European Journal of Wood and Wood Products (2024) 82:147–158
https://doi.org/10.1007/s00107-023-01998-5

ORIGINAL ARTICLE

Modified pine needles as a formaldehyde scavenger for urea-formaldehyde resin in plywood production

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Received: 7 June 2023 / Accepted: 20 September 2023 / Published online: 12 October 2023

Abstract

The aim of the present work was to investigate whether it is possible to use ground pine needles as formaldehyde-scavenging filler for urea-formaldehyde resin in the production of plywood. The scope of the research included determinations of both optimal amount of introduced filler and the effect of its modification (silanization, hydrothermal and alkaline treatments). Properties of adhesives such as viscosity, gel time and pH were investigated and their morphology was assessed using scanning electron microscopy. The manufactured plywood panels were tested in terms of their wet shear strength, tendency to delamination in varying conditions and formaldehyde emission. It was found that the addition of pine needles lowers the pH and reduces gel time of the adhesive. Moreover, it was shown that despite the significant reduction in formaldehyde emission, the addition of non-modified needles causes a decrease in bonding quality of plywood. Based on the results, 10 parts by weight of needles per 100 parts by weight of resin can be considered as an optimal loading. The use of ground needles modified hydrothermally and with silane allows to minimize the negative effect on the strength of glue lines and leads to further reduction of formaldehyde emission. Therefore, it can be concluded that pine needle powder has strong potential for the application as a formaldehyde-scavenging filler for urea-formaldehyde adhesive in plywood production.

1 Introduction

Plywood is a valuable wood-based material characterized by a layered structure, widely used in construction, furniture manufacturing, internal design, as packing material etc. The wide range of its applications results from many beneficial properties, among others, great durability, tensile strength and resistance to deformation. However, its production requires the use of large amounts of adhesives, which according to Bekhta et al. (2021) may constitute a considerable share in the weight of finished plywood. These are mainly phenol-formaldehyde (PF), melamine-urea-formaldehyde (MUF) and urea-formaldehyde (UF) adhesives, which additionally require the addition of fillers (Réh et al. 2021; Jeżo et al. 2023). The main purpose of filling material implementation is to lower the overall production costs, facilitate resin spread and reduce over penetration of resin into wood veneer surface (Cao et al. 2020). Moreover, the use of materials with high content of proteins or phenolic substances for this purpose may also contribute to the reduction of formaldehyde emission from the resultant products (Liu et al. 2022; Kristak et al. 2023). The problem of formaldehyde emission from wood-based materials, especially those bonded with UF adhesive, has attracted the attention of scientists since the mid-1960s up to the present day (Kawalerczyk et al. 2022). Formaldehyde release from plywood is a complex issue which can be affected by

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many factors related to both physicochemical characteristics of the material and the environmental factors (Zhang et al. 2018a; Shao et al. 2022). However, many studies are constantly being conducted on this subject due to its negative impact on humans. As shown by the research results, long-term exposure to formaldehyde can cause respiratory and immune diseases or even cancer (Antov et al. 2020; Jalali et al. 2021). Consequently, more stringent regulations regarding permitted emission levels are being developed which forces the progress of research towards their limitation (Mantanis et al. 2018).

Numerous research works aimed to determine the effect of phenolics-rich fillers, such as: walnut shell (Sellers et al. 2005), chestnut shell (Oh 2022), pecan shell (Sellers et al. 1990), furfural residues (Sellers 1989), pine nut shell (Yong-Sung and Sellers 1999), walnut dregs (Li et al. 2019), coffee bean post-extraction residues (Danilowska and Kowaluk 2020), hazelnut husk extract (Bilgin and Colakoglu 2021) etc., on the properties of plywood have been carried out before. The use of rich in phenolics bark powder for this purpose is also an interesting concept (Réh et al. 2019; Tudor et al. 2020). Studies have shown that in the case of ground bark, its effectiveness in terms of capacity of formaldehyde removal from UF adhesive varied depending on, for example, dimensional fraction (Mirski et al. 2020a) or tree species (Walkiewicz et al. 2022), but the overall effect was very satisfactory.

An interesting type of forest biomass that could potentially find such use as well are pine needles. Due to the large share of coniferous species in Polish forests, they constitute a biomass which has not found yet any significant industrial application (Salzano de Luna et al. 2023). Finding a way of needle utilization is important because every year, the large amount of fallen dry needles accumulate in the forests. In excessive amounts they reduce water permeability of soil which lowers the groundwater level and inhibits the growth of other plants. Furthermore, the presence of large amounts of dry needles can also contribute to the uncontrolled spread of forest fires (Salzano de Luna et al. 2023). In response to this problem, studies determining their usefulness as fillers for epoxy composites (Gairola et al. 2019), polyester composites (Kumar et al. 2017), poly(lactic) acid composites (Sinha et al. 2018) and polyethylene composites (Barton-Pudlik and Czaja 2016) have been conducted, however, none of them investigated the possibility to implement them as a filler for UF adhesive in plywood production.

Therefore, taking into account the lack of knowledge on the possibility to use ground pine needles as a formaldehyde-scavenging filler for UF adhesive, the aim of the present study was to determine the effect of their implementation into the UF resin formulation on the properties of manufactured plywood. The research was also aimed at determining whether the modification of pine needles with various methods influences properties of the resultant plywood panels.

