ACTA TEHNICA CORVINIENSIS – Bulletin of Engineering
Tome VII [2014] Fascicule 2 [April – June]
ISSN: 2067 – 3809

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THE INVESTIGATION OF NEW POLYMERIC COMPOUNDS FOR LEATHER TREATMENT

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Abstract: *Physical and chemical properties of modern polymeric compounds have been investigated. The influence of polymers on the properties of collagen containing materials – gelatin, chrome leather and leather semi-finished item has been examined. Presumptive nature of the interaction between polymeric compounds and collagen has been ascertained. Reasonability of their usage for leather processing before dyeing has been shown. Implementation of research results in the production will help to get a leather product of high quality and to make rational use of material resources.*
Keywords: *modern polymeric compounds, physical and chemical properties*

INTRODUCTION

In the conditions of the market economy only high quality items with high consumer properties are in great demand and all these properties are defined by the state of raw materials treatment and the efficiency of applied chemical materials, especially in tanning and after tanning processes. So the actual problem to the branch is searching and motivated using of modern chemical materials for natural leather production from available raw materials. Taking into account the above mentioned the main our investigation concept is the improvement of leather treatment with the application of modern materials in order to simplify technological schemes and decrease material capacity while providing with finished goods of high quality [1-3]. The literature analysis and the practical experience of the work of leather industry enterprises testify about promising application of polymeric compounds of a new generation that impart to derma the desired properties [4-6].

This work is continuation of investigation of modern polymeric compounds properties, their influence on the collagen of derma to ascertain the efficiency of these materials usage in leather production.

The following objectives have been formulated to achieve this goal: to investigate the physicochemical properties of new polymeric compounds and compare them with the results of previous studies, to determine the effect of these materials on the properties of leather; to ascertain the nature of polymers interaction with collagen, to show the reasonability of their usage for leather treatment.

Liquid leather finishing using modern polymeric compounds has been chosen as the object of research; as a subject of research new polymeric compounds in the form of derivatives of unsaturated maleic acid (product Kro), acrylic acid (product CP) and its derivatives (product TP) have been taken, as well as the properties of collagen after treatment with these materials.

The scientific novelty of this research consists in determination of the influence of the kind and flow of polymeric compounds on the isoelectric point of gelatin and collagen thermal stability, establishing a possible mechanism of interaction between these materials and protein.

The practical meaning of the work is the experimental confirmation of the efficiency of new polymeric compounds for leather treatment.

EXPERIMENT

We have used both common in leather and fur production and modern research methods: viscometric, fusiometric, photometric, potentiometric, infrared spectroscopy and microscopic, mathematical statistics.

For establishing viscosity of investigated polymers Ostwald viscometer was applied (relative error ± 1 %), choosing its diameter so that obtained data have been the most trustworthy. Surface tension was defined with the help of stalogmometer CT-2 (Corund-Chem, Russia) (absolute error ± 0.06 mN/m); density – areometer AOH-1 (Steklopribor, Ukraine) (absolute error ± 0.01 g/cm³); pH – pH meter HI 2210 (Hanna Instruments, Great Britain) (absolute error ± 0.1 pH); dry residue – by weight method. Resistance to electrolytes was determined after coagulation threshold at adding to polymers, wide-spread in leather production, electrolytes (sodium chloride, ammonium hydroxide, acetic and salt acids and others).

For measuring polymer particle size laser correlation analyzer – spectrometer Zeta Sizer Nano (Malvern Instruments, Great Britain) was used. As to the advantages of the device the range of material measurement from 0.02 μm to 2000 μm can be attributed; wide spectrum of samples types (it is possible to measure emulsions, suspensions, dispersions, powder); convenience in usage; full reconstruction of obtained data; high exactness of measurement (relative error ± 1 %).

The influence of temperature on derma collagen and its derivative – gelatin was defined according to the melting temperature 10 % gels of gelatin at fusiometer [7] (absolute error ± 0.1 °C) at corresponding apparatus [8] (absolute error ± 1 °C). In order to define isoelectric point of protein photometer (Econix Expert, Russia) was used (absolute error – 0.005) and pH meter HI 2210 (Hanna Instruments, Great Britain) (absolute error ± 0.1 pH).

