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Lowering of formaldehyde emission from modified UF resin with collagen polymers

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Abstract: *Lowering of formaldehyde emission from modified UF resin with collagen polymers.* Presented work describes the possibility of lowering the formaldehyde emission from wood products glued with urea-formaldehyde (UF) adhesive. Results of laboratory tests confirmed, that collagen prepared from leather waste is suitable additive for lowering of formaldehyde emission from wood products glued with UF adhesive. Increased efficiency of collagen was obtained by modification with urea and di-aldehyde. Tests confirmed the decrease of formaldehyde content in comparison with the standard down to 50 % stated by perforator method.

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

INTRODUCTION

The research of modification of adhesives is aimed on utilisation of products, which are easy accessible and their application save the costs for resin production. On the market, there is large amount of biopolymers, which as secondary raw material can be used for modification of adhesives with the aim to keep and/or increase the quality of adhesives and also glued joints. Leather and food industry produces amount of different biopolymer waste, which pollutes the environment (**Pünterer 1995, Buljan et al. 1997, Matyašovský et al 2011**).

Protein waste arising at the processing of leather consist approx. of 55% carbon, 21% oxygen, 7% hydrogen, 17% nitrogen, and/or sulphur and phosphorus and their properties are conditioned by the chemical composition, amino acid sequence, molecular size, and dimensional structure. Besides peptide bond, in proteins there are very often covalent disulphide bond (disulphide bridge) and other covalent bonds, e.g. ester (**Blažej et al. 1978, Blažej A. et al. 1980, Blažej A. et al. 1984**).

For the preparation of adhesives, they have special importance modifying reactions of proteins. By affecting of formaldehyde (fd), proteins lose their original solubility. This property is used to reduce formaldehyde emission of UF adhesives, increase the resistance of leather glue against moisture, and also the increase resistance of albumin glues, and at the manufacture of artificial horn. Fibril character of collagen is analogic with cellulose fibres and its structure can be stabilised by chemical bond e.g. formaldehyde, glutaraldehyde etc. Substantial advantage of biopolymers is their non-toxicity and ability of biodegradation into their constituent elements (**Blažej et al. 1975, Langmaier et al. 2005**).

The shear strength of glued joint directly depends on the resistance against humidity. Suitable modification of adhesive mixtures can reach better cross-linking of the structure of hardened adhesive, increase of durable chemical bonds and lowering of the hydrolysis of adhesive. The research aimed not only on the study of properties of wood and adhesives, but as glued products are also the subject exposed to the environment in which they are located, and also to study their interactions (**Šmidriaková et al. 2011, Matyašovský et al. 2001**).

In woodworking industry, at present, the most used adhesives are polycondensation urea-formaldehyde (UF) resins. Their wide application in wood and furniture industry enables their

relative low price, high reactivity, availability of raw materials and easy applicability, after hardening they provide transparent, but fragile joints. UF adhesives are thermo-reactive resins, they cross link in wide interval of temperatures, they have relatively short condensation time and they are resistant against micro-organisms.
Emission of formaldehyde and harmful effect of formaldehyde is still a problem mainly for products used in interior. Adversely affects the respiratory system, eyes, skin, genetic material, reproductive organs, it has a strong effect on the central nervous system (Příhoda 1988). The International Agency for Research on Cancer (IARC) categorises formaldehyde as carcinogen, which can cause allergies.
Langmaier et al 2004 in his experiments used hydrolysate of chromium waste from leather industry obtained by enzymatic hydrolysis. Nonisothermal thermogravimetric method (TGA) was used at investigation of condensation reactions of dimethylolurea (DMU) and its 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, which is completely crosslinked into the structure of the adhesive.
Maminski et al. 2006 investigated melamine-urea-formaldehyde (MUF) adhesive, they added GA into the hardener in form of 50 % water solution. Shear strength of birch samples glued with modified adhesive was significantly higher in comparison with the reference sample. Also, there is a direct bond of GA with chemical compounds of wood, what significantly increase the strength of glued joint. The percent of fibre destruction was much higher, modified adhesive proved stronger interaction adhesive-wood.
The stability of amino-plastic thermoset adhesives is important hygienic parameter, therefore the research effort is aimed on reduction, and/or avoiding of formaldehyde release from glued material.
When curing adhesives, present acidic hardeners increase the rate of both types of cross-linking bonds of adhesive structure (non-stable dimethyl-ether and also more stable methylene bonds), but also influence the transformation of dimethyl-ether bonds to methylene. With lowering of amount of dimethyl-ether cross link bonds in hardened adhesive film of amino plastic, we are able to reduce the emission of formaldehyde in hardened film.

