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WOOD-BASED PANELS WITH LOW FORMALDEHYDE EMISSION BY COLLAGEN AND KERATIN BIOPOLYMERS

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ABSTRACT

Urea formaldehyde (UF) adhesives are the most commonly used for wood-based panels, but their main disadvantage is an intensive formaldehyde emission. The aim of the investigation was to reduce the release of formaldehyde from UF bonded wood materials by developing and testing new and more efficient modifiers that bind formaldehyde and form more stable methylene bonds resistant to hydrolysis of the adhesive. Methylol pre-condensate additives with varying ratios of glutaraldehyde and urea modified by fibril proteins based on collagen and keratin were tested. The measurements confirmed the decrease of formaldehyde at all concentrations of methylol pre-condensate compared to the reference sample. Formaldehyde emissions were evaluated from five-layer plywood according to JIS A 1460 (2001): "Building boards. Determination of formaldehyde emission. Desiccator method". The most significant decrease of formaldehyde emission up to 37% was achieved with the application of 5% methylol pre-condensate into UF adhesive standard. The gluing quality has been assessed according to standards EN 314-1 and EN 314-2 and the tested plywood meet the requirements of the standard for Class 1 – suitable for application in the interior.

Key words: wood-based panels, urea-formaldehyde resin, collagen, keratin, plywood.

INTRODUCTION

Bonding has an important role in the creation of wood based materials and it is a key process in the efficient utilisation of wood sources. There is a growing interest in the utilisation of renewable resources for the development of environmentally friendly adhesive systems for production of bonded wood products. Polycondensation adhesives are obtained from non-renewable resources and emitting formaldehyde is known as potential carcinogen (He 2017). Proteins are gaining interest in this field due to their inherent adhesive properties and capability in formaldehyde scavenging. Collagen and keratin are renewable materials, and their sources are almost unlimited. Therefore, there is an effort to constantly improve existing products and find new options for their application and processing (Matyašovský et al. 2014).

Collagen occurs in the entire world of living organisms, and belongs to the technically most important fibril proteins. Collagen represents 25-30% of all proteins in an animal body. It creates the main organic factor of skin, bones, cartilages, tendons, and connective tissues. Collagen is the main material of leather industry for the production of leather (about 4 mil ton of collagen is processed every year).

Keratins are defined as certain filament-forming proteins with specific physicochemical properties. They are extracted from the cornified layer of the epidermis. Currently, the term ‘keratin’ covers all intermediate filament-forming proteins with specific physicochemical properties and produced in any vertebrate epithelia (Bragulla and Homberger 2009).

The stability of aminoplastic thermosetting adhesives and the problem of toxicity of urea-formaldehyde (UF) adhesives is generally solved by the addition of additives that releasing formaldehyde (fd) binds or creates more stable methylene linkages. They are more resistant to reversible hydrolysis of the adhesive to achieve increased resistance to weathering and humid conditions (Langmaier et al. 2004, Maminski et al. 2006, Wang and Pizzi 1997).

The aim of the research was to determine the influence of methylol pre-condensate additives based on glutaraldehyde, urea, collagen and keratin on the basic parameters of adhesive mixtures as adhesive system lifetime, condensation time, viscosity, formaldehyde emission and quality of glued joint.

EXPERIMENTAL METHODS

Two variants of modifier samples with varying ratios of glutaraldehyde and urea were prepared for application to UF polycondensation resin: MOD-I and MOD-II.

Composition of UF adhesive systems:

1. Standard – UF.
2. Addition of 1.25, 2.5, 5.0 and 10% methylol pre-condensate MOD-I.
3. Addition of 1.25, 2.5, 5.0 and 10% methylol pre-condensate MOD-II.

Prepared adhesive systems were tested for their lifetime, condensation time and viscosity. Formaldehyde emission and quality of glued joint were determined on three resp. five layer plywood. Rotary-peeled alder wood veneers (*Alnus glutinosa*) with nominal thickness of 1.5 mm and moisture content of ~5% were used. Tangential sheets of veneer were cut into 300 ×300 mm pieces for plywood assembly. Only veneer sheets without visible defects were selected. Conditions of plywood pressing (laboratory hydraulic press FONTIJNE) were as follows: pressing temperature 105 °C, specific pressure 1.8 MPa and pressing time 5 min for three layer and 7 min for five layer plywood. Prepared plywood were conditioned at the ambient temperature of (20 ± 2) °C and relative humidity (65 ± 5) %.

