APPLICATION OF ADVANCED POLYMERIC COMPOUNDS FOR DEVELOPMENT OF LEATHER PRODUCTION

A Nikonova¹, O Andreyeva¹, L Maistrenko¹

¹Kyiv National University of Technologies and Design, str. Nemirovich-Danchenko, 2, Kyiv, 01011, Ukraine
E-mail: nikonovaav@mail.ua

Abstract. Abatement of negative impact of leather industry on the environment is associated with scientifically grounded use of chemical materials and raw materials, with the development of low-toxic and low-waste technologies. A solution of this problem can be development and implementation of pre-tanning and tanning processes alternative technologies with the use of polymeric compounds. To replace traditional pickling process advanced polymeric material based on acrylic acid has been used. It has been found experimentally that application of the polymeric processing intensifies the tanning process, increases the thermostability of leather with more rational use of chemical materials. The content of chrome (III) compounds, chlorides and sulphates in waste water are reduced.

1. Introduction

One of the most important processes of natural leather production is tanning, during which the main formation of the structure and many properties of derma takes place. More than 80% of the leathers in the world are processed by using compounds of chrome which is connected with easiness of technology, reliability of the process, high technological and operational properties of chrome tanned leathers, the possibility to manufacture products of different kinds. Using of known production technologies have negative impact on the environment because of formation of waste waters that contain toxic compounds of chrome (III), sulphates, chlorides, products of protein degradation etc. Depending on the technology of the production nearly 4.0-8.0 g/l of chrome is contained in waste solutions after the process of chrome tanning. At the same time the effectiveness of tannins using is nearly 50-60%, and the rest is transferred to waste waters and solid production wastes [1-2]. In addition to carrying out the process of pickling before tanning is increases concentration of sulphates in the waste solutions, which together with other salts present danger are formation of hydrogen sulphide and acid. Hereupon, the purification of drains by using biological methods becomes complicated and needs additional expenses [3].

Manufacturers try to remove the above mentioned drawbacks at the expense of partial replacement compounds of chrome by other mineral and organic tanning agents, optimization of tanning parameters according to the index of chrome exhaustion, repeated using of tanning solutions, and introduction of masking and alkali reagents. Herewith, it is not always possible to conduct the process in the way when during rational using of material and energetic resources the finished leather was of high value. The development and introduction of new technologies into production which decrease negative impact, presents scientific and practical interest. One of the most perspective directions of formation of such technologies is using of available, nontoxic chemical materials, which are able to increase considerably the diffusion component of tanning process and provide maximum fixation of chrome tanning agent by the leather tissue [4].

The previous work shows that the using of polymeric material on the basis of maleic acid before chrome tanning the increases interstructural distance in the collagen. This improves the diffusion of the tanning agent into the derma and as a result of its interaction with collagen the shrinkage temperature is raise. Duration of tanning process is decreases in 1.2 – 9.0 times. The processes of polymeric processing and chrome tanning are carried out non-traditionally at temperature 36-38°C [5].

The aim of this research is to study the influence of advanced polymeric material on the bases of acrylic acid (PMAA) on the process of chrome tanning with purpose to define the effectiveness of its
using in leather production. In order to decrease harmful impact on the environment the possibility to exclude the technological cycle of pickling process was investigated.

2. Materials and methods
2.1. Raw and chemical materials
For all groups bated pelt of sheep skin (90 sq.dm area) was used. Polymeric material PMAA (Codyeco S.p.A., Italy) was applied for experimental groups. It is one of commercial technical materials for leather production on the world market. The specification of PMAA used in the present study: solubility in water – soluble; active agent content (dry residue) – 32.5%; pH of 10% solution – 5.5±1.0; resistant to electrolytes action; ability to interact with the collagen [6].

Sodium chloride (97%), sulphuric acid (96%), formic acid (85%), chrome tanning agent (38.0% basicity, 25.0% of chrome oxide), sodium hydracarbonate (96%) for control group and the same chemical material except of sulphuric and formic acids for experimental groups were used in the present study. All indicated materials for leather processing are the technical products. Materials for chemical analysis are the analytical grade.

