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ВВЕДЕНИЕ ШЛАМА ЦЕЛЛЮЛОЗЫ И ОТХОДОВ ДРЕВЕСНОЙ КОРЫ ДЛЯ СНИЖЕНИЯ ЭМИССИИ ФОРМАЛЬДЕГИДА ИЗ ФАНЕРЫ НА ОСНОВЕ КАРБАМИДОФОРМАЛЬДЕГИДНОЙ СМОЛЫ

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В производстве древесных плит очень важен выбор клея, влияющий на гигиенические свойства плит. Наибольшее внимание уделяется эмиссии формальдегида, потому что формальдегид вреден для здоровья человека и поэтому определяет токсичность плит. Целью исследования является модифицирование карбамидоформальдегидной (КФ) смолы целлюлозным шламом и древесной корой с целью снижения выделения формальдегида. Порошок древесной коры представляет собой смесь, содержащую 50 % буковой коры и 50 % еловой коры. Эмиссию формальдегида и прочность на сдвиг клеевых соединений тестировали на пяти образцах трехслойной фанеры ольхи. Эмиссию формальдегида определяли эксикаторным методом в течении 24-часов и контролировали семь недель после склеивания. Через 7 недель выделение формальдегида из КФ клея, модифицированного порошком древесной коры, снизился на 39 %. Эмиссия формальдегида из фанеры с использование КФ клея, модифицированного шламом целлюлозы уменьшилась на 34 %. Наиболее значительное снижение эмиссии (на 45 %) наблюдали при тестировании КФ клея с древесной корой . Добавки, используемые для модификации КФ клея, имели положительное влияние на снижение эмиссии формальдегида из фанеры при сохранении прочности на сдвиг, которая соответствовала стандартным требованиям.

Ключевые слова: эмиссия формальдегида, гигиенические свойства, КФ клей, мебель, фанера

CELLULOSE SLUDGE AND WOOD BARK AS FORMALDEHYDE SCAVENGERS FOR PLYWOOD BONDED WITH UREA FORMALDEHYDE RESIN

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Abstract

In production of wood-based panels, the choice of adhesive is very important; the adhesive influences hygienic properties of boards. Most attention is given to emission of formaldehyde, because formaldehyde is harmful to human health. The aim of the research was to modify urea-formaldehyde resin (UF) by cellulose sludge and wood bark in order to reduce formaldehyde emission. Wood bark powder was a mixture containing 50 % of beech bark and 50 % of spruce bark. Release of formaldehyde and shear strength of the adhesive joints was tested on five resp. three-layer alder plywood. Formaldehyde emission was determined by 24-hour desiccator method and monitored during seven weeks after gluing. After 7 weeks of the experiment the reference UF adhesive showed formaldehyde emission decreased by 39 %. Emission from plywood glued with UF adhesive modified with cellulose sludge was lower by 34 %. The most significant decline in emission was measured at the UF adhesive with wood bark – reduction by 45 %. Additives used for modification of the UF adhesive confirmed a positive impact to reduce formaldehyde emissions from plywood and shear strength met the standard requirements.

Keywords: formaldehyde emission, hygienic properties, UF adhesive, furniture, plywood

INTRODUCTION

Formaldehyde is a colourless gas commonly found in interiors. Typical household sources are wood based panels (plywood, particleboard) bonded with adhesives containing formaldehyde, decorative laminates, fiberglass, coatings, household cleaners, and others. Formaldehyde is a respiratory irritant and sensitizer. In 2006 World Health Organization (WHO IARC) evaluated formaldehyde as carcinogenic to humans (Group 1). In the last decades, there is an increasing concern over indoor air quality. Both indoor and outdoor air pollution have been recognized to contribute to global health burden. The reported health effects range from cardiovascular, respiratory diseases, neuronal to cancer.

Much of the recent focus has been on formaldehyde levels indoors. The formaldehyde concentration is dependent on humidity, temperature, and season. Dannemiller *et al.* (2013) developed and evaluated the use of a simple, inexpensive, and replicable method for formaldehyde testing in homes. They searched correlations between formaldehyde sources and formaldehyde concentration, and concentration and asthma control. They have found that increased formaldehyde concentration showed an association with decreased asthma control. This fact suggests that decreasing formaldehyde concentration may improve health control.