Spectral analysis has been holding on spectrophotometer TENSOR 37 (Brucer, Germany). Belonging of the absorption bands on the spectra to materials under test of the different types of compounds (groups of atoms) was ascertained on the basis of numerous publications in the field of infrared spectroscopy [9-10]. The resulting absorption spectrogram in the range of 400-4000 cm^{-1} was treated by the methods of «baseline» and «internal standard» [2]. For the internal standard bands with frequencies in 2930 and 1337 cm^{-1} was chosen (deformative vibrations of CH_3 and CH_2 groups correspond to the valent), since at these frequencies the optical density of substances under test is changed insignificantly.

Chemical and physico-mechanical tests of chrome leather were carried out according to standard methods [8] with the use of modern equipment: tearing machine PT 250M; drying cabinet SNOL 24/200 (Umega, Lithuania); thickness gauge SGM (Filetta, Netherland); microscope L1500A 600x (Paralux, France). The uniformity of dyeing of leather semi-finished item in modern photometer of whiteness and colour characteristics «Kolir» (Trigla, Ukraine) was determined under such conditions as: measurement geometry/ observation – D/65; regime: a) colour distinction; b) source – A; c) observer – 2°; error according to coordinate of colour – not more than ± 0.02.

Accuracy of the results, the validity of the ascertained regularities and the assumptions are provided by sufficient quantity of the conducted experiments, the use of modern exact methods, of computer technologies to attain the objective.

RESULTS AND DISCUSSION

The results of physicochemical studies of new polymeric compounds indicate their anionic nature and such valuable properties as non-toxicity, complete water solubility, stability to electrolytes (Table 1).

Table 1. The main physical and chemical properties of investigated polymers

Index	Polymer		
	Kro	TP	CP
Component (acid) derivative of	maleic acid	acrylic acid	acrylic acid
Activity, %	15.0±5.0	17.0±3.0	29.0±3.0
Solubility in water	complete	complete	complete
Resistance to electrolytes	high	high	high
pH (10 % solution)	7.6±0.5	5.7±0.5	5.5±1.0
Dry residue, %	21.5	13.5	32.5
Density, g/cm³	1.015	1.011	1.040
Surface tension, mN/m	54.09	76.59	76.88
Relative viscosity (20 % solution)	1.14	3.40	14.90
Intrinsic viscosity	0.700	1.472	2.507
Molecular weight	11599	33538	71756

It was ascertained by the method of laser correlation spectroscopy that average size of maleate particle is 17 nm, while particles of acrylates are larger in 4.6-252.4 times. On the basis of the results of viscometric study polymer solutions of different concentrations (0.3-5.0 g/l) their molecular weight was defined according to the equation of Mark-Houwink (Table 1). Depending on the molecular weight the investigated compounds can be arranged in the sequence of CP > TP > Kro, which is quite correlated with the particles size. The effect of polymeric compounds on the properties of collagen, using gelatin as an example, leather semi-finished item and leather has been defined. It is ascertained that after treatment with polymers melting temperature of 10 % gelatin gels increases by 3-4 °C (Fig. 1).

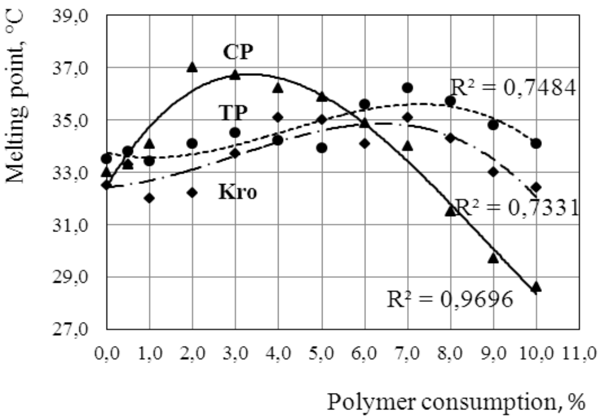

Figure 1. Influence of polymeric compounds on the melting point of gelatin gels

It is fully consistent with hydrothermal stability index – the shrinking temperature of collagen of untanned leather semi-finished item from cow hides. The index increases after treatment with the products Kro and CP at 5-10 °C [3]. It indicates the formation of some, though not very strong, bonds in the structure of the derma.

With the help of potentiometric and photocolorimetric methods it has been ascertained that gelatin treatment by investigated polymer shift the isoelectric point of protein from a position of 4.89 to the lower pH by 0.16-0.53 units: for product Kro − to 4.73, for product TR - to 4.55, for product CP – to 4.6.

The shift of the isoelectric point of gelatin to more acidic area indicates the presence in polymeric compounds of active mainly unbound carboxyl groups, which are inclined to interact with the basic and the other nitrogen-containing groups of collagen. The above stated is confirmed by spectral analysis of gelatin films treated by polymers (Table 2).

