ACTA FACULTATIS XYLOLOGIAE ZVOLEN, 65(1): 57−62, 2023
Zvolen, Technická univerzita vo Zvolene
DOI: 10.17423/afx.2023.65.1.05

KERATIN AS A FORMALDEHYDE SCAVENGER FOR ENVIRONMENTALLY FRIENDLY WOOD-BASED PANELS

Ján Sedliačik – Ján Matyašovský – Peter Duchovič – Igor Novák – Peter Jurkovič

ABSTRACT

The use of polycondensation urea-formaldehyde (UF) resins in the woodworking and furniture industries is widespread due to their relatively low price, high reactivity, availability of raw materials, and ease of use. After curing, they provide a transparent, brittle joint, but their main disadvantage is the continuous emission of formaldehyde. The naturally occurring biopolymer keratin and the amino acid cysteine prepared from sheep wool were chosen and tested as possible agents for UF adhesives, allowing the reduction of formaldehyde emissions from wood-based panels. Emissions of formaldehyde were determined in accordance with EN ISO 12460-4. The gluing quality was tested according to standard EN 314-1, and the tested plywood met the requirements of standard EN 314-2. The most significant decrease in formaldehyde emission by up to 44.0% was achieved by applying 1% MOD-I (pre-condensate of glutaraldehyde and urea + cysteine) to the reference UF adhesive. Therefore, samples prepared for this study have great potential for application as environmentally friendly formaldehyde scavengers.

Keywords: keratin, urea-formaldehyde resin, plywood, formaldehyde emission, scavenger

INTRODUCTION

It is generally known that biopolymers, especially proteins, have the ability to bind free formaldehyde and thus act as formaldehyde scavengers. Research conducted on the modification of adhesives for the woodworking industry is aimed at natural, non-toxic, biologically degradable, and cheap biopolymers. The industry offers a large number of biopolymers, e.g., collagen and keratin, and waste sources from food and leather production can be used for technical applications, e.g., as modifiers of adhesives for the woodworking industry. Possibilities of effective processing and applications of sheep wool, leather tanned, and non-tanned waste for different products were described earlier by several authors (Pünterer 1995, Buljan *et al*., Matyašovský *et al*. 2011). Controlled enzymatic hydrolysis of leather waste has the advantage of lower energy consumption, especially when using available commercial proteases of microbial origin (Kolomazník *et al*. 2000, Sun and Zhong 2000). The advantage of this procedure may be the control of the average molecular weight of the hydrolysate by selecting the reaction time of the enzymatic hydrolysis. Proteins of amino-acids with peptide bonds are the source of a large number of amino-groups – NH_2, which are reactive with formaldehyde. The fibrous character of collagen presents a similar analogy with cellulose fibres and its structure can be stabilized with chemical bonds, e.g., formaldehyde, glutaraldehyde, etc. Another advantage of biopolymers is their non-toxicity and biodegradation ability for basic structural elements (Matyašovský *et al.* 2001).

For adhesives, the modification reactions of proteins have significance. Proteins lose their original solubility by affecting of formaldehyde. This property is used for lowering formaldehyde emission from UF adhesives, increasing the water resistance of leather glue, and increasing the resistance of albumin glues (Sedliačik and Sedliačiková 2009).

The shear strength of a glued joint directly depends on its resistance to humidity. The research aimed not only at the study of the properties of wood and adhesives but also as glued products are exposed to the environment in which they are located, and to study their interactions.

Langmaier *et al*., (2004) used a hydrolysate of chromium waste from the leather industry obtained by enzymatic hydrolysis. The non-isothermal thermogravimetric method (TGA) was used for the investigation of condensation reactions of dimethylol-urea (DMU) and its mixtures with different weight contents of urea, hydrolysate, and acid hardener. The proteins extracted from waste leather production, which are known for their reactivity with formaldehyde, can be used as selected modifying additives. Langmaier *et al*., (2005) used non-isothermal gravimetry and studied the condensation kinetics of dimethylol urea with urea and collagen prepared by enzymatic hydrolysis. They have found that the addition of collagen decreases the rate of formation of unstable dimethylenether crosslinks in favour of more stable methylene bonds. The thermo-oxidative stability of different materials and biopolymers was tested by differential scanning calorimetry (DSC). The method is based on determining the end of the induction period or the beginning of the primary oxidation process (Šimon and Kolman 2001, Šimon 2006).