Amino resins such as urea-formaldehyde (UF) resin, urea-melamine-formaldehyde (MUF) resin and melamine-formaldehyde (MF) resins are polymeric condensation products of formaldehyde with urea, copolymers of urea and melamine, or melamine. UF adhesive is the major binder in particleboard industry which has many advantages, such as water solubility, fast curing, good performance in the wood-based panel, and low price. Disadvantages are formaldehyde emission from the panels and low resistance to water. The formaldehyde emission from the panels used for interior applications was one of the factors affecting sick building syndrome in an indoor environment. Therefore, the formaldehyde emission issue has been one of the most important aspects of UF resin in the last few decades.

It is known that hydrolysis of cured UF resin is a major factor affecting formaldehyde emission of UF adhesive bonded wood panels. The curing reaction is reversible under hydrolysis, and subsequently the formaldehyde is emitted into the environment. Another way how to improve UF adhesive properties is modifying the UF adhesive with various substances. Results of testing of UF adhesive added with melamine showed that that a higher F/U mole ratio and greater melamine content in the MUF resin decreased formaldehyde release. However, the hydrolytic stability of cured MUF resin could quite differ from the one in wood-based composite panels (Park *et al.* 2009). The incorporation of the modified starch in UF resins at different stage of the synthesis was studied by Zhu *et al.* (2014). With the increasing addition amount of modified starch, the bonding strength of plywood first improved and then decreased. Formaldehyde emission of plywood was decreased significantly. To diminish formaldehyde emission, Ghafari *et al.* (2016) investigated replacement of the formaldehyde by furfural in UF resin. Urea formaldehyde furfural (UFF) resin was synthesized approximately the same as synthesis of UF resin by replacement of the formaldehyde by furfural. Results indicated that formaldehyde emission and modulus of rupture of panels reduced. Internal bonding strength of panels made using modified resin was superior to others.

There have been published a lot of experimental results concerning the reduced formaldehyde emission from wood based materials glued with UF adhesives. Research was aimed at various substances added into UF adhesives such as organic polymers, starch, collagen, chemical substances, minerals, sorbents (Khodosova *et al.* 2010, Costa *et al.* 2014, Kim et al. 2007, Sedliačik *et al.* 2011).

Pulp and paper secondary sludge was tested as co-adhesive and formaldehyde scavenger for particleboard bonded with UF adhesive (Xing *et al.* 2013). The results indicated that the use of sludge gives a possibility to produce particleboards at reduced UF resin content. What was the most important, formaldehyde emission was reduced. The reduction on formaldehyde emission and recycling of pulp and paper secondary sludge as co-adhesive was the most important environmental benefits.

The mechanism of reduction of formaldehyde emission is still not fully understood. It could be linked to presence of reactive functional groups in modifiers added into UF adhesive and their ability to capture free formaldehyde emitted from panels. Wood mass, whether it is wood or recyclable wastes from forestry and wood processing industry, is a prospective source of lignocellulosic raw material. In the technological process of hydrolysis pretreatment of lignocellulosic biomass, hemicelluloses are hydrolyzed to soluble sugars and cellulose is spited into shorter chains. To monitor changes in the structure of macromolecules, the infrared spectroscopy is used. By interpretation of spectrum of cellulose, the functional groups can be identified (Kučerová and Výbohová 2014).

The aim of this study was to modify UF adhesive in order to reduce the formaldehyde emission by testing of two various waste products – cellulose sludge and wood bark – as formaldehyde scavengers. Another of our goals was to monitor the formaldehyde emissions within a few weeks after gluing of experimental plywood.

MATERIAL AND METHODS

UF adhesive and additives

In the experiments a commercially available UF adhesive was used. The adhesive was modified with two various additives – cellulose sludge or wood bark. The cellulose sludge (CS) powder particles were smaller than 0.06 mm. Wood bark (WB) powder was a mixture consisting of 50 % of beech bark (*Fagus sylvatica*) and 50 % of spruce bark (*Picea abies*).