2 Materials and methods

2.1 Characteristics of raw materials

For the production of plywood, rotary-cut birch veneers obtained in industrial conditions with a thickness of 1.4–1.5 mm and a moisture content of 7.0 ± 0.5% were used. Urea-formaldehyde resin commonly applied in the plywood industry was used as a binding agent. It was characterized by the following properties: viscosity of 750 mPa·s, density of 1.321 g/cm^3, solids content of 64.5%, pH 7.72 and gel time at 130 °C of 143 s. A 20% aqueous solution of ammonium nitrate was introduced as a hardener to the adhesive formulation in the amount of 2% based on the solid weight of the resin. Plywood panels bonded with UF adhesive mixture containing rye flour in the amount of 10 parts by weight (PBW)/100 PBW of resin were then used as a reference variant for the analysis and interpretation of the obtained results. Ground Bosnian pine (*Pinus heldreichii*) needles were applied as a substitute for the traditionally used technical flour. They were characterized by exceptional length reaching values of 45–100 mm and thickness of 1.5–2.0 mm (Fig. 1a, b). The implementation of this type of material as a filler for adhesive required getting rid of mineral particles by rinsing the needles several times in cold water. Then, they were dried in a laboratory oven at 100 °C for 24 h and ground in a laboratory mill to obtain the powder (Fig. 1c). After being prepared this way, the moisture content of the filler was approx. 1.5%. The fractional compositions of the fillers used in the study (i.e. rye flour and pine needle particles) are shown in Fig. 2.

The needle powder prepared according to the described method was introduced into the adhesive mixture in various amounts of 5, 10 and 15 PBW/100 PBW of UF resin. The effect of needle powder modification was investigated for an optimal amount of filler selected based on the outcomes of plywood properties obtained during the first stage of the research (10 PBW of needle powder/100 PBW of resin). The modifications were carried out by applying three different methods: silanization, hydrothermal treatment and alkaline treatment.

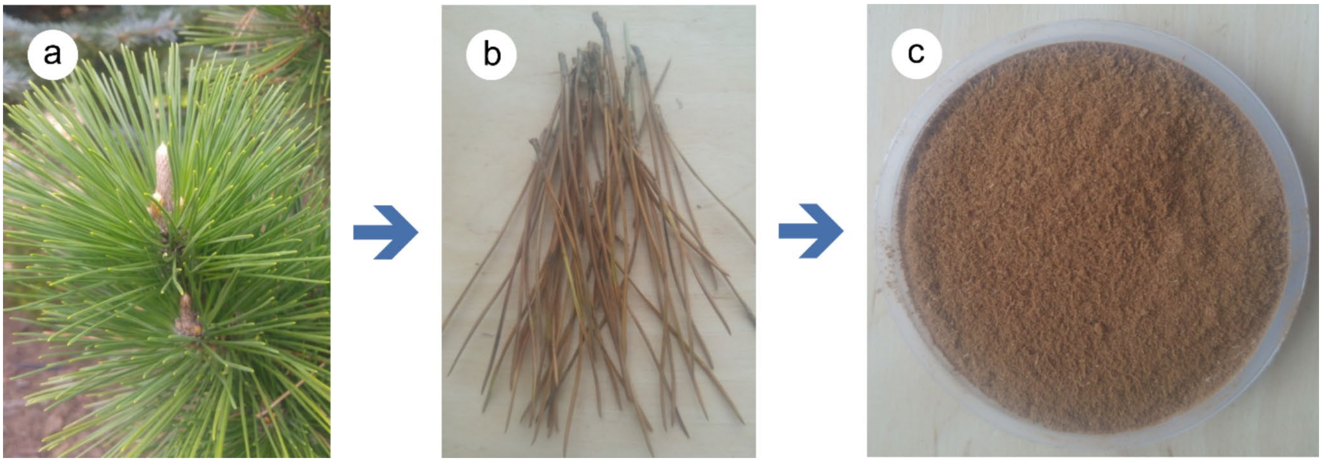
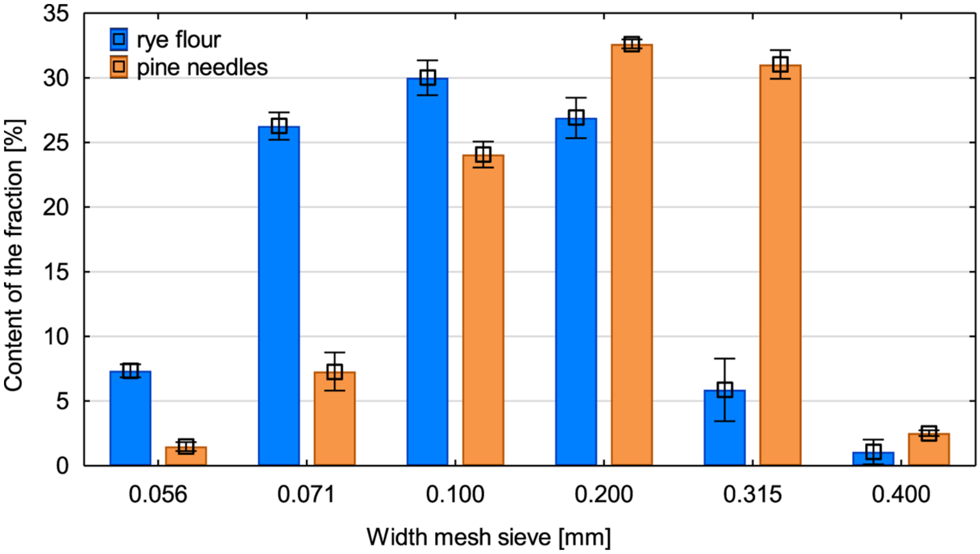


Fig. 1 Needles of Bosnian pine (*Pinus heldreichii*): **a, b -** initial form, **c** – after grinding

Fig. 2 Fractional composition of rye flour and ground pine needles applied as a filler for plywood production