2.2. Experimental conditions
Bated pelt from sheep skin were divided into 14 groups and completed in two samples in group by the method of asymmetric trimming [7]. The samples were prepared in size 10x20 cm and the edge portions was removed. Samples of pelt control group 14c was fully treated using traditional chrome-pickling tanning at temperature 18-20°C, known as production technology of garment leather [8]. All processes before pickling in the experimental groups 1-13 were performed using typical method, by without process of pickling. Polymeric processing was performed directly before tanning, bath was poured. Consumption of PMAA was in amount 1.0-3.0%, temperature 36-38°C, process time 1.0-3.0 hour (h) and consumption of water in amount 100%. The pH after polymeric processing was 6.0±0.2. Then the solution was drained. The next processing was carried with sodium chloride during 15 min to prevent acid swelling. Consumptions of sodium chloride was in amount 5%, water in amount 100% Chrome tanning agent was added to the same solution in amount 1.2-1.6% (% of chrome oxide) and temperature 36-38°C (for traditional chrome-pickling tanning the processing temperature is 20°C). After 1.0h after beginning of tanning, sodium hydrocarbonate was added in amount 0.3% (1:20 w/v) in few feeds and section pH was controlled. In all cases, the end of the tanning process was determined by a positive boiling test. Consumption of chemical materials and water is depending on limed pelt mass of samples. Conditions of polymeric processing and tanning are presented in table 1.

All processing was carried out in a laboratory setting for shaking glass containers of size 1.0 liter were used, providing required temperature and shaking. The frequency of shaking was 10 min⁻¹.

| Parameters                      | Group |
|--------------------------------|-------|
| PMAA (%)                       | 1 2 4 3 5 6 7 8 9 10 11 12 13 14c |
| Chrome tanning agent (%)       | 1.6 1.2 1.6 1.2 1.4 1.4 1.4 1.6 1.6 1.2 1.2 1.4 1.6 |
| Time of polymeric processing (h)| 2.0 2.0 1.0 1.0 2.0 2.0 1.0 1.0 1.5 1.5 1.5 1.5 1.5 |

For determining of the parameters of non-pickling chrome-polymeric tanned (NPCPT) process in all existing methods of experimental planning was chosen widespread in practice no-compositional symmetric quasi-D-optimal plan that allows getting a good statistical model which has the minimal number of experiments. The factors influencing this method vary at three levels: +1, 0, −1 [9].
After a series of previous experiments the three most important factors are determined: $X_1$ – consumption of polymeric material, %; $X_2$ – consumption of chrome tanning agent, %; $X_3$ – time of polymeric processing, h, along with zero level and interval of variation, that is shown in table 2.

Table 2. Zero level and variation interval of factors.

| Factor                  | PMAA | Chrome tanning agent | Time of polymeric processing (h) |
|-------------------------|------|----------------------|----------------------------------|
| Coded designations      | $X_1$| $X_2$                | $X_3$                            |
| Zero level $x_{i0}$     | 2.0  | 1.4                  | 1.5                              |
| Range of variation $\Delta x_i$ | 1.0  | 0.2                  | 0.5                              |

According to primary variables (response function) values of tanned leather that efficiency describe tanning process were selected: the mass part of volume yield, shrinkage temperature, mass part of chrome oxide (equation 2-4).

The necessary calculations and visuals construct the optimal area of NPCPT process was fulfilled using MathCAD 15 [10].

2.3 Research methods

Tanned leather and exhaustion solutions were subjected to physical and chemical analysis.

The pH control of solutions was determined using a pH-meter PATECH PH-013M.

Shrinkage temperature, which is the measure of degree of tanning, was analysed for experimental and for control tanned leathers. The measurements were carried out using a shrinkage tester as per official testing method (ISO 3380:2015). Boiling test was carried out in accordance [7].