Shear strength of UF adhesive mixtures

The strength properties of the adhesive bonds were tested on plywood. UF adhesive mixtures were prepared as follow: the reference UF adhesive and the UF adhesive modified with 5 % additives added (cellulose sludge or wood bark). The adhesive spread was 160 g.m^2. Three-layer alder plywood was pressed at temperature of 105 °C, specific pressure of 1.8 MPa, and pressing time 5 minutes. The plywood was conditioned in normal climate (temperature 20 ± 5 °C, 65 % relative humidity) for 7 days. The shear strength test was performed in accordance to the standard EN 314-1 and EN 314-2 after preliminary conditioning. Shear strength was measured and evaluated using a tensile testing machine LabTest 4.050 (LaborTech) with 5 kN head. The speed of the jaws was 2 mm/min, the bonds collapsed within 30 ± 10 seconds. Ten specimens were tested for each adhesive mixture for both ways of conditioning (conditioning in normal climate or immersing in water of 20 °C for 24 hours).

The differences between the mean values of shear strength of specimens bonded with various adhesive mixtures were evaluated statistically by one-factor ANOVA.

Formaldehyde emission

To determine formaldehyde emission, five-layer alder plywood was made. Emission was determined by 24-hour desiccator method in accordance with JIS 1460 standard. The emitted quantity of formaldehyde was obtained from the concentration of formaldehyde absorbed in distilled water when the test pieces of specified surface area (1800 cm^2) were placed in the desiccator filled with 300 ml of water and 24 h has elapsed. Concentration of formaldehyde absorbed in water was determined according to the principle based on the Hantzsch reaction, in which the formaldehyde reacts with ammonium ions and acetylacetone. Formaldehyde emission was measured for seven weeks in 7 days intervals.

RESULTS AND DISCUSSION

Shear strength

UF adhesives are generally tested according to EN 314-2 for class 1, the test specimens were conditioned according to the relevant procedure; the test specimens were immersed in water at 20 °C for 24 hours and then tested wet. The results of the shear strength measurement after soaking are shown in Tab. 1.

After 24 hours soaking, the highest average strength of 2.93 MPa was reached by UF adhesive modified with CS. The reference UF adhesive strength was almost the same – 2.91 MPa. Adhesive bond of UF adhesive with WB added reached the lowest shear strength of 2.12 MPa. All adhesive compositions

Table 1

Table of descriptive statistics for shear strength

Adhesive mixture	Shear strength [MPa]	Confidence interval		[n]	Standard deviation [MPa]	Shear strength [MPa]		Coefficient of variation [%]
		- 95.00 %	95.00 %			Min.	Max.	
UF ref.	2.91	2.680	3.134	10	0.32	2.43	3.45	10.9
UF + CS	2.93	2.787	3.075	10	0.20	2.40	3.10	6.8
UF + WB	2.12	1.926	2.308	10	0.27	1.72	2.53	12.6

Note: Required shear strength 1.0 [MPa]

achieved the shear strength more than two-times higher than the strength required by the standard (1.0 MPa). All adhesive bonds meet criteria according to the EN 314-2 for bonding in Class 1. Examining the pattern of the break, it was seen that the break surface for all samples was covered with wood fibres.

The obtained results were processed statistically using one-factor analysis of shear strength. One-way analysis of variance for adhesive composition shows that the factor "adhesive mixture" affects the shear strength statistically significant (significance level $p < 0.05$). From the results of Duncan test (Tab. 2) it can be assessed whether the difference between two mean values of shear strength of each adhesive composition is statistically significant.

According to the results of Duncan test, it can be seen that between reference UF adhesive and the adhesive mixture modified by SC is not any significant difference. But the adhesive with WB achieved significantly lower shear strength when compared with strength of the reference UF adhesive and also the strength of the adhesive with CS added. The differences between shear strength of the three adhesive mixtures are shown in the Figure 1 (95 % confidence intervals).

Formaldehyde emission

To measure formaldehyde emission, the desiccator method according to JIS A 1460 was chosen. Formaldehyde emission was tested at 5-layer plywood glued with examined adhesive mixtures. The emission was measured on the 7th day after pressing. The values of formaldehyde emission are presented in Table 3.

Formaldehyde emission from 5-layer reference plywood (UF ref. adhesive) reached the value of 0.604 mg/l. If the value is taken as 100 %, the emission from the boards bonded with UF with SC was lower by 10.4 %. The board with WB showed no significant reduction in emission (emission reached the value of 96.7 %).