The aim of the research is to decrease the formaldehyde content in UF adhesives by application of collagen colloid, hardener and additives. In laboratory conditions, there were optimised the technology of collagen preparation and their modifications.

MATERIAL AND METHOD

In the experimental research, UF resin KRONORES CB 1639F and hardener ammonium nitrate (R-60) was used. Natural modifiers of UF resins were raw materials based on collagen prepared from waste of leather industry. For modification of collagen hydrolysate were applied: urea, di-aldehyde, and glycerol.
Collagen samples:
Collagen No. 1 – collagen hydrolysate prepared from waste of leather industry,
Collagen No. 2 – collagen hydrolysate modified with urea,
Collagen No. 3 – collagen hydrolysate modified with urea and glutaraldehyde.
Laboratory tested plywood was prepared form beech wood (*Fagus sylvatica*); the spread of adhesive mixture was 160 $g.m^{-2}$. The pressing conditions (laboratory hydraulic press FONTIJNE): pressing temperature 105 °C, specific press 1,8 MPa, pressing time 5 min. The formaldehyde content in glued material was determined by perforator method FESYP according to EN 120. Dry matter content was determined gravimetrically according to EN 322.

EXPERIMENTAL PART

Experimental research was aimed on testing the influence collagen hydrolysate prepared from leather waste and its modifications on adhesive properties – mainly on lowering of fd emission, viscosity, surface tension, life time and strength of glued joint. Parameters of collagen colloid for application into UF resins are in Table 1.

Table 1. Physical and chemical parameters of dry collagen colloid

Size of particles	60 Mesh or 0.25 mm
Bloom at concentration 6.67% and temperature 10 °C	191
Viscosity at concentration 6.67% and temperature 60 °C	2.6 mPa.s
pH	5.2
Dry content matter	90.8%
Ash	< 2%

Composition of UF adhesive mixtures:

Standard – KRONORES CB 1639F + 3 % hardener R-60,

Modification 1 – KRONORES CB 1639F + 3 % hardener R-60 + (2, 5, 8, 10%) substitution of resin with collagen,

Modification 2 – KRONORES CB 1639F + 3 % hardener R-60 + (2, 5, 8, 10%) substitution of resin with collagen modified with urea,

Modification 3 – KRONORES CB 1639F + 3 % hardener R-60 + (2, 5, 8, 10%) substitution of resin with collagen modified with urea and glutaraldehyde.

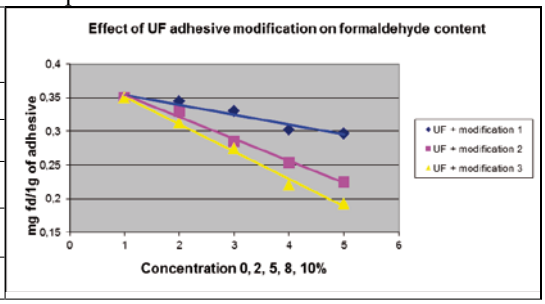
RESULTS AND DISCUSSION

The influence of collagen modification on the content of formaldehyde in UF adhesives

Results of the influence of UF resin modification on the content of free fd in 1 g hardened UF adhesive mixture are presented in Table 2.

Table 2. Formaldehyde content in modified samples

Sample	Mod 1 fd mg/g	Mod 2 fd mg/g	Mod 3 fd mg/g
Standard (0%)	0,35	0,35	0,35
Concentration 2%	0,33	0,31	0,29
Concentration 5%	0,28	0,27	0,27
Concentration 8%	0,25	0,22	0,21
Concentration 10%	0,22	0,19	0,17



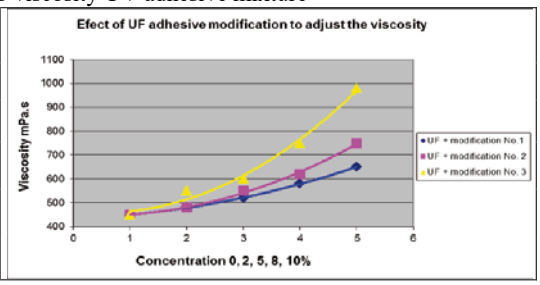
From obtained results follow, that collagen is suitable modifier for lowering of fd content in hardened UF adhesive mixtures. Collagen modified with urea and glutaraldehyde most significantly lowers fd content, and this effect is stronger with increasing concentration from the value of the reference sample 0,35 mg fd/g down to 0,17 mg fd/g of hardened adhesive.