The quality of gluing was determined on three layer plywood test pieces prepared according to standards EN 314-1 and EN 314-2 for the Class of gluing 1 (interior normal conditions): immersion for 24 h in water at (20 ± 3) °C.

Formaldehyde emission was tested from five layer plywood of alder according to standard testing method JIS A 1460 (2001). Building boards. Determination of formaldehyde emission. Desiccator method.

RESULTS AND DISCUSSION

Testing the influence of additives MOD-I and MOD-II on lifetime and condensation time of UF adhesive systems at 45 °C and 100 °C.

The influence of addition of MOD-I and MOD-II with the concentration of 1.25, 2.5 and 5.0% on condensation time and lifetime of UF adhesive systems is described in Tables 1 and 2.

Table 1: Influence of MOD-I on lifetime of UF adhesive mixtures at 45 °C and condensation time at 100 °C

Sample No.	Lifetime and condensation time of adhesive mixture at the temperature of	
	45 °C	100 °C
0 – Reference sample	75 ± 2 min	55 ± 2 s
1.25% MOD-I	73 ± 2 min	52 ± 2 s
2.5% MOD-I	70 ± 2 min	50 ± 2 s
5.0% MOD-I	74 ± 2 min	53 ± 2 s
10.0% MOD-I	78 ± 2 min	65 ± 2 s

Table 2: Influence of MOD-II on lifetime of UF adhesive mixtures at 45 °C and condensation time at 100 °C

Sample No.	Lifetime and condensation time of adhesive mixture at the temperature of	
	45 °C	**100 °C**
0 – Reference sample	75 ± 2 min	55 ± 2 s
1.25% MOD-II	72 ± 2 min	53 ± 2 s
2.5% MOD-II	68 ± 2 min	50 ± 2 s
5.0% MOD-II	73 ± 2 min	54 ± 2 s
10.0% MOD-II	78 ± 2 min	60 ± 2 s

Adhesive systems have a comparable lifetime and condensation time with a reference sample of unmodified UF adhesive. The measurements confirmed a slight decrease in the lifetime of the adhesive mixtures at 1.25 and 2.5% concentration of methylol pre-condensate MOD-I and II compared to the reference sample.

Testing the influence of additives MOD-I and MOD-II on formaldehyde emission.

Resulting effect of methylol pre-condensate MOD-I and II on the emission of releasing fd from prepared plywood is shown in Figure 1.