Within further research, formaldehyde emissions from boards were measured over seven weeks in 7 days intervals. The results are shown in Fig. 2.

During the experiment the emission from the panel bonded with reference UF adhesive was decreasing from the value of 0.604 mg/l to 0.366 mg/l (decrease by 39.4 %).

At start of the experiment the plywood glued with

Table 2

Duncan test for shear strength

Adhesive mixture	{1}	{2}	{3}
Shear strength	M = 2.9070	M = 2.9310	M = 2.1170
UF ref. {1}		0.842	0.000
UF+CS {2}	0.842		0.000
UF+WB {3}	0.000	0.000	

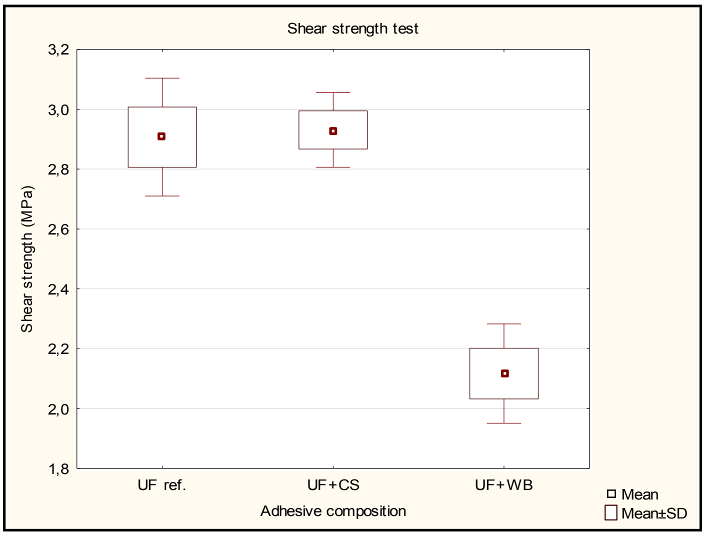

Fig. 1. Graph 95 % confidence intervals for shear strength at wet specimens

Table 3

Formaldehyde emission from plywood (desiccator on day 7 after gluing)

Adhesive mixture	Formaldehyde emission [mg/l]	Emission compared to reference [%]
UF ref.	0.604	100.0
UF + SC	0.541	89.6
UF + WB	0.584	96.7

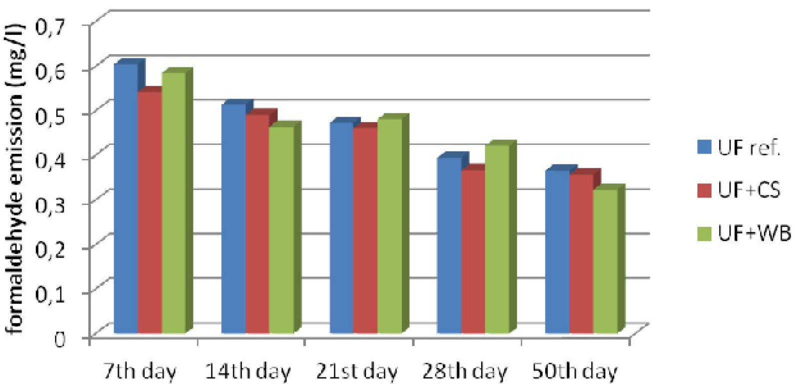

Fig. 2. Formaldehyde emission during experiment

UF with CS added showed the emission of 0.541 mg/l. When compared to the other adhesive compositions, it was the lowest value. During the experiment the emission has decreased to the value of 0.357 mg/l (decrease by 34.1 %).

The board glued with the UF adhesive with WB added showed the emission of 0.584 mg/l at start of the experiment. During the experiment the emission has decreased to the value of 0.323 mg/l (decrease by 44.7 %). When compared to the other adhesive compositions, the board glued with UF with WB added showed the lowest value at the end of the experiment.

When comparing the results of measurements of formaldehyde emissions for various UF adhesive compositions (Fig. 3), can be seen that each adhesive mixture shows the same trend with time. If compared to the previous week each following week, the emissions were lower and lower. The only exception was the board glued with UF with WB added. After 21 days of the experiment, the measured value of emission was higher (0.481 mg/l) than previous week value (0.465 mg/l). But the difference in values of emission was minimal.