2.2 Modification of pine needles

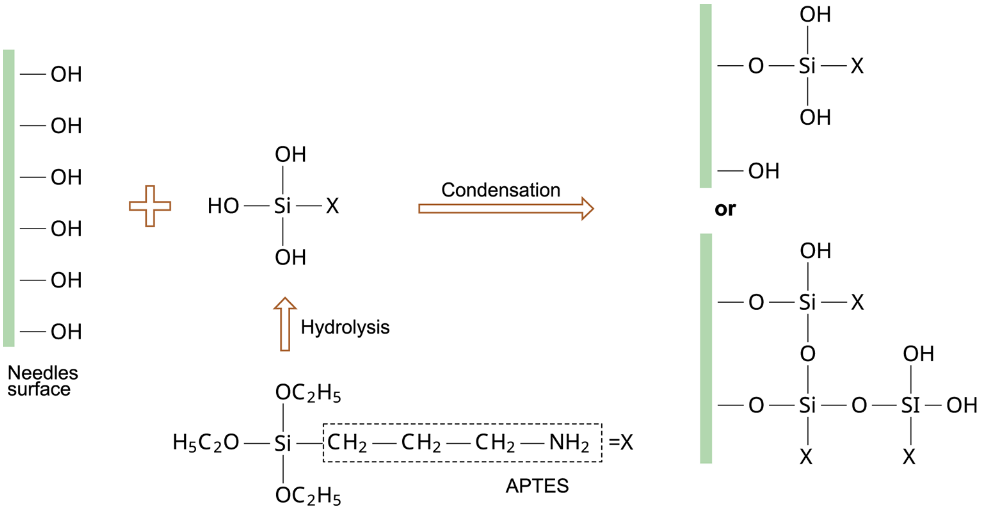
2.2.1 Modification of needle powder with 3-aminopropyltriethoxysilane

3-aminopropyltriethoxysilane (APTES) with the trade name U-13 was purchased from Unisil Sp. z o.o. (Tarnów, Poland). It is a chemical agent mainly applied as an adhesion promoter and surface modifier of organic and inorganic fillers for polymers such as for example phenolic, acrylic, cellulosic materials. This compound, characterized by a density of 0.951 g/cm^3, is soluble in anhydrous alcohols, aliphatic and aromatic hydrocarbons and ethers. Silanization of the needle particles was carried out in order to achieve the maximum degree of their dispersion in the adhesive mixture and to increase the chemical compatibility between the filler and the adhesive matrix. Modification of needles was conducted after grinding by applying APTES on their surface using an atomizer, at a powder to silane solution weight ratio of 10:1 (Ratajczak et al. 2015; Miedzianowska et al. 2020). Silane solution was prepared by dissolving APTES in the mixture of ethyl alcohol and distilled water in a weight ratio of 4:1, and stirring for 1 h at 23 °C. Then, the obtained silane-modified needle powder was dried at 105 °C for 2 h. Possible reaction between the hydroxyl groups of needles and APTES is shown in Fig. 3, according to the work of Song et al. (2017).

2.2.2 Hydrothermal modification of needle powder

Hydrothermal treatment of needles (HT) was carried out mainly in order to remove wax substances from the surface and to improve the wettability of the particles by the adhesive mixture. It was performed by boiling the ground needle powder in water for 3 h (Singha and Thakur 2009). After assumed time, the particles were filtered, dried in the

Fig. 3 Possible reaction of needles with APTES



laboratory oven at 105 °C for 12 h, and then ground in the laboratory mill again.

2.2.3 Modification of needle powder with NaOH solution

The alkaline modification of needles was carried out in order to remove wax substances from their surface as well, but also to activate it (Yamamoto et al. 2017). The ground needles were soaked in 1% NaOH solution and stirred vigorously with the use of a magnetic stirrer at 100 rpm for 180 s. Then, it was filtered and washed with distilled water until the pH of approx. 7 was achieved. The obtained powder was dried in the laboratory oven at 105 °C for 12 h, and then ground again using the laboratory mill.

2.3 Properties of adhesives

To assess the effect of the experimental filler introduction on the properties of obtained adhesive mixtures, their characteristics commonly used for industrial quality control of resins were determined. Viscosity, which is a crucial parameter for plywood production, was investigated with the use of Brookfield DV-II + Pro viscometer (Middleboro, USA) at 50 rpm, 23 °C using a spindle no. 5. In addition, the pH of the adhesive mixtures was tested with the use of Testo 206 pH-meter (Pruszków, Poland). Their curing was evaluated based on the results of gel time measurements at 100 °C, performed in accordance with the Polish standard PN-C-89352-3 (1996). Morphology of the cured adhesives was assessed based on scanning electron microscopy (SEM) images taken with the use of Hitachi SU3500 microscope (Tokyo, Japan) at an accelerating voltage of 15 kV.