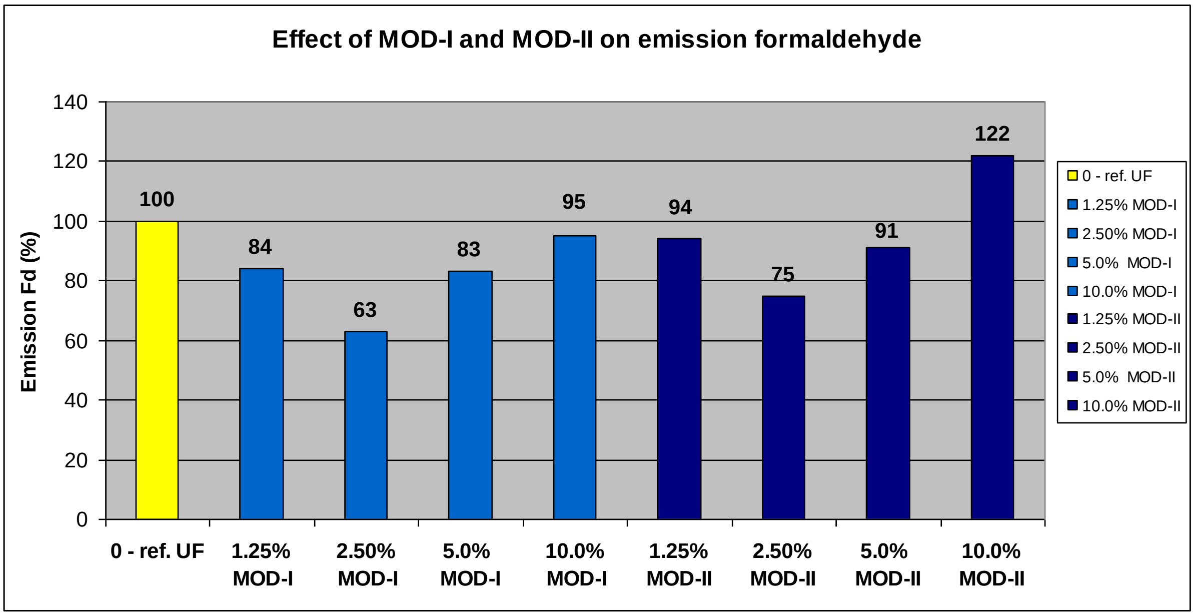

Figure 1: Formaldehyde emission stated by desiccator method

Performed measurements confirmed the decrease of formaldehyde emission for all MOD-I concentrations compared to the reference sample. The most significant decrease in fd emission up to 37% was achieved for 2.5% methylol pre-condensate application into UF resin. The measurements also confirmed the decrease of formaldehyde for MOD-II compared to the reference sample. The most significant decrease in fd emission up to 25% was achieved for 2.5% MOD-II application into the UF standard. Formaldehyde emissions were increased by 22% compared to the reference sample for application of 10% of MOD-II.

Testing the influence of methylol pre-condensate MOD-I and II on bonding quality

The results and basic statistical evaluation of the influence of modifications on the shear strength of the plywood test pieces are shown in Table 3 and are shown graphically in Figure 2. European standard EN 314-2 requires the value of shear strength above 1.0 MPa.

Table 3: Shear strength of plywood test pieces

Sample No.	Shear strength and statistic evaluation					
	avg x (MPa)	stdev s (MPa)	var coeff v_k (%)	min value (MPa)	max value (MPa)	n
0 – UF standard 1, 2, 3 – (1.25, 2.5, 5)% methylol pre-condensate MOD-I						
0	1.95	0.17	9.2	1.65	2.22	15
1	2.11	0.16	7.0	1.85	2.44	15
2	2.41	0.16	6.7	2.22	2.64	15
3	2.15	0.19	9.2	1.82	2.44	15
4, 5, 6 – (1.25, 2.5, 5)% methylol pre-condensate MOD-II						
4	2.05	0.21	10.2	1.71	2.26	15
5	2.70	0.21	7.2	2.40	3.15	15
6	2.11	0.14	7.4	1.85	2.24	15

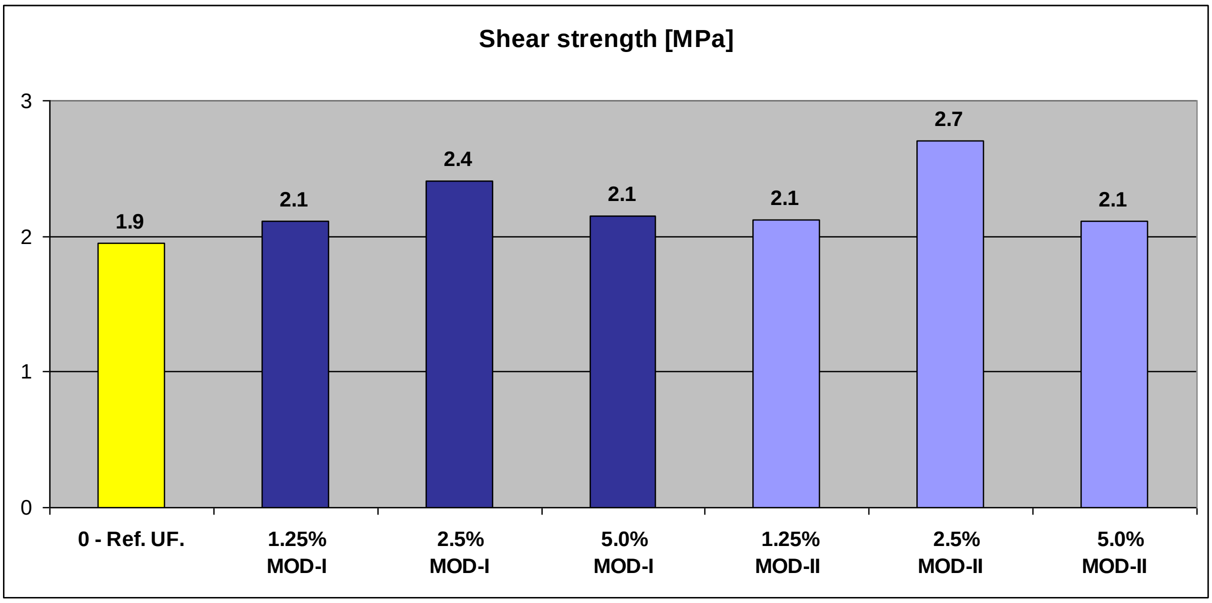

Figure 2: Influence of MOD-I and MOD-II on shear strength of plywood

The measurements confirmed the increase in shear strength of the bonded joint for all MOD-I and MOD-II concentrations compared to the reference sample.

