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Influence of modified collagen on parameters of adhesive mixtures Part: II. Parameters of collagen adhesive and its microbiologic stabilisation with colloid silver

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Abstract: *Influence of modified collagen on parameters of adhesive mixtures. Part: II. Parameters of collagen adhesive and its microbiologic stabilisation with colloid silver.* This work presents the possibility to use the modified biopolymer collagen for preparation of ecologic, biologically degradable thermoplastic adhesives. Glued joint obtained high strength and flexibility after application of modification plasticisation agents based on collagen. Industrial tests of gluing of book sheets confirmed the possibility to process adhesive in all types of machines at standard required quality. Ecologic hot-melt adhesives based on proteins are not produced in Slovakia at present.

Keywords: collagen, hot-melt adhesive, viscosity, antibacterial stability, colloid silver, plasticizer,

INTRODUCTION

Possibilities of effective processing and applications of leather tanned and non-tanned waste for different products are described in [1-5]. Controlled enzymatic hydrolysis has the advantage in lower consumption of energy, especially when using commonly available commercial proteases of microbial origin[6-8]. The advantage of this procedure can be the control of medium mole weight of hydrolysate by selection of reaction time of enzymatic hydrolysis.

Collagen is the main component of connective tissues and also belongs among technically most important fibrous proteins. Characteristic property of collagen molecule is the strength and three dimensional spiral structure created with α-chains, which rotate to regular right-handed scroll. Molecules are created mostly of glycine (26-28 %) and proline (over 15 %). Native collagen without modification is relatively difficult to process for proposed application. Collagen, similarly as other proteins, has character of amphoteric polyelectrolyte, what causes, that its ion reactions run in the dependence on pH value. Isoelectric point of native collagen is at value of pH 7,5 and it can be changed by mild affect with chemicals in the interval pH 4,5 – 8,0. Most of physical and chemical parameters of collagen have in this interval extreme values, stability is changing, reactivity, ability of hydration etc.[9,10]. This property of collagen was used at modification of adhesives for woodworking industry and production of modified thermoplastic collagen adhesives. Mutual combination of individual components of the mixture and their concentrations is enable to modify physical and mechanical properties of adhesives and their biologic degradation.
Obtained experimental results confirmed, that modified collagen gel is possible to use for preparation of ecologic thermoplastic adhesives with comparable parameters of competitive adhesives e.g. DAVIS and PLAKAL.

For increasing of microbial stability, modification with s colloid silver was laboratory tested, with regard to the significant antibacterial properties with the aim to prolong the life time of protein adhesives.

The aim of our work is the proposal of technology of adhesives preparation and investigation of the influence of obtained modified collagen on parameters of adhesive dispersions and gluing. For increasing of the life time of modified thermoplastic collagen adhesives, application of colloid silver was laboratory tested. Silver colloid was prepared form silver nitrate and silver sulphate. Antibiotic and fungicide effect of nano-silver is given by its direct penetration into bacteria and reaction of silver with –SH groups of oxidation metabolic enzymes of bacteria. A bacterium suffocates, because nano-silver creates active oxygen. Bacteria do not acquire resistance against these metals, what is the advantage opposite classical antibiotics[11].

EXPERIMENTAL PART

Used material

- Chemicals and raw materials for modification of adhesive mixtures:
  - collagen biopolymers,
  - acids, alkalies, proteases,
  - urea, glycerine,
  - paper glued materials with different thickness,
  - calcium sulphate, titanium dioxide,
  - $AgNO_3$, Ag_2SO_4 etc.
- Equipment and apparatus:
  - equipment for modification of collagen gel,
  - laboratory equipment for filling of adhesive,
  - digital pH meter,
  - refract meter,
  - viscometer.

RESULTS AND DISCUSSION

Experiments were aimed to testing the influence of modification of collagen colloids on properties of thermoplastic collagen adhesive. Laboratory tests confirmed biopolymers of animal origin (e.g. technical leather glue, gelatine etc.) as suitable raw materials for preparation of thermoplastic collagen adhesives.

Tab. 1 Technical leather glue – basic parameters of input raw material.