2.4 Plywood manufacturing and testing

The prepared adhesive mixtures were applied on the veneer surfaces in the amount of 160 g/m^2. The process of pressing three-layer plywood was conducted at a high temperature of 120 °C for 240 s, using a unit pressure of 1.6 N/mm^2. The manufactured panels were conditioned for 7 days under conditions of 22 ± 1 °C and 65% relative humidity. After this period, plywood characterized by an average moisture content of 7.5% was tested for bonding quality and emission of free formaldehyde. Bonding quality was determined according to the requirements of EN 314-1 (2004), by investigating the shear strength after pre-treatment consisting of soaking in water at 20 °C for 24 h. Tests were conducted on 12 samples from each variant. Free formaldehyde emission was determined in triplicates using the flask method according to EN 717-3 (1996). Content of formaldehyde in the obtained water solution was measured using commonly applied ammonium acetate and acetylacetone method with the use of Biosens UV-5600 spectrophotometer (Warsaw, Poland) at wavelength of 412 nm. Furthermore, the susceptibility of the manufactured plywood to delamination was assessed according to the ANSI/HPVA HP-1 (2004) protocol. It is a method widely used to determine water resistance of experimental adhesive formulations applied to plywood bonding (Damodaran and Zhu 2016; Mousavi et al. 2018; Taghiyari et al. 2020). Samples with the dimensions of 130 mm × 50 mm were subjected to a treatment procedure including soaking in water at 24 ± 2 °C for 4 h followed by drying in a laboratory oven for 19 h at 50 ± 1 °C. After this time, the delamination, which is considered as a continuous opening between two veneer layers deeper than 6.35 mm, longer than 50 mm, and wider than 0.08 mm, was assessed using 10 samples from each variant.

2.5 Statistical analysis

One-way analysis of variance (ANOVA) was performed to analyse the results of shear strength after pre-treatment and free formaldehyde emission. Moreover, Tukey's test at the significance level of $\alpha = 0.05$ was performed using Statistica 13.3 software in order to distinguish homogeneous groups and assess significance of observed changes.

3 Results and discussion

3.1 Properties of adhesive mixtures with pine needles

In order to determine the suitability of pine needles as UF resin filler for the plywood production process, the prepared adhesive mixtures were tested for their basic properties such as viscosity, pH and gel time. These parameters are helpful in determining the optimal amount of filler that is necessary to provide the required technological parameters. An adhesive mixture prepared according to an industrial recipe with rye flour was used as a reference. The obtained results are presented in Table 1.

Based on the obtained results, it can be concluded that the increase in the amount of pine needles leads to a gradual decrease in the pH values of the adhesive mixtures. In relation to the resin with the addition of rye flour, a significant reduction in its gel times was also observed. Moreover, as the share of needle powder increased, its viscosity also increased. In the case of introduction of needles in the amount of 5 PBW, the viscosity of the adhesive was almost twice lower when compared to the reference mixture. Such low value may cause major difficulties in the gluing process considering the flow of the adhesive mixture from the wavy veneers and creation of the so-called glue stains on the surface of finished plywood, which is a significant drawback in terms of its quality. Therefore, it seems as if this amount of powder was insufficient to provide the required viscosity of the adhesive mixture. The introduction of needles in the amount of 10 PBW resulted in the increase in viscosity but the obtained average value was still 50% lower than the reference mixture. It should be emphasized that during the adhesive spreading on the surface of the veneer sheets, the application of this variant did not cause any major difficulties and moreover, no glue stains on the surface of resultant panels were observed. As could be expected, the variant containing 15 PBW of ground pine needles demonstrated the highest viscosity. It was still 20% lower compared to the reference one, but such a high amount of experimental filler caused considerable difficulties during the gluing operation which resulted mainly from the tendency of fine fraction of needles to form the agglomerates. This tendency can lead to uneven application of the adhesive mixture, which is crucial for obtaining the high-quality bond lines. Therefore, it seems that despite lower viscosity comparing to the flour-filled reference variant, the optimal formulation of the UF adhesive mixture should contain 10 PBW of pine needle powder. The reason for lower viscosity values observed in the case variants filled with needles comparing to the reference one was probably the high protein content of approx. 12.5% in the composition of rye flour (Kawalerczyk et al. 2021b). The protein molecules show the ability to form a network, and consequently, they increase the viscosity more effectively than pine needles. In addition, flour has the ability to absorb water (up to 30%), which promotes the increase in viscosity of the mixtures. Similar conclusions were drawn by Mirski et al. (2020b), who observed a very similar effect for the adhesives filled with ground oak bark.

Table 1 Properties of UF resin with the addition of various amounts of fillers

Type of filler	Amount of filler (PBW/100 PBW of resin)	pH	Viscosity (mPa·s)	Gel time (s)
Rye flour	10	7.05 (0.08)*	2680 (11.3)	341 (10.6)
Pine needles	5	7.22 (0.10)	928 (13.2)	161 (2.6)
Pine needles	10	6.80 (0.08)	1384 (11.8)	163 (6.1)
Pine needles	15	6.57 (0.06)	2184 (16.7)	172 (3.5)

*standard deviation

Both gel time and pH are important parameters indicating the effect of experimental fillers on the reactivity of UF resin. It was observed that as the amount of filler increased, the pH of the adhesive mixtures decreased, which led to shortening of gel time. In the case of the variant assuming the highest content of needle powder, gel time was shortened by 50% in comparison with the reference containing rye flour. It can also be noticed that the shortest gel times were observed for the mixtures containing 5 and 10 PBW of pine needle powder. In some cases, too high a filler loading can lead to its uneven dispersion within the resin due to the formation of agglomerates, which could potentially delay the curing process (Nabinejad et al. 2017). Overall, it seems as if the addition of needles increased the reactivity of the UF adhesive which probably came from the increased acidity of the solution. This is a favourable effect looking from the industrial perspective considering the emerging opportunity to reduce pressing time of plywood (Mahrdt et al. 2016). This effect is consistent with the outcomes of studies

Table 2 Effect of pine needle modification on the properties of UF adhesive mixtures

Method of modification	pH	Viscosity (mPa·s)	Gel time (s)
Non-modified	6.80 (0.08)*	1384 (11.8)	163 (6.1)
HT	6.70 (0.09)	2520 (10.0)	167 (2.1)
APTES	7.12 (0.06)	2016 (7.6)	201 (10.4)
NaOH	7.08 (0.05)	2014 (5.6)	205 (14.6)

*standard deviation

performed by Mirski et al. (2020a, b) regarding the effect of introducing the acidic bark powder to amino adhesives on their enhanced curing behaviour.