Based on obtained results, the research was continued by modification of UF adhesive mixtures with multifunctional aldehyde and urea (MOD-I and MOD-II) together with natural biopolymer based additives.

Type and marking of prepared natural biopolymer additives:

0. Reference sample UF resin – KRONORES CB 1639F
1. MOD-I + keratin 10% – prepared from sheep wool at VIPO
2. MOD-I + cysteine 10% – amino-acid prepared at VIPO from keratin of sheep wool
3. MOD-II + keratin 5%
4. MOD-II + cysteine 5%

Composition of adhesive systems:

0 – Reference – 100 % UF resin + 20% technical flour + 4% hardener.

1–4 – 98% UF resin + 20% technical flour + 2% additive (1–4) + 4% hardener.

Testing the viscosity of proposed adhesive systems

The results of the dynamic viscosity stated on rotational viscometer at the temperature of 20 °C of the prepared adhesive systems were comparable with the reference sample of UF adhesive composition, all variants were about 5000 mPa.s.

Testing the bonding quality

Obtained results of the influence of modifications on the shear strength of the test pieces of plywood are shown graphically in Figure 3.

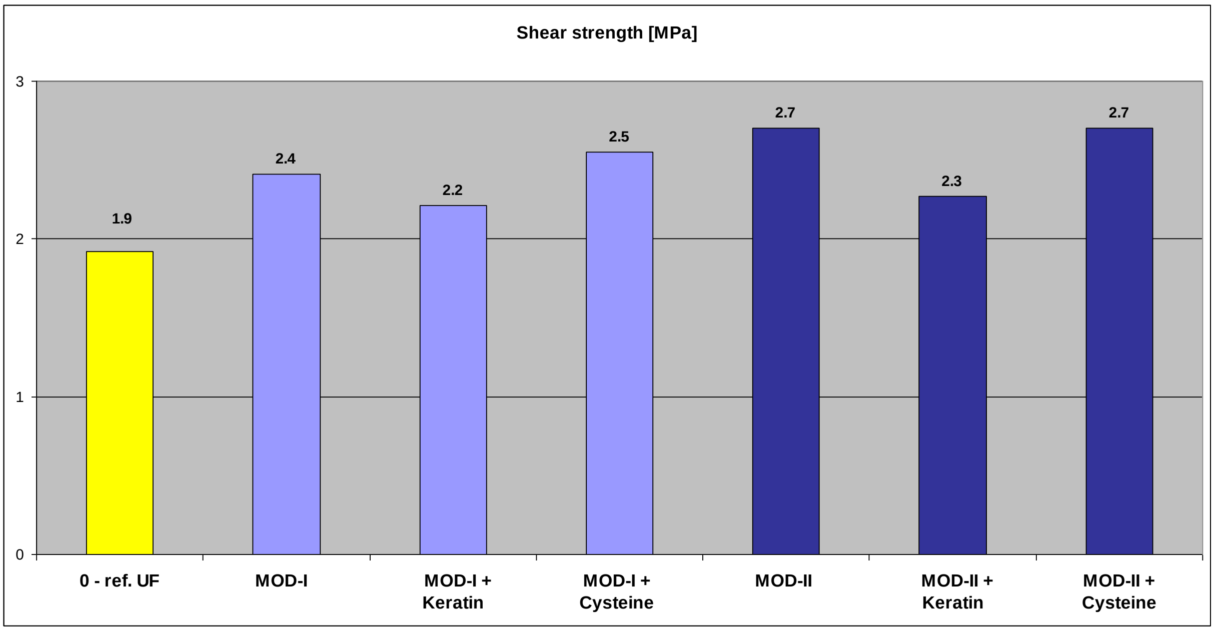

Figure 3: Results of shear strength of plywood

The tested plywood is suitable for use in normal interior conditions. The best result compared to the reference sample was achieved with the modification MOD-I + 5% cysteine and MOD II + 10 % cysteine.

Testing the formaldehyde emission

The measured values of the extinction of the tested solutions with formaldehyde are graphically presented in Figure 4. They confirmed the strong decrease of formaldehyde emission for all additives compared to the reference sample. The most significant decrease in fd emission up to 39% was achieved with modifications of MOD-I + Cysteine = 0.223 (mg/l) and MOD-II + Cysteine = 0.225 (mg/l).