No.	**Parameter**	**Methods**	**Results**
1	viscosity 12,5 % (mPa.s)	ISO EN 9665	7,2
2	viscosity 17,7 % (°E)	TP - 03/95	3,13
3	strength of gel (Bloom)	ISO EN 9665	267
4	pH	ISO EN 9665	6,2
5	content of water (%)	ISO EN 9665	13,7
6	content of fat (%)	ISO EN 9665	1,70
7	content of ash (%)	ISO EN 9665	2,11
8	foam (ml)	TP - 03/95	2
9	decrease of viscosity (%) 40 °C – 24 h	TP - 03/95	0

Parameters of modified collagen for application into thermoplastic adhesives:

1. Temperature of collagen melting (130 – 170) °C – depends on amount of modification additives,
2. Moisture content (10,0 – 15,0) %,
3. Decomposition temperature – DSC (242,7 – 268) °C,
4. Size of collagen particles (50 – 60) in Mesh.

Tab. 2 Hot-melt indexes of samples – collagen + modifier Urea

Sample No.	Composition of the sample	MFI (g/10 min.)
1.	Collagen – non-crosslinked, non-modified	–
2.	Collagen +10 % modifier	0,85
3.	Collagen + 20 % modifier	2,52
4.	Collagen + 30 % modifier	9,60
5.	Collagen + 40 % modifier	23,7

Increasing content of modification matter in collagen ensured higher tensile elongation and higher melting indexes of the composite.

Tab. 3 DSC °C – Differential scanning calorimetry of biopolymer samples

Sample No.	Composition of the sample	**DSC °C**	**moisture content %**
1.	Collagen – non-crosslinked	242,7	4,15
2.	Collagen – non-crosslinked	250,3	4,09
4.	Collagen – crosslinked	268,0	0
5.	Thermoplastic collagen adhesive	do not decompose	40,12

Crosslinking of collagen and lowered content of water in collagen caused increasing of the temperature of decomposition of the composite. Technology of preparation of collagen hydrolysate was realised in the duplicator with heating to temperature max. 80 °C with the possibility to add chemicals in liquid and solid form. Chemicals – water, collagen, HCl, lyotropic agent were used for preparation of collagen standard. Hydrolysed, non-modified collagen is indefinitely soluble in water, after drying creates transparent, strong but very fragile film.

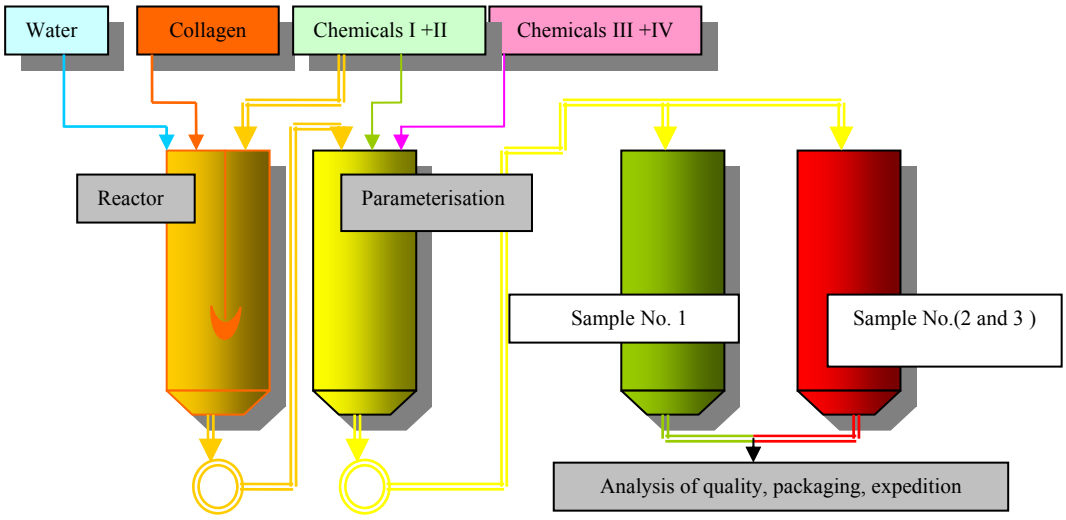

Fig. 1 Scheme of equipment for production of collagen adhesive

Equipment is accompanied by a dosing of modified collagen dispersion into polyethylene packs, where dispersion after cooling creates strong gel and at the same time, there is prevented from secondary microbiological contamination of animal hot melt adhesive. Parameters of developed hot-melt adhesives were compared with parameters of competitive adhesives e.g. DAVIS BL 150, CM 50 and PLAKAL (825, 830W, 850) RF.

