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Influence of modified collagen on parameters of adhesive mixtures. Part: I. Influence of collagen modifications on adhesion, biodegradability and formaldehyde emission

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Abstract: *Influence of modified collagen on parameters of adhesive mixtures. Part: I. Influence of collagen modifications on adhesion, biodegradability and formaldehyde emission*. The work describes possibility to lower formaldehyde emission in wood products glued with urea-formaldehyde (UF) adhesives at keeping of required strength of glued joints. Results of laboratory and industrial tests confirmed, that collagen biodegradable additive modified with urea is suitable modifier for lowering of formaldehyde emission from hardened UF adhesive mixtures. Increased efficiency of collagen was reached by modification of standard hardener with di-aldehyde. Industrial tests at plywood production confirmed lowering of formaldehyde emission in comparison with standard production down to 30 %, stated according to EN 120.

Keywords: collagen, UF resin, glutaraldehyde, formaldehyde, viscosity, modifier, starch

INTRODUCTION

Research of modification of adhesives for woodworking industry is aimed on natural non-toxic, biologically degradable and cheap biopolymers. Market offers large amount of biopolymers (e.g. collagen waste from food and leather productions), which can be used as modifiers of adhesives for woodworking industry. Proteins of amino-acids with peptide bond are the source of large amount of amino-groups $-NH_2$, which are reactive with formaldehyde (fd). Fibril character of collagen presents similar analogy with cellulose fibres and its structure can be stabilised with chemical bond e.g. formaldehyde, glutaraldehyde etc. Another advantage of biopolymers is their non-toxicity and biodegradation ability to basic structural elements[1,2].

For adhesives, modification reactions of proteins have the significance. Proteins lose their original solubility by affecting of formaldehyde. This property is used for lowering of formaldehyde emission from UF adhesives, increasing of water resistance of leather glue and also increasing of resistance of albumin glues[3,4].

Langmaier et al.[5,6] in their experiments used hydrolysate of chromium waste from leather industry obtained with enzymatic hydrolysis. Non-isothermic thermo-gravimetry (TGA) was used for investigation of condensation reactions of di-methylol-urea (DMU) and their mixtures with different weight content of urea, hydrolysate or acid hardener.

Glutaraldehyde (GA) is chemical matter, which is often tested for modification of hardeners, there is the assumption, that will be completely built-in cross-linked structure of adhesive. MAMINSKI et al.[7] investigated addition of GA as 50 % water solution into hardener for melamine-UF adhesive. Shear strength of birch samples (*Betula verrucosa*) glued with modified adhesive was significantly higher as control. There is a direct chemical bond of GA with chemical chains of wood, what significantly improves the strength of glued joint. This is proved by higher ratio of wood fibre failure, modified adhesive had much stronger interaction adhesive – wood.

Wood is hygroscopic material due to hydrophilic behaviour of cellulose, hemicellulose and lignin. It was proved, that proteins are able to create bonds with different forms of cellulose, what is used at purification and separation of different types of proteins on cellulose. Polus-Ratajzak et al.[8] prepared experiments with proteins in interaction with cellulose and lignin. Chemical changes of cellulose and lignin during the reaction were evaluated by infra-red spectroscopy (IRS). Changes of spectra proved chemical reaction between peptide chain and reactive groups present in chains of cellulose and lignin.

EXPERIMENTAL PART

Material and methods

In experimental work, we used urea-formaldehyde (UF) adhesive KRONORES CB 1639F (Diakol Strážske, s.r.o.) and hardener R-60 (Duslo, a.s. Šaľa). Natural polymers were based on collagen, obtained from waste in leather industry (leather collagen – hydrolysate). Activator based on glutaraldehyde (VIPO a.s. Partizánske) – water solution of aldehyde mixture (AG) was used for modification of hardener R-60. Sample plywood we prepared from beech (*Fagus sylvatica*) veneer, spread of adhesive mixture was 160 $g.m^{-2}$. Other pressing conditions (laboratory hydraulic press FONTIJNE): pressing temperature 105 °C, specific pressure 1,8 MPa, pressing time 5 min. The content of formaldehyde in plywood was determined by perforator method according to EN 120:1995. Dry content matter was determined gravimetrically according to EN 322.

RESULTS AND DISCUSSION

Experimental work was aimed on testing the influence of modification of collagen colloids on adhesive properties – above all lowering of formaldehyde emission, viscosity, surface tension, life time and strength of glued joint.