In order to improve the effect of pine needles implementation as a filler for UF resin even more, the modification of powder was carried out. The effect of applied methods on the properties of adhesive mixtures is presented in Table 2.

The applied modifications contributed to slight extension of gel time and an increase in the viscosity of adhesive mixtures. The extended gel time observed in the case of implementing APTES-modified and NaOH-modified needles probably resulted from the increase in the pH, which in turn was caused by the alkaline nature of modifiers. Nevertheless, it is noteworthy that even for the adhesive mixture containing alkali-treated needles, the gel time was 40% shorter (205 s) than for the reference mixture containing the traditional filler in the form of rye flour (341 s). The highest viscosity values were found in the case of introduction of hydrothermally treated needles. Compared to variants containing non-modified needles, viscosity was 80% higher and reached a similar level to the reference mixture filled with flour. In contrast, needle modification with APTES and NaOH solution led to an increase in viscosity by approx. 45%. The reason for such significant changes which occurred as a result of filler treatment was probably better dispersion of particles within the adhesive. Furthermore, removal of hydrophobic wax layers from the surface of needles due to the applied modifications could contribute to the increased water absorption of their particles (Zhang et al. 2018b).

3.2 Pine needles as scavengers of formaldehyde

The results of formaldehyde emission investigations aimed at assessing the suitability of pine needles for the use as natural formaldehyde scavenger for UF adhesive-bonded plywood are shown in Fig. 4. As shown in Fig. 4a, the introduction of ground pine needles into the UF adhesive significantly reduced the emission of formaldehyde, which indicates their potential as environmentally friendly and natural formaldehyde scavenger. It was found that the amount of needles had a significant effect on the obtained results. Comparing to the reference variant, the most noticeable decrease in formaldehyde emission by 40% was observed in the case of the addition of needle powder in the amount of 15 PBW. Lowering the loading of introduced experimental filler to 10 PBW also allowed for a significant, but slightly smaller reduction of formaldehyde emission by 30%.

However, the introduction of 5 PBW of needles did not cause any statistically significant changes comparing to the reference plywood. Observed improvement in the hygienic characteristic of resultant panels most likely resulted from

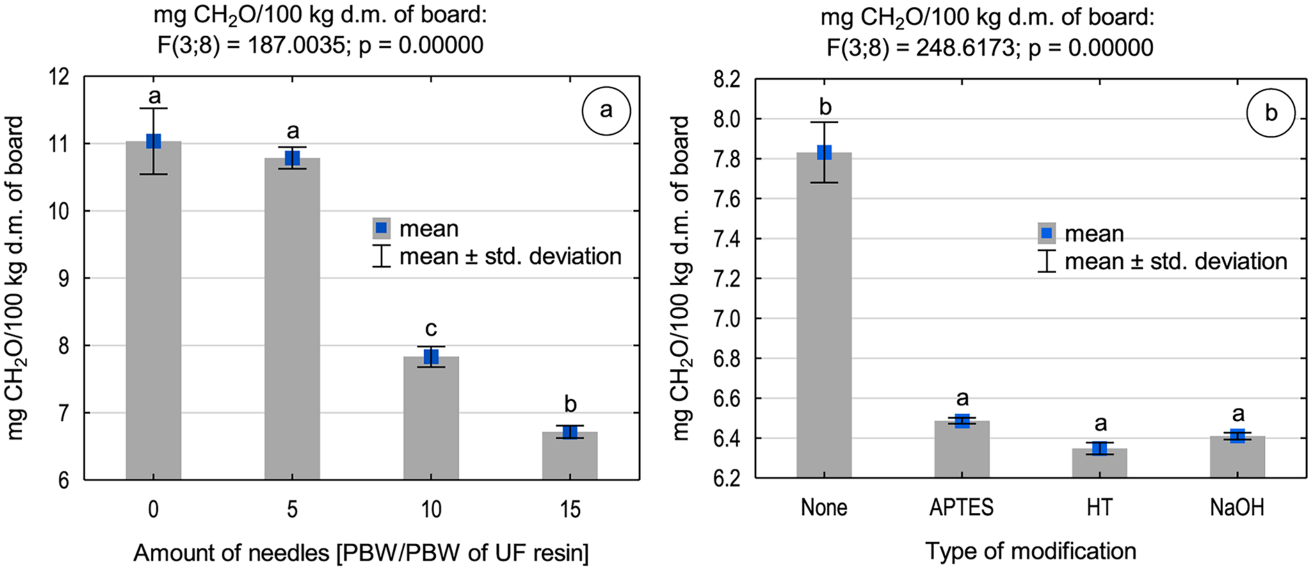


Fig. 4 Effect of pine needle powder on the formaldehyde emission depending on: **a** – amount of introduced filler, **b** – modification of introduced filler