Literary reviews and practical requirements indicated the existence of the potential to apply modifiers of protein hydrolysates for adjusting the parameters of wood adhesives, particularly polycondensation UF resins. Biologically active natural products are suitable to be used for new applications in the technology of polycondensation adhesives (Ružiak *et al*., 2017, Sedliačik *et al*., 2011, Zhao *et al*., 2012). Experimental research was aimed at the preparation of adhesive mixtures and testing their influence on formaldehyde emission and the strength of glued joints.

The aim of the study was to reduce the release of formaldehyde from wood materials by developing and testing new, more effective keratin-based environmental modifiers that bind formaldehyde and form more stable methylene bonds and their effect on the bond strength of wood-based panels.

MATERIALS AND METHODS

Commercial UF resin, generally used for plywood production, with a solid content of 66.2%, a density of 1.27 g/m^3, a pH of 7.6, a viscosity of 1250 mPa.s at 20 °C, and ammonium nitrate as a hardener, was used to prepare the basic adhesive mixture.

The modification of UF adhesives was investigated by the preparation and application of four samples of keratin hydrolysates and amino acid cysteine, which were laboratory prepared from sheep wool ‘Merino’ of the following composition: nitrogen 12.15 %, ash 2.53 %, sulphur 2.21 %, and fat 7.16 %. Before the process of hydrolysis, the wool was separated, washed, defatted, and dried at room temperature. An increase in stability and efficiency of the amino acid cysteine was solved by its modification with the additive MOD-I, which was prepared by pre-condensation of glutaraldehyde and urea. Description and labelling of originally prepared samples:

- Keratin K-1 – prepared by acid hydrolysis and neutralized with NaOH,
- Keratin K-2 – prepared by oxidative hydrolysis,
- Keratin K-9 – prepared by alkaline hydrolysis and neutralized with HCl,
- Keratin K-11 – prepared by alkaline-oxidative hydrolysis.
- Cysteine – prepared from sheep wool that was modified with glutaraldehyde and urea, and marked as (MOD-I),

Modified adhesive mixtures were prepared as 0, 0.5, 1, and 3% solutions of added biopolymers into UF resin, e.g., reference 100% UF; 99.5% UF + 0.5% biopolymer; 99.0% UF + 1.0% biopolymer; 97.0% UF + 3.0% biopolymer. Furthermore, wheat flour was added in an amount of 10% as an extender and ammonium nitrate in an amount of 5% as the hardener.

Plywood quality of gluing and shear strength testing were performed according to standards EN 314-1 and EN 314-2. Five-layer plywood panels of birch (*Betula*) veneer with dimensions of 32×32 cm were prepared for the determination of physical and mechanical properties under the following conditions: adhesive consumption of 160 g/m^2, pressing (laboratory hydraulic press FONTIJNE) pressure of 1.8 MPa, temperature of 105 °C and time of 6 min. Plywood samples were conditioned at a temperature of 20 ± 2 °C and a relative humidity of 65 ± 5 % for 7 days and cut into 20 pieces of each variant. Tested pieces were pre-treated for class 1 and tested according to these conditions:

- immersion in water at 20 °C for 24 hours,
- constant rate loading,
- disruption after 30 ± 10 seconds,
- accuracy of 1 N.

Formaldehyde emissions from prepared plywood were tested by the desiccator method according to the test method EN ISO 12460-4 complying with the following conditions:

- volume of desiccator: 9-11 dm^3,
- loading coefficient: 1 800 cm^2,
- temperature of 20 ± 0.5 °C,
- test duration: 24 h.

The concentration of formaldehyde absorbed in distilled water was evaluated by the acetyl-acetone method with spectrophotometric evaluation using the ultraviolet spectrophotometer UviLine SI 5000 at 412 nm wavelength and counted as an average of two parallel measurements.

RESULTS AND DISCUSSION

Reduction of formaldehyde emission

Formaldehyde emissions from prepared plywood were tested according to the test method EN ISO 12460-4. The results and evaluation of the effect of the presented modifications on formaldehyde emissions from wood-based boards (plywood glued with UF adhesives) expressed in percentages are graphically shown in Figure 1.