Tab. 4 Qualitative parameters of collagen after plasticisation

Change of viscosity of collagen adhesives with temperature developed in VIPO					
Sample No. 1		Sample No. 2 – white adhesive		Sample No. 3 – white adhesive + inorganic filler	
Temperature	Viscosity	Temperature	Viscosity	Temperature	Viscosity
50 °C	3125 mPa.s	50 °C	8013 mPa.s	50 °C	12550 mPa.s
55 °C	2513 mPa.s	55 °C	5613 mPa.s	55 °C.	8663 mPa.s
60 °C	2113 mPa.s	60 °C	4500 mPa.s	60 °C	6825 mPa.s
65 °C	1825 mPa.s	65 °C	3713 mPa.s	65 °C	5575 mPa.s

During the industrial test, parameters of gluing of different materials were investigated: combinations: paper – (textile, leather, leatherette) etc. Qualitative parameters of adhesive sample No. 1 of non-diluted adhesive at 60 °C:

pH: 6,5 ± 0,5,
viscosity: 2100-2200 mPa.s,
refraction value: 55-60 % – dry content matter,
open time: short,
surface stickiness of adhesive: immediate.

Tab. 5 Parameters of collagen adhesives developed in VIPO in comparison with DAVIS BL 150 used in printing company FINIDR according to EN 3376

Thermoplastic adhesive	MPa concentrated	MPa diluted 1:1	MPa diluted 1:2	MPa diluted 1:4
DAVIS BL 150 – standard	1,33	0,77	0,18	0,14
Sample No. 1	1,58	1,25	0,32	0,16
Sample No. 2	2,40	0,92	0,29	0,08

Evaluation of the test

According to obtained results, adhesives prepared in VIPO reached higher tensile strength as standard commercial adhesive DAVIS. Highest tensile strength was reached with the application of non-diluted white adhesive – sample No. 2. Lowering of concentration of adhesives caused lowering of strength of white adhesive. Thermoplastic adhesives based on collagen have the value of pH in interval (6-7) and temperature of application must not exceed 70 °C, because adhesive will degrade.

Research was also aimed on preparation and application of colloid silver with the aim to prolong life time of collagen adhesives. For preparation of Ag nano-particles with controlled size, two-stage reduction was applied, where combination of smaller (approx. 10-20 nm) and bigger particles with dimensions up to hundred nm is created. Colour shade of colloidal silver depends on wavelength of the spectra and from the size and shape of nano-particles and surrounding, in which are dispersed. For example, small nano-particles of silver in water are yellow, as they have absorbency peak at wave length approx. 400 nm.

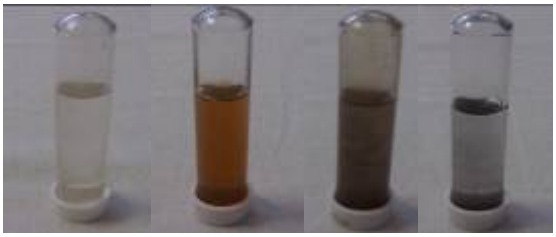

Fig. 2 Images of water dispersions of silver particles prepared by reduction of Ag^+ in ammonia. From left: dispersions – ion silver; nano-particles of silver with the size approx. 25 to 50 nm; dispersions of colloid particles of silver with the size > 100 nm; dispersions of aggregates sediment of silver particles.

Scanning electron microscope (SEM) - JEOL JIB-4000 was used for control measurements of the size and aggregation of silver particles. Procedure: polymer foil was powdered by fine layer of Au (with the thickness of 4 nm), and then, thin layer of colloid Ag was spread and water evaporated at laboratory temperature.