Collagen additive for UF adhesives

Influence of collagen modifications on formaldehyde emission from UF adhesives

The aim of research was lowering of formaldehyde emission from UF adhesives with application of modified collagen hydrolysates, hardeners and additives. In laboratory conditions, technology of preparation of modified collagen hydrolysate marked as **VIPOCOL TM** was optimised for application into UF adhesives.

Tab. 1 Parameters of collagen hydrolysate VIPOCOL TM for application into UF and MUF adhesives

Physical and chemical parameters		
1.	General information Look, smell	Light brown water dispersion, characteristic as amino-acids
2.	Important health, safe and environment information Combustibility, solubility in water Consistency Ford 4	Non-combustible liquid, dry content matter 55 ± 2 %, pH 5,5 ± 0,2, boiling temperature 100 °C, mix with water unlimited, 15 ± 2 s.
3.	Storage ability	min. 3 month

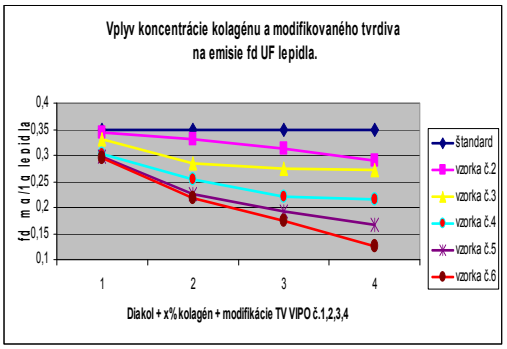
Composition of adhesive mixtures with collagen:

1. UF + 3 % hardener – standard,
2. UF + 3 % hardener + (2,5,8,10) % substitution of adhesive with collagen modified by urea,
3. UF + 3 % VIPO N.1 + (2, 5, 8, 10) % substitution of adhesive with collagen colloid modified with urea,
4. UF + 3 % VIPO N.2 + (2, 5, 8, 10) % substitution of adhesive with modified collagen,
5. UF + 3 % VIPO N.3 + (2, 5, 8, 10) % substitution of adhesive with collagen,
6. UF + 3 % VIPO N.4 + (2, 5, 8, 10) % substitution of adhesive with collagen.

Hardeners VIPO N.1, 2, 3, 4 = Hardener R-60 standard + modification (1, 2, 3, 4) % of dialdehyde. Results of measurements of the influence of modifications of hardeners VIPO and collagen colloid on the content of free fd in 1 g of hardened UF adhesive mixture are described in the Table 2.

Tab. 2 Formaldehyde emission from modified samples

Modification samples	Emission Fd mg/1g	Emission Fd mg/1g	Emission Fd mg/1g	Emission Fd mg/1g
standard N.1	0,35	0,35	0,35	0,35
sample N.2	0,344	0,33	0,313	0,29
sample N.3	0,33	0,285	0,274	0,272
sample N.4	0,302	0,254	0,22	0,215
sample N.5	0,297	0,225	0,192	0,167
sample N.6	0,296	0,219	0,174	0,126



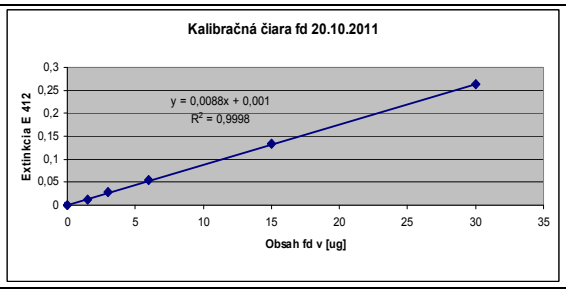
From measured results follow, that collagen colloids are suitable modifiers for lowering of fd emissions in hardened UF adhesive mixtures. The efficiency of collagen is possible to increase with modification of standard hardener R 60 by dialdehyde, and this efficiency is increasing with concentration of collagen and dialdehyde. Measurements in VIPO confirmed lowering of fd content in comparison with reference sample down to 50 %. Industrial experiments were done in the company DYAS – Czech rep. at plywood production.