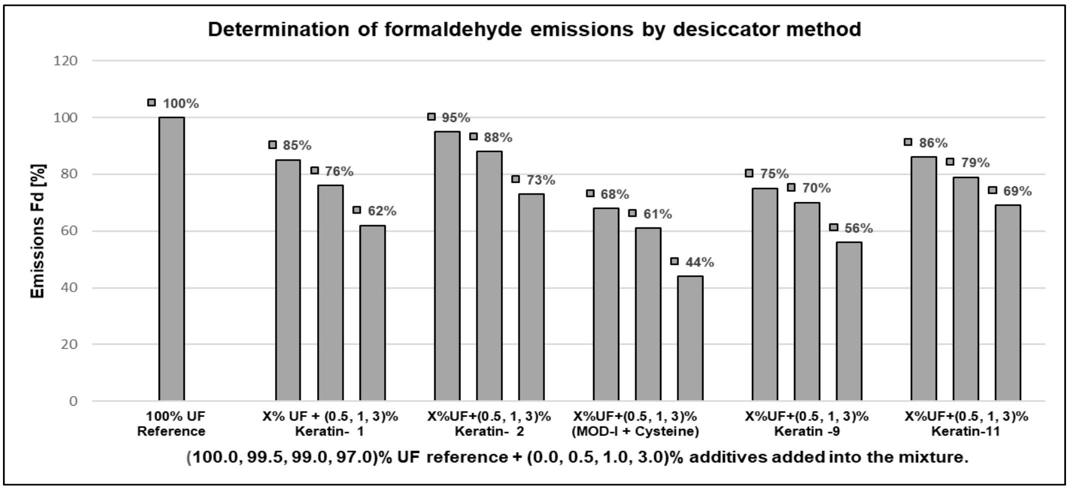

Fig. 1 Results of formaldehyde emission by desiccator method.

Measured values of extinctions of samples of UF glue confirmed the lowering of formaldehyde emissions for each concentration of additives prepared from biopolymer keratin in comparison with the reference sample. The most significant decrease in formaldehyde from wood-based panels, up to 44%, was achieved with the modification of sample No. 6. e.g., 97% UF + 3% cysteine (prepared from sheep wool) + MOD I (prepared by modifying glutaraldehyde with urea).

Shear strength of plywood panels

The quality of gluing was tested on five-layer plywood according to standards EN 314-1 and EN 314-2. The results and evaluation of the effect of the presented modifications on the shear strength of wood-based panels (plywood glued with UF adhesives) expressed in percentages are graphically shown in Figure 2.

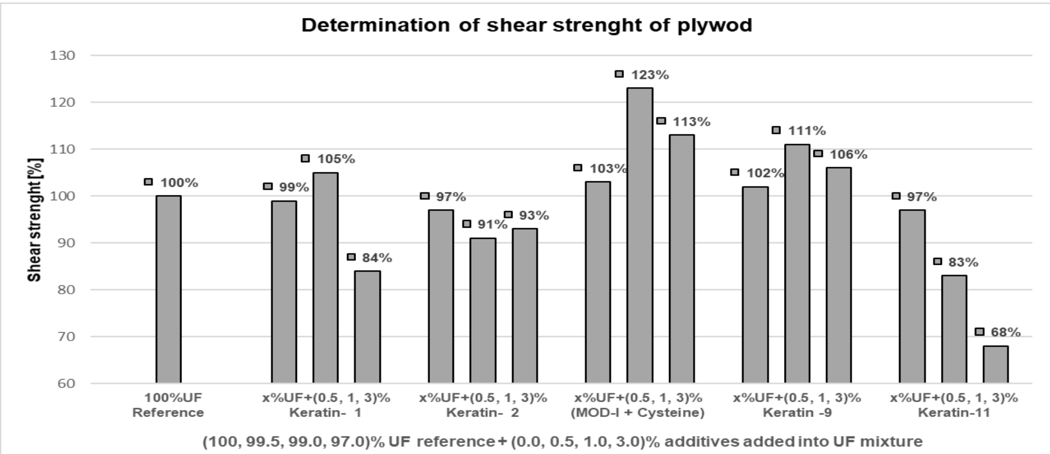

Fig. 2 Influence of modifications UF adhesive by additives prepared from keratin on shear strength of plywood.

European standard EN 314-2 requires a value of shear strength above 1.0 MPa. Tested plywood fulfils the requirement of the standard for class of gluing 1 – they are suitable for application in a normal interior environment. The highest shear strength of 2.24 MPa was obtained for sample No. 6 – 99% UF adhesive + 1% (MOD-I prepared by modification glutaraldehyde with urea + cysteine prepared from sheep wool), which corresponds to an increase in shear strength of 123% compared to the reference UF sample.

Shear strength above 2.0 MPa was also achieved with samples of the following compositions: 97% UF adhesive + 3% (MOD I modified with cysteine) and 99% UF adhesive modified with 1.0% Keratin K-9. The shear strength of the plywood test pieces decreases slightly with increasing concentrations of biopolymers in the mixture of UF adhesives.