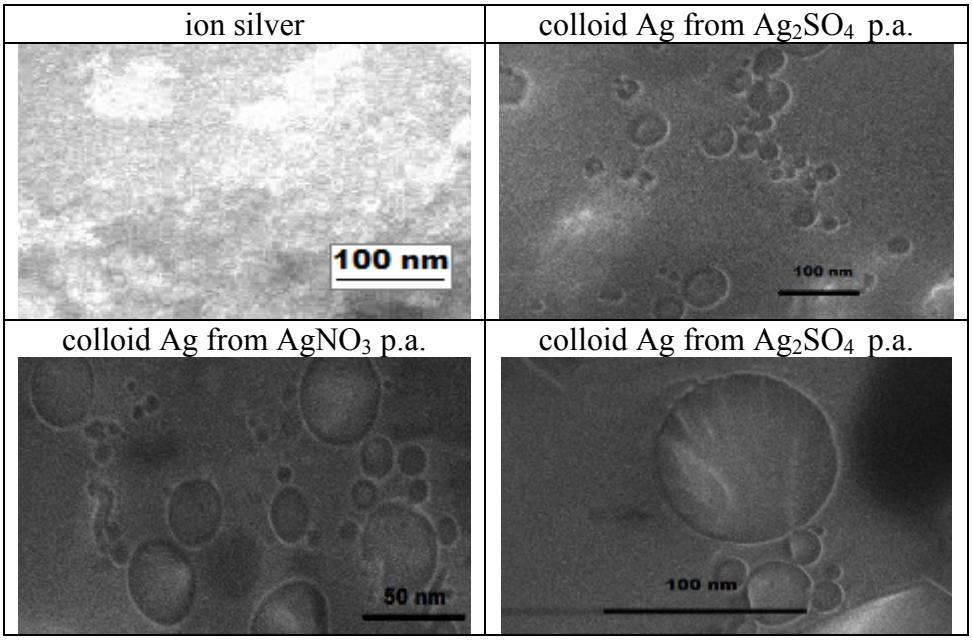

Fig. 3 SEM images illustrating the aggregation of nano-particles of silver prepared by reduction of Ag^+ in the surrounding of inorganic reducing salt of sulphur, in ammonia surrounding and following treatment of pH weak reduction matter. Shape and size of particles is comparable in the case of both applied silver salts ($AgNO_3$ p.a. and Ag_2SO_4 p.a.)

Control determination of silver was realised according to EN 31427 – Determination of silver in silver jewellery alloys. Volumetric (potentiometric) method using potassium bromide (ISO 11427:1993).

Collagen modified with colloid silver

Morphology of collagen samples with colloid silver was investigated by dual scanning microscope SEM FEI Quanta 3D (The Institute of Electrical Engineering of Slovak Academy of Sciences). Procedure: metallisation of underlay foil was realised by powdering of Au in thin layer with the thickness of 3 nm.

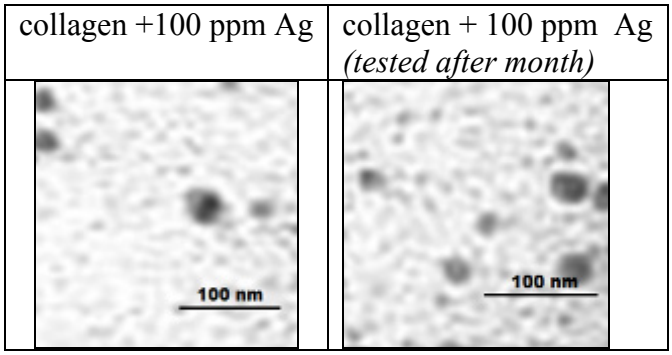

Fig. 4 SEM images of colloid silver particles and collagen hydrolysate – images illustrate long-term stability of nanoparticles of silver with collagen at the value of pH=5,7.

In laboratory conditions, there were prepared 2 samples of collagen hydrolysates, one without modification with colloid silver and another with its modification with the aim to compare IR spectra of these samples. IR spectra of samples of collagen and collagen modified with colloid Ag were comparable even after one month.

CONCLUSIONS

Evaluation of raw material from leather industry from renewable sources was investigated with the aim to apply them after modification for gluing of book sheets. Tested modifications of collagen enable to prepare thermoplastic collagen adhesive with required parameters. For increasing of the lifetime of adhesive, application of colloid silver was laboratory tested. Obtained results in VIPO Partizanske and in industrial conditions of printing company FINIDR confirmed, that collagen adhesive prepared in VIPO is possible to use without limits and parameters of gluing are comparable with commercially used adhesives.

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Streszczenie: *Wpływ zmodyfikowanego kolagenu na parametry klejów. Część II: Parametry kleju kolagenowego i jego mikrobiologiczna stabilizacja za pomocą srebra koloidalnego.* Praca prezentuje możliwość zastosowania biopolimeru kolagenowego do wytworzenia ekologicznego, biodegradowalnego kleju termoplastycznego. Połączenie klejowe wykazało wysoką wytrzymałość oraz elastyczność po modyfikacji plastyfikatorami opartymi na kolagenie. Testy przemysłowe klejenia grzbietów książek potwierdziły możliwość zastosowania otrzymanego kleju we wszystkich stosowanych maszynach przy utrzymaniu właściwej jakości. Ekologiczne kleje topliwe bazujące na białkach nie są obecnie produkowane na Słowacji.

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