Tab. 3. Analysis of fd emission from industrial test – 3-layer plywood, EN 120

Sample	E 412 nm	Content fd mg/1000 ml	Dry content matter [%]	Weighed moist [g]	Weighed dry [g]	mg fd/100g dry board
1,5% TV VIPO	0,0251 0,0259	2,8986	94,96	102,9551	97,766	**2,96**
3,5% TV VIPO	0,0288 0,0287	3,2680	94,27	102,6993	96,815	**3,37**
Dukol – standard	0,0342 0,0341	3,8873	94,31	102,9117	97,056	**4,00**

Tab. 4 Calibration line of formaldehyde

[µg fd] in 10 ml off solution stated with acetyl acetone	E 412
0	0
1,5	0,0128
3	0,0278
6	0,0546
15	0,1346
30	0,2632



Results of laboratory and industrial tests confirmed, that collagen additive modified with urea is suitable modifier for lowering of formaldehyde emission from hardened UF adhesive mixtures. Increased efficiency of collagen was reached by modification of standard hardener with di-aldehyde. Industrial tests at plywood production confirmed lowering of formaldehyde emission in comparison with standard production down to 30 %, stated according to EN 120.

CONCLUSIONS

The problem of recovery of raw material of leather industry from renewable sources with the aim to apply for lowering of formaldehyde emission from hardened UF adhesives was investigated. Tested modifications of collagen and standard hardener enable to lower formaldehyde emission from hardened UF adhesives.

Obtained results in VIPO Partizánske and in industrial conditions of DYAS (Czech rep.) confirmed, that collagen additives prepared in VIPO Partizánske are possible to use for lowering of formaldehyde emission at keeping mechanical and physical parameters of gluing.

REFERENCES

1. ŠMIDRIAKOVÁ, M., SEDLIAČIK J., MATYAŠOVSKÝ J. 2011: Prírodné polyméry na báze modifikovaného kolagénu ako čiastočná náhrada UF lepidla In Adhesives in Woodworking Industry. Zvolen, p.14-20.
2. MATYAŠOVSKÝ J., KOPNÝ J., MELUŠ P., SEDLIAČIK J., SEDLIAČIK M. 2001: Modifikácia polykondenzačných lepidiel bielkovinami. In: Pokroky vo výrobe a použití lepidiel v drevopriemysle. TU Zvolen, s. 37-42.
3. BLAŽEJ A. et al. 1980: Polyméry v kožiarskom, obuvníckom a galantérnom priemysle. Praha: SNTL, Bratislava: ALFA. p. 279-283.
4. 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.
5. LANGMAIER F., KOLOMAZNÍK K., MLÁDEK M., ŠIVAROVÁ J. 2005: Curing urea-formaldehyde adhesives with hydrolysates of chrome-tanned leather waste from leather production. In: International Journal of Adhesion and Adhesives. 2005, 25, p. 101-108.
6. LANGMAIER F., ŠIVAROVÁ J., KOLOMAZNÍK K., MLÁDEK M. 2004: Curing of urea-formaldehyde adhesives with collagen type hydrolysates under acid condition. In: Journal of Thermal Analysis and Calorimetry. 76, p. 1015-1023.
7. MAMINSKI M.L., PAWLICKI J., PARZUCHOWSKI P. 2006: Improved water resistance and adhesive performance of a commercial UF resin blended with glutaraldehyde. In: The Journal of Adhesion. 82, p. 629-641.
8. POLUS-RATAJCZAK I., MAZELA B., GOLINSKI P. 2003: The chemical interaction of animal origin proteins with cellulose and lignin in wood preservation. In: Annals of Warsaw Agricultural University. No. 53. SGGW Warszawa, p. 296–299.
9. STN EN 120: 1995: Drevné materiály. Zisťovanie obsahu formaldehydu. Extrakčný postup zvaný „perforátorová metóda“.
10. STN EN 322: 1995: Dosky z dreva. Zisťovanie vlhkosti.

Streszczenie: *Wpływ zmodyfikowanego kolagenu na parametry klejów. Część 1: Wpływ modyfikacji kolagenu na adhezję, biodegradowalność oraz emisję formaldehydu*. Praca opisuje możliwości obniżenia emisji wolnego formaldehydu w wyrobach z drewna klejonych przy pomocy żywic mocznikowo-formaldehydowych przy zachowaniu wymaganej wytrzymałości połączeń. Badania laboratoryjne oraz testy przemysłowe potwierdziły że dodatek biodegradowalnego kolagenu zmodyfikowanego mocznikiem jest odpowiednim dodatkiem do obniżenia emisji wolnego formaldehydu z utwardzonych spoin mocznikowo-formaldehydowych. Zwiększona wydajność kolagenu została zapewniona poprzez modyfikację utwardzacza za pomocą bi-aldehydu. Testy przemysłowe przy produkcji sklejek powwierdziły obniżenie emisji wolnego formaldehydu do 30% standardowych wartości, zgodnie z normą EN 120.

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