The influence of addition of modified collagen colloids No.1, 2, 3 on viscosity of UF adhesive mixture

The influence of addition of modified collagen colloids in different concentrations on the viscosity of UF adhesive mixture is presented in Table 3.

Table 3. Effect of modification of collagen to viscosity UV adhesive mixture

Sample	Mod 1 mPa.s	Mod 2 mPa.s	Mod 3 mPa.s
Standard (0%)	450	450	450
Concentration 2%	480	480	550
Concentration 5%	520	550	600
Concentration 8%	580	620	750
Concentration 10%	650	750	980

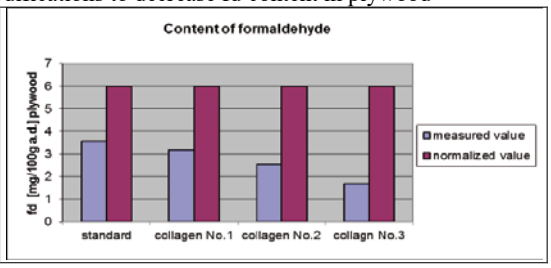


Modification 1 increases the viscosity of UF adhesive at 10% concentration up to 650 mPa.s.
Modification 2 increases the viscosity of UF adhesive at 10% concentration up to 750 mPa.s.
Modification 3 most significantly increases the viscosity of UF adhesive at 10% concentration up to 980 mPa.s.
Investigation the changes of viscosity of UF adhesive mixtures confirmed, that collagen jellies are suitable modifiers of UF adhesive viscosity.

The influence of collagen modifications on hygienic properties of plywood
The formaldehyde content in wood material was tested by the perforator method according to EN 120. The addition of different concentrations of modified samples of collagen with reactive amino-groups was tested on ecologic parameters of wood products. Obtained results confirmed the decrease of formaldehyde content in comparison with the reference sample. Results of measurements of the influence of modification and concentration of collagen colloids No. 1, 2, and 3 on the formaldehyde content in prepared plywood with UF adhesive mixtures are presented in Table 4.

Table 4. Effect of collagen colloid and its modifications to decrease fd content in plywood

Standard – KRONORES CB 1639F + 3 % hardener R-60 – reference sample 3,57 fd /100g absolutely dry (a.d.) sample
Collagen No. 1 – lowers fd emission to 3,17 fd /100g a.d. sample
Collagen No. 2 – lowers fd emission to 2,54 fd /100g a.d. sample
Collagen No. 3 – most significantly lowers fd emission to 1,68 fd /100g a.d. sample



Results of laboratory tests confirmed, that collagen prepared from leather waste is suitable additive for lowering of formaldehyde emission from wood products glued with UF adhesive. Increased efficiency of collagen was obtained by modification with urea and di-aldehyde. Tests confirmed the decrease of formaldehyde content in comparison with the standard down to 50 % according to perforator method.

CONCLUSION
The recovery of secondary raw material of renewable resources from leather industry was solved with the aim to apply it after modification for lowering of the formaldehyde content in hardened UF adhesive and treatment of the viscosity of UF adhesive mixtures. Tested modifications of collagen confirmed significant decrease of formaldehyde content in hardened UF adhesives and emissions from plywood and possibilities to treat the viscosity of adhesive mixtures.

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Streszczenie: *Obniżenie emisji formaldehydu w modyfikowanej żywicy UF z polimerami kolagenowymi.* Prezentowana praca opisuje możliwości obniżenia emisji formaldehydu z materiałów drewnopochodnych spajanych klejami UF. Wyniki badań laboratoryjnych potwierdziły, że kolagen wytwarzany z odpadów skórnych jest odpowiednim dodatkiem do zmniejszania emisji formaldehydu. Zwiększoną wydajność kolagenu uzyskuje się przez modyfikację mocznikiem i di-aldehydem. Badania potwierdziły 50% zmniejszenie emisji formaldehydu, w porównaniu ze standardowymi wyrobami.

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