Table 2. Change of gelatin optical density after treatment by polymers

λ, cm^{-1}	Connection type, group	Z* Kro	TP	CP
1554	Amide II (CN; NH); Carboxylic acids (COO^-)	1.05	1.05	0.95
1405	Alcohols, phenols (OH); Carboxylic acids (CO; OH) Primary amides (CN)	1.35	1.42	1.33
1280	Amines secondary, tertiary (CN); Esters (COC)	1.01	1.01	1.50
1240	Amide III (CO; CN; NH; O = CN) Amines secondary, tertiary (CN); Esters (COC)	1.01	1.06	1.00

** Ratio of adducing optical density of the initial gelatin to adducing optical density of gelatin after treatment by polymer*

After polymer treatment of gelatin index Z, which characterizes the decrease of the intensity of the gelatin absorption bands on the IR spectrograms, increases at frequency 1405 cm^{-1}; after treatment with some of them − at frequencies 1554, 1280 and 1240 cm^{-1}. This can be explained by the interaction between polymeric compounds and nitrogen (Amide II − 1554 cm^{-1}, amines secondary, tertiary − 1240-1280 cm^{-1}) and hydroxyl (1405 cm^{-1}) protein groups (Table 2). Results of kinetic research of the system «polymer-gelatin» indicate the chemical nature of the interaction between polymers and collagen: for all products under test the activation energy is not less than 125 KJ [2].

Expediency of polymeric compounds use in leather processing has been studied at the stage of dyeing and fatliquoring processes an example of maleic acid derivative. Processing scheme of shaved semi-finished item of cow hide has been chosen by according to the standard method of chrome-tanned leather production for the upper of shoes, from cattle hides [11]: washing – neutralization – washing – dyeing – fatting – vegetable tanning agents retannage – washing.

The difference in processing of the investigated leathers consisted in the application of polymer before dyeing (a product Kro) in the amount of 6.0 % of weight of shaved semi-finished item, reducing the consumption of tannins and dye in 2 times as *compared with control ones (2.0 and 1.0 % respectively). As a vegetable tanning agents quebracho tannins have been used as a dye – brown anionic Y. Polymer processing and dyeing temperature was at 36 °C, the duration of each of these processes – 1 hour, consumption of water – 200 %. Control leathers have not been treated by polymers. No complications due to polymer processing have not occurred, the finished product was dyed uniformly, it was soft and filled to the touch, had a nice grain. As a result of leather physical and chemical testing it has been found (Table 3) that the use of maleate promotes the obtainment of quality leather goods, which is characterized by high hydrothermal stability, the strength of leather as a whole and its grain (σ_g, σ_s), good fullness (yield in thickness), good elastic and plastic properties (elongation at 10 MPa L10). Increase of distribution uniformity of the strength and elongation indices by 10-17 %, the yield in area by 1.5 %, reducing the consumption of tannins and dye by 50 % indicates a more rational use of scarce raw stock and chemical materials.*

Table 3. Indices of chrome leathers

Index		Value: Investigated leather	Value: Control leather
Temperature of shrinkage,°C		126.1	123.3
Limit tensile strength σ_g, MPa		22.0	21.6
The strength of grain layer σ_s, MPa		16.7	16.2
$\Delta\sigma = \sigma_g - \sigma_s$, MPa		5.3	10.4
Elongation at stress 10 MPa L_{10}, %		41.5	40.0
Uniformity of distribution of indices to directions of leather	$K\sigma_g$	0.80	0.72
	$K\sigma_s$	0.69	0.59
	K_{L10}	0.90	0.75
Porosity, %		54.0	42.1
Vapour permeability, %		85.2	69.5
Yield in thickness, %		92.0	92.1
Yield in area, %		94.7	93.3
Volume yield, cm^3/100 g protein		233.0	231.3
Penetration level of dye, %		76.2	66.6
Uniformity of colouring ΔE(D65)		2.51	7.45

CONCLUSIONS

On the basis of the research of new polymeric compounds − derivatives of unsaturated maleic and acrylic acids − it has been suggested that due to the peculiarities of their structure and properties (definite particle size, presence of active groups and bonds, reaction to the action of water and electrolytes) investigated polymers can not only be sorbe by derma, filling the space between its structural elements, but also to interact with the active (amine, imine, peptide, hydroxyl) groups of collagen and to impart to the natural leather high consumer, health, aesthetic and cutting-out properties. The introductions of research results into the manufacture give the possibilities to get a high quality leather item with more rational use of material resources.

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