the chemical composition of applied needles. It should be emphasized that their formaldehyde-scavenging ability is a complex issue and may depend on many factors, such as: species, age of the tree, growth conditions, habitat etc. In general, pine needles are characterized by the high concentration of tannins, flavonoids and other phenolic compounds (Karapandzova et al. 2015). Condensed tannins due to their phenolic nature can easily react with formaldehyde in both acidic and alkaline environments (Jahanshaei et al. 2012; Gangi et al. 2013; Ferreira-Santos et al. 2020). Formaldehyde reacts with tannins which leads to polymerization through the formation of methylene bridge linkages to the reactive positions of the polyphenols molecules (Pizzi 1979; Réh et al. 2021). Demonstrated reduction in formaldehyde emission can also be attributed to the high content of lignin in the chemical composition of needles. According to Asadullah et al. (2006) they contain approx. 35% of lignin, and as found by Van Der Klashorst and Strauss (1986), resulting benzyl alcohols react with a model lignin compound which leads to the formation of methylene-linked dimers. Additionally, similarly as in the case of rye flour, pine needles also contain several amino acids which are an integral component of biomass (Körner 2021). They include for example alanine, aspartate, aspartic acid, cysteine, glutamic acid, glutamate, glycine, histidine, arginine, lysine and phenylalanine (Raitio and Sarjala 2000; Qi et al. 2020; Ramay and Yalçın 2020). According to Kamps et al. (2019), formaldehyde reacts with amino acids such as cysteine, arginine or histidine under various conditions, giving cyclised, hydroxymethylated, N-formylated and N-methylated products characterized by very different stabilities, which could influence the formaldehyde emission as well. It was found that among mentioned amino acids, cysteine reacts most effectively with formaldehyde, forming a stable thiazolidine. Furthermore, studies performed by Metz et al. (2004) showed that formaldehyde reacts with the amino group of N-terminal amino acid residue and the side chains of arginine, cysteine, histidine and lysine residues to form methylol groups, Schiff bases and methylene bridges. It is worth emphasizing that so far no works regarding the possibility of using pine needles as the bio-based formaldehyde scavenger have been conducted. Nevertheless, the obtained results correspond to the outcomes of other studies concerning the introduction of phenolics-rich forest biomass as a filler for UF adhesive, an example of which was ground bark of various tree species. Emission-reducing effect was confirmed in the case of bark of the following species: walnut, chestnut, fir, spruce (Aydin et al. 2017), birch, beech, maple and pine (Walkiewicz et al. 2022). Beech bark was also used by Ružiak et al. (2017), Bekhta et al. (2021) and Réh et al. (2021).

Based on the results presented in Fig. 4b, it was found that modification of needles with APTES, hydrothermal treatment and NaOH solution contributed to a further decrease in formaldehyde emission. However, statistical analysis showed no statistically significant effect of the applied modification method. Compared to the reference plywood and plywood bonded with an adhesive mixture containing 10 PBW of non-modified pine needles, a reduction in formaldehyde emission, regardless of the method of modification, was approx. 42% and 18%, respectively. The favourable effect observed in the case of APTES-modified needles probably resulted from the introduction of an amino group located on top of the modifier molecule. According to Hassannejad et al. (2018) these groups are the most effective reactive groups which can be used for formaldehyde adsorption and they can react with both free and hydrolysed HCHO (Park and Jeong 2011; Kawalerczyk et al. 2022). As a result, methyl groups are formed, which in turn, can form methylene bridges due to further reactions (Resetco et al. 2016). Moreover, in the case of modification with APTES, the reduction of emission was probably also caused by the change in the surface characteristic of the filler. It could lead to the reduction of agglomeration of fine needle particles and therefore, to the increase in the formaldehyde-absorbing surface. As stated by Ayrilmis et al. (2016) agglomeration of filler introduced to the adhesive can negatively affect the formaldehyde emission. In the case of hydrothermal and alkaline treatments, the observed decrease seems to be a more complex issue and may result from several factors. Firstly, both methods can change the chemical composition of needles by dissolving some part of organic compounds (e.g. terpenes and oils) and removing layer of wax from the needle surface, which consequently may influence the formaldehyde emission (Gupta et al. 2010). In addition, the use of hot water and NaOH solution changes the pH of the needles, which in turn can affect the content of amino acids. Alkaline amino acids such as arginine, lysine and histidine are more stable in neutral and alkaline environment, while acidic amino acids, such as aspartic acid and glutamic acid, are more stable in an acidic environment. The pH of solutions affects solubility of amino acids as well because they dissociate into different ions in aqueous solutions (Lee et al. 2013). Furthermore, both hot water and NaOH solution can break peptide bonds between the amino acids and thus, degrade proteins into smaller molecules (Averina et al. 2021). As a result, some amino acids contained in the needles may be degraded and others may be released which may influence their overall content and consequently, the hygienic properties of plywood as well.