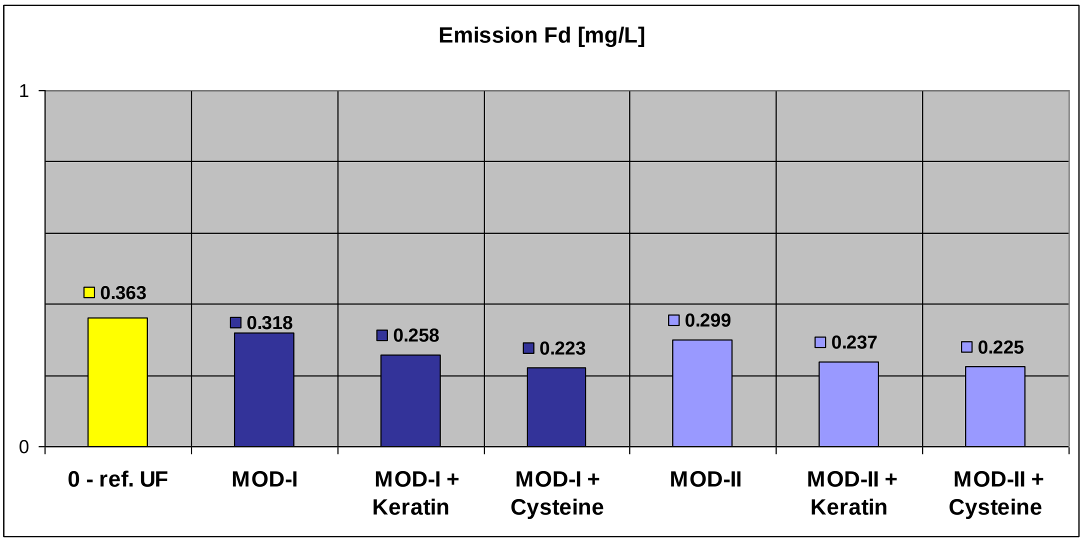

Figure 4: Formaldehyde emission stated by desiccator method

CONCLUSIONS

These carried out experiments confirmed the proposal of modification of polycondensation adhesives, mainly urea-formaldehyde, used for production of wood-based materials with improved hygienic properties with minimized content and emission of volatile formaldehyde. The application of natural biopolymer based additives into urea-formaldehyde adhesive systems do not influence their lifetime, condensation time and viscosity. All measurements of formaldehyde emission confirmed that used additives significantly reduce formaldehyde release from plywood compared to the reference sample. The most significant decrease was recorded at the sample of UF resin + technical flour + MOD-II + cysteine. The quality of gluing of plywood with all proposed UF adhesive systems fulfils requirements of the standard for class of gluing 1 – they are suitable for normal interior applications.

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REFERENCES

BRAGULLA, H.H., HOMBERGER, D.G. 2009. Structure and functions of keratin proteins in simple, stratified, keratinized and cornified epithelia. Journal of Anatomy, 214(4): 516–559.

EN 314-1: 2005. Plywood. Bonding quality. Part 1: Test methods.

EN 314-2: 1998. Plywood. Bonding quality. Part 2: Requirements.

HE, Z. 2017. Bio-based wood adhesives. Preparation, characterization, and testing. CRC Press, Taylor&Francis Group. Boca Raton, FL: 356 p.

JIS A 1460: 2001. Building boards. Determination of formaldehyde emission. Desiccator method.

LANGMAIER, F., ŠIVAROVÁ, J., KOLOMAZNÍK, K., MLÁDEK M. 2004. Curing of urea-formaldehyde adhesives with collagen type hydrolysates under acid condition. Journal of Thermal Analysis and Calorimetry, 76: 1015-1023.

MAMINSKI, M.L., PAWLICKI, J., PARZUCHOWSKI, P. 2006. Improved water resistance and adhesive performance of a commercial UF resin blended with glutaraldehyde. The Journal of Adhesion, 82(6): 629–641.

MATYAŠOVSKÝ, J., SEDLIAČIK, J., MATYAŠOVSKÝ, J.JR., JURKOVIČ, P., DUCHOVIČ, P. 2014. Collagen and keratin colloid systems with a multifunctional effect for cosmetic and technical applications. 2014. Journal of the American Leather Chemists Association, 109(9): 284–295.

WANG, S., PIZZI, A. 1997. Succinaldehyde-induced water resistance improvements of UF wood adhesives. Holz als Roh- und Werkstoff 55: 9–12.

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