Emission from the reference UF adhesive was decreasing almost regularly: 0.604 – 0.514 – 0.473 – 0.395 – 0.366 mg/l. During the experiment the emission has decreased by 39.4 %. Emission from the UF adhesive mixture with WB showed a more pronounced downward trend between the first and second week after gluing and then in the last two weeks of the experiment. 0.584 – 0.465 – 0.481– 0.421– 0.323 mg/l. During the experiment the emission has decreased most significantly, by 44.7 %. The value of the emission form the UF adhesive composition with CS added was gradually reducing throughout the experiment, but during the last two weeks it has reduced minimally. Emis-

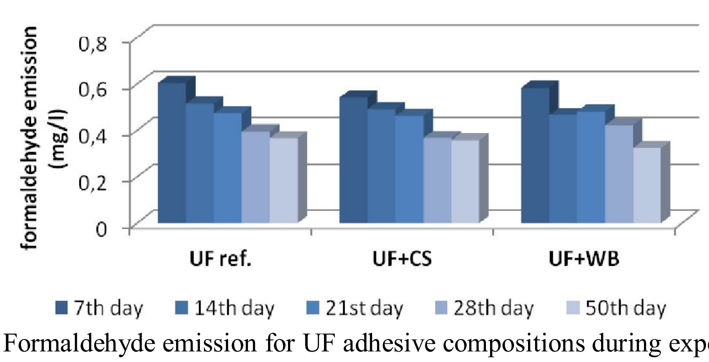

Fig. 3 Formaldehyde emission for UF adhesive compositions during experiment

sion values were 0.541 – 0.491 – 0.461 – 0.367 – 0.357 mg/l. During the experiment the emission has decreased by 34.1 %.

Secondary sludge from three pulping processes was used as co-adhesive in particleboard production and tested by Xing *et al.* (2013). The results showed formaldehyde emission decreased if compared to emission of control panels. Depending on the type of sludge and its proportion in UF adhesive, the emission was decreased by 6.7 %, 25.2 % or 48.3 %. Emission decreased as the sludge was added into UF adhesive, but the amount of UF did not decrease. So the decrease in emissions was not due to replacement of the UF adhesive by the sludge. Emission decreased markedly with the sludge content. Secondary sludge can have high nitrogen content, inferring the presence of proteins. Substances rich in proteins are expected to reduce formaldehyde emission. Protein macromolecules contain functional groups that may react with formaldehyde.

CONCLUSIONS

Industrial UF adhesives are designed to be able to glue in the environmental grade of E1. But there is still a need to study about environmental friendly materials for solving indoor air quality problem. The research was aimed at modified UF adhesive in order to reduce formaldehyde emission. The commercial available UF adhesive was modified by cellulose sludge powder or wood bark powder, added in amount of 5 %.

Shear strength of the adhesive bond was tested on three-layer alder plywood. Shear strength of all the tested UF adhesive mixtures met the standards. When tested according to EN 314-2 for class 1, the mean shear strength reached the values from 2.1 to 2.9 MPa.

Formaldehyde emission was determined by 24-hour desiccator method. On the 7th day after gluing emission from the reference adhesive was 0.604 mg/l. Emission from the modified adhesive mixtures was a little lower (0.541 mg/l for cellulose sludge and 0.584 mg/l for wood bark). All formaldehyde emission values were of grade F*** (average 0.5 mg/l) according to JIS A 1460.

After 7 weeks of the experiment, the reference UF adhesive showed formaldehyde emission decreased by 39 %. Emission from plywood glued with UF adhesive with cellulose sludge was lower by 34 %. The most significant decline in emission was measured at the board with wood bark – reduction by 45 %. All formaldehyde emission values were of grade F**** (average 0.3 mg/l) according to JIS A 1460, which is approximately equivalent of class E1 to requirements of EN 636.

Based on obtained results, it can be concluded that the tested additives for UF adhesive have a positive impact to reduce the formaldehyde emissions from wood-based panels. Also, using waste (cellulose sludge from paper production industry, and wood bark) in modifying of UF adhesives can contribute to the quality of the environment.

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