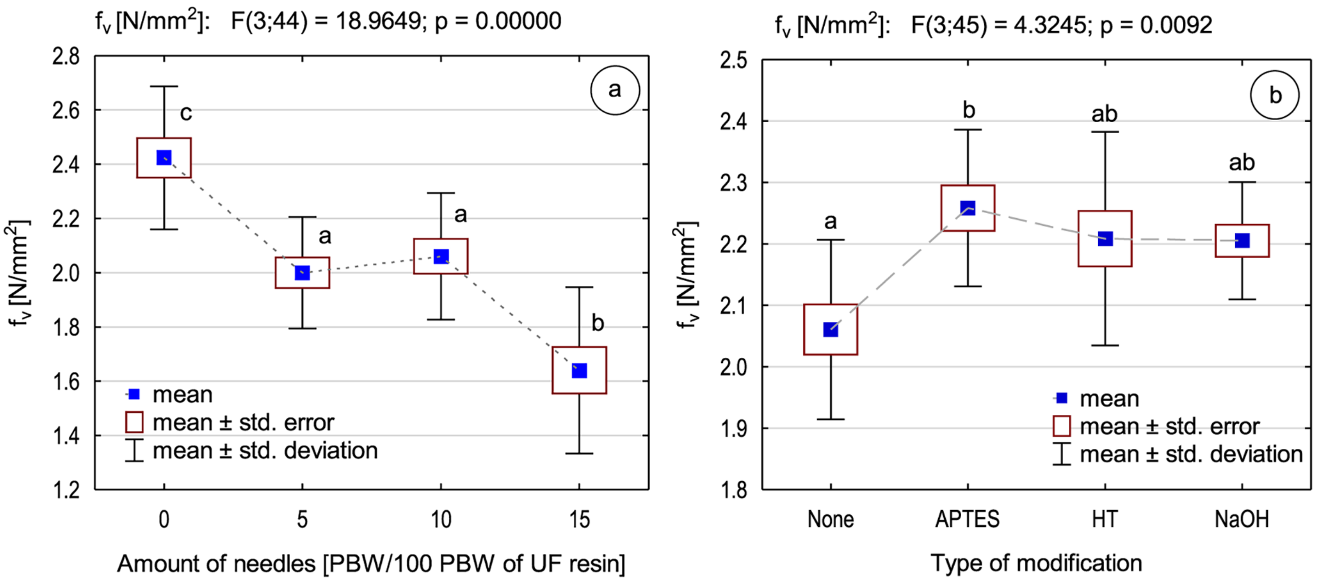


Fig. 5 Effect of pine needle powder on shear strength of plywood depending on: **a** – amount of introduced filler, **b** – modification of introduced filler

Table 3 Delamination of plywood depending on the amount of introduced needle powder

Amount of filler (PBW/100 PBW of resin)	Number of delaminated samples	Result
Reference	0/10	P*
5	0/10	P
10	3/10	F
15	2/10	F

*P – test passed; F – test failed

Table 4 Delamination of plywood depending on the modification of introduced needle powder

Method of modification	Number of delaminated samples	Result
Non-modified	3/10	F*
APTES	0/10	P
HT	0/10	P
NaOH	1/10	F

*P – test passed; F – test failed

3.3 Bond quality of plywood

The effect of needles application and their modification on strength of the obtained glue joints in plywood was assessed on the basis of the outcomes of both shear strength (f_v) test and delamination test, the results of which are presented in Fig. 5 and Tables 3 and 4.

According to Singha and Thakur (2009), the introduction of pine needles to the UF-based polymer composite contributes to the improvement of their properties due to strong bonding between the methylol groups of polymer matrix and hydroxyl groups of cellulose contained in the needles.

However, results obtained in the case of plywood showed the opposite tendency. It was found that the use of ground needles as a filler of UF adhesive led to a decrease in plywood bonding quality as demonstrated by the results of wet shear strength test and delamination test. It was particularly noticeable when the larger amounts of filler were introduced to the mixture, i.e. more than 10 PBW. Compared to the reference variant, the addition of pine needles in the amount of 10 PBW and 15 PBW resulted in a statistically significant decrease in shear strength by approx. 13% and 30%, respectively. These loadings of needles increased the tendency of plywood to delamination as evidenced by test failures. It is especially important since delamination is considered as a valuable indicator of bond lines water resistance and accurate predictor of plywood behaviour in various conditions (El Moustaphaoui et al. 2019). However, shear strength of all panels, regardless of the amount of introduced needle powder, exceeded 1 N/mm^2 required by EN 314-2 (2001). The decrease in bonding quality observed in needle-filled variants may result from several reasons. Replacing the flour with the experimental filler led to deterioration of the morphological structure of cured UF adhesive.

The SEM (Fig. 6a and b) images showed that the application of pine needles led to the formation of greater number of microcracks and micropores in the structure of the cured adhesive resulting from the release of water during the condensation reaction and resin curing (Gao et al. 2012). Limiting the occurrence of cracks and inhomogeneities within the structure may have a crucial influence on the bonding quality of resultant plywood (Kawalerczyk et al. 2021). Moreover, as already shown, needle-filled mixtures were