CONCLUSIONS

This investigation was focused on modifications of natural biopolymer keratin and their possible application, mainly for the reduction of formaldehyde release from wood-based materials. Adding keratin and cysteine prepared from sheep wool to UF adhesives proved to lower formaldehyde emission from plywood panels in all cases. It was confirmed that a sample of amino acid cysteine modified with glutaraldehyde and urea (MOD-I) achieved the highest decrease in formaldehyde emissions and the highest shear strength of plywood samples compared to the reference UF sample.

ACKNOWLEDGEMENTS

This work was supported by the Slovak Research and Development Agency under the contracts No. APVV-18-0378 and APVV-19-0269. This work was supported by the project VEGA 1/0264/22.

REFERENCES

Buljan, J., Reich, G., Ludvík, J., 1997. Mass Balance in Leather Processing". Centenary Congress of the IULCS, London, 138–156.

Kolomazník, K., Mládek, M., Langmaier, F., Janáčová, D., Taylor, M.M., 2000. Experiences in Industrial Practice of Enzymatic Dechromation Shavings. Journal of the American Leather Chemists Association 95, 55–63.

Langmaier, F., Kolomazník, K., Mládek, M., Šivarová, J., 2005. Curing urea-formaldehyde adhesives with hydrolysates of chrome-tanned leather waste from leather production. International Journal of Adhesion and Adhesives 25, 101–108.

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.

Matyašovský, J., Kopný, J., Meluš, P., Sedliačik, J., Sedliačik, M., 2001. Modifikácia polykondenzačných lepidiel bielkovinami. Pokroky vo výrobe a použití lepidiel v drevopriemysle. TU Zvolen, 37–42.

Matyašovský, J., Sedliačik, J., Jurkovič, P., Kopný, J., Duchovič, P., 2011. De-chroming of chromium shavings without oxidation to hazardous Cr^{6+}". Journal of the American Leather Chemists Association 106, 8–17.

Pünterer A. 1995. The Ecological Challenge of Producing Leather. Journal of the American Leather Chemists Association 90, 206–215.

Ružiak, I., Igaz, R., Krišťák, L., Réh, R., Mitterpach, J., Očkajová, A., Kučerka, M., 2017. Influence of Ureaformaldehyde Adhesive Modification with Beech Bark on Chosen Properties of Plywood. BioResources 12(2), 3250–3264.

Sedliačik, J., Matyašovský, J., Šmidriaková, M., Sedliačiková, M., Jurkovič, P., 2011. Application of Collagen Colloid from Chrome Shavings for Innovative Polycondensation Adhesives. Journal of the American Leather Chemists Association 106(11), 332–340.

Sedliačik J., Sedliačiková M., 2009. Innovation tendencies at application of adhesives in wood working industry. In: Annals of Warsaw University of Life Sciences – SGGW. Forestry and Wood Technology, Warszawa, No 69, s. 262–266.
Sun, S., Zhong, Z., 2000. Adhesives from modified soy proteins. In Wood Adhesives 2000. Extended Abstracts. Nevada: Forest Products Society, 5–6.
Šimon, P., 2006. Induction periods – theory and applications. Journal of Thermal Analysis and Calorimetry 84, 263–270.
Šimon, P., Kolman, L., 2001. DSC study of oxidation induction periods. Journal of Thermal Analysis and Calorimetry 64, 813–820.
Zhao, Y., Ding, Z., 2012. The Application of Keratin in the Field of Wood Adhesive. World Automation Congress Proceedings, Puerto Vallarta; Mexico, 1–5.
EN 314-1: 2004. Plywood. Bonding quality. Part 1: Test methods. European Committee for Standardization: Brussels, Belgium.
EN 314-2: 1993. Plywood. Bonding quality. Part 2: Requirements. European Committee for Standardization: Brussels, Belgium.
EN ISO 12460-4: 2016. Wood-based panels. Determination of formaldehyde release. Part 4: Desiccator method. European Committee for Standardization: Brussels, Belgium.

AUTHORS' ADDRESSES

Prof. Ing. Ján Sedliačik, PhD.
Technical University in Zvolen
Department of Furniture and Wood Products
T.G. Masaryka 24
960 01 Zvolen
Slovakia
sedliacik@tuzvo.sk

Ing. Ján Matyašovský, PhD.
Ing. Peter Jurkovič, PhD.
Ing. Peter Duchovič
VIPO, a.s.
958 01 Partizánske
Slovakia
jmatyasovsky@vipo.sk
pjurkovic@vipo.sk

Ing. Igor Novák, CSc.
Slovak Academy of Sciences
845 41 Bratislava
Slovakia
igor.novak@savba.sk