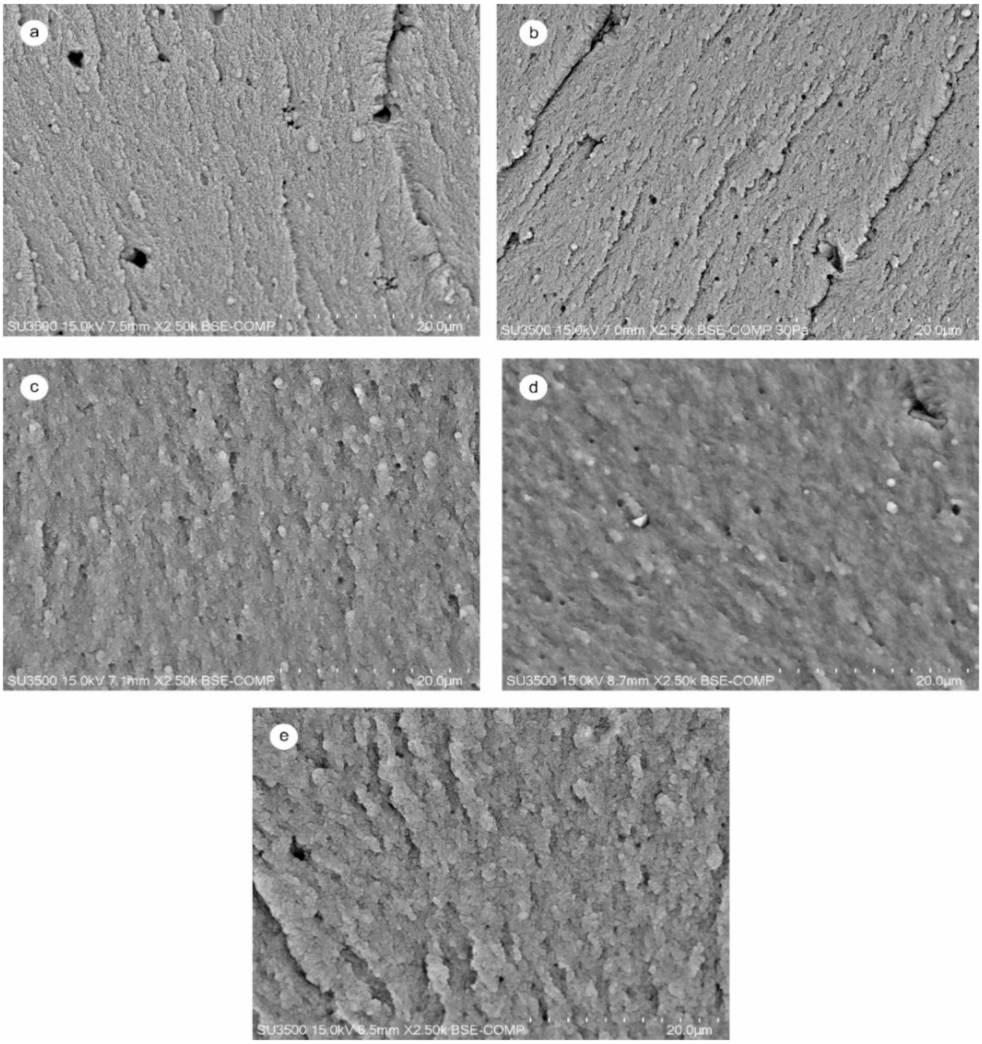


Fig. 6 SEM images of cured UF resin filled with: **a** – rye flour (reference), **b** – unmodified pine needles, **c** – APTES-modified needles, **d** – hydrothermally modified needles, **e** – NaOH-modified needles

characterized by significantly lower viscosity compared to the reference mixture. Highly hydrophilic rye flour swells due to absorbed water and, in conditions of high temperature, starch grains begin to crack, which in turn leads to their gelation and increase in the overall viscosity of the adhesive. This effect prevents an excessive penetration of the glue into the porous veneer surface. Thus, lower viscosity of mixtures filled with needle powder can cause over penetration of the adhesive and consequently, its amount remained on the surface can be insufficient to provide a joint characterized by the required strength. Negative effect on bonding quality could also result from the tendency of fine needle particles to form the agglomerates, which made it difficult to evenly spread the adhesive mixture on the veneer surface. It is important because filler particles play the role of stress carriers along the glue line and their concentration at some points may weaken the bonding strength (Mirski et al. 2020b).

Singha and Thakur (2009) also stated that compatibility between pine needles and UF resin matrix depends on the surface characteristic of applied needles. Therefore, their modification seemed to be an especially reasonable solution, which was confirmed by the outcomes presented in Fig. 4b and Table 4.

Particularly effective and statistically significant influence on plywood bonding quality, assessed based on the results of wet shear strength and delamination test, was achieved by implementing the modification with APTES. The use of hydrothermally modified needles only led to the reduction in a number of delaminated samples. Both silanization and hydrothermal treatment of the particles probably allowed to limit their agglomeration and thus, to obtain proper homogenization of the adhesive mixtures. As a result, created bonds were characterized by a more composed and uniform morphology (Fig. 6c and d). Better dispersion of needle particles modified using these methods reduced the number of cracks and void spaces in the bond line, which can indicate that the adhesion was improved (Gao et al. 2012). Moreover, according to Li et al. (2015), a denser morphology of the cured adhesive can prevent water penetration into the joint, which improves its overall water resistance. In the case of modification with APTES, the introduction of amino groups could enhance cohesion and increase the compatibility between the filler and UF resin as well. On the other hand, as shown in Fig. 6e, treatment of needles with NaOH solution resulted in deterioration in the morphology of the cured adhesive. Obtained glue lines were characterized by a layered structure full of cracks. According to Taghiyari et al. (2020), it contributes to the decrease in bonding quality of plywood and increased tendency to delamination which was confirmed by the outcomes presented in Table 4.

4 Conclusion

Based on the results of the performed research, it can be concluded that as the amount of introduced pine needle powder increases, the viscosity of the adhesive also increases. Moreover, the pH of the mixtures decreases with the increase in the loading of pine needles, which consequently leads to the reduction of gel time. The optimal amount of pine needles allowing to achieve the required technological parameters of the adhesive mixture and the bonding quality of the manufactured plywood is 10 PBW/100 PBW of resin. Further increase in the amount of introduced experimental filler causes major difficulties in spreading the adhesive on the veneer surface and leads to a decrease in bonding quality as well. The addition of needle powder enhances the hygienic properties of plywood as shown by significantly decreased formaldehyde emission. Furthermore, both hydrothermal treatment and silanization of pine needles allow to improve the bonding quality of plywood as evidenced by the increase in shear strength and reduced tendency to delamination after aging test. Modification with NaOH solution does not allow for the improvement in strength of the glue lines. Each of the applied modification methods additionally increases the ability of needles to reduce the formaldehyde emission. Thus, ground pine needles can be used as a valuable substitute for the traditional fillers applied in the production of UF adhesive-bonded plywood. The resultant panels are characterized by good bonding quality and significantly reduced formaldehyde emission.

Author contributions Conceptualization, Methodology, Investigation, Data curation, Formal Analysis, Resources, Writing–original draft, Writing–review & editing: DD; Conceptualization, Methodology, Investigation, Data curation, Formal Analysis, Resources, Writing–original draft, Writing–review & editing: JKa; Investigation, Data curation, Formal Analysis, Resources: JKm.

Funding No funding was received to assist with the preparation of this manuscript.

Data Availability The datasets collected, generated and analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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