A full penetration of tanning agent into derma was measured performed at intervals of 30 min using Bresser Researcher Bino optical microscope with increasing 40-1000 (Bresser, Germany).

Physical and chemical analysis of leather were carried out as per official methods: mass part of chrome oxide ISO 5398-1:2007, moisture content ISO 4684:2005, hide substance ISO5397:1984), apparent density ISO 2420:2002, thickness ISO 2589:2002.

Tanned solutions was analysed using a photocolorimeter AE - 30F (ERMA Inc, Japan) for determination of chrome content (Cr$_2$O$_3$) as per official analytical method ISO 5398-2:2009.

Collecting and analysis of waste waters was made as per official methods of chemical analysis for BOD ISO 5815-1:2003, ISO 5815-2:2003, COD ISO 15705:2002, sulfates content ISO 6844:1983, chlorides content ISO 3566:1976.

Volume yield VR, cm$^3$/100g of protein was calculated using the formula (1) [11]:

$$VR = \frac{100^2 \cdot d_a}{HS}$$

where $d_a$ is the apparent density, g/cm$^3$; HS is the hides substance, (per absolutely dry substance), %.

Leathers after tanning were subjected to visual and feel assessment for functional properties such as softness, fullness, grain smoothness characteristics and general appearance by hand and visual examination. The absence of complications should be noted during processing of experimental groups the samples are soft and fulling, have a clean and silky grain smoothness.

3. Results and discussion

Adequate mathematical models in the encoded units were obtained. These models describe the dependence of the most important indices of leather after NPCPT process of expenses of chrome tanning agent, PMAA and time of polymeric processing.

The mathematical on down.
• **Volume yield:**

\[ Y_1 = 225.0 + 9.81X_2 + 7.75X_1X_2 + 19.02X_1^2 + 9.2X_3^2 \]  

(2)

• **Shrinkage temperature:**

\[ Y_2 = 1085 - 0.75X_1 + 1.56X_2 + 1.75X_1X_2 - 1.75X_1X_3 + 0.81X_1^2 + 0.94X_2^2 \]  

(3)

• **The mass part of chrome oxide:**

\[ Y_3 = 6.22 + 0.35X_1 + 0.19X_2 - 0.23X_3 + 0.17X_1X_2 - 0.29X_1X_3 - 0.24X_2X_3 - 0.41X_1^2 + 0.85X_2^2 - 0.36X_3^2 \]  

(4)

For full description of tanning process in choosing the rational parameters of NPCPT process the several factors were tested additionally: penetration of tanning agent, duration of tanning, exhaustion of tanning agent, thickness and volume yield (table 3).

The experimental results shows that in comparison with the traditional chrome-pickling tanning at temperature 18-20°C, processing with PMAA at temperature 36-38°C improved next parameters: penetration of tanning agent into derma increased in 0.7-3.0 times, duration of tanning process reduced to 2.5-5.0 times, exhaustion of chrome tanning agent from solution increased to 13.5-38.6%.

The use of PMAA over 2.0h has no effect on exhaustion of chrome tanning agent from working solution that is at the level 62.9-70.0%. At lower time of polymeric processing (1.0h) the exhaustion of tanning agent better on 3.7-18.6%. Best rate (88.6%) was obtained for polymeric processing during 1.0h and consumption 1.0% of PMAA. Regardless of exhaustion of chrome tanning agent (79.2-88.6%), the best exhaustion of tanning agent was achieved at lower consumption of PMAA (1.0%) and less time of polymeric processing (1.0h), or higher consumption of PMAA (3.0%) and less time of polymeric processing (1.0h). In other conditions tanning processes rate decreased at 11.5-25.7%.

### Table 3. Rational parameters choosing of NPCPT process.

| Group | Full penetration of tanning agent (h) | Duration of tanning (h) | Exhaustion of tanning agent (%) | The mass part of chrome oxide (%) | Shrinkage temperature (°C) | Volume yield (cm³/100g) | Yield of thickness relative to bated pelt (%) |
|-------|--------------------------------------|-------------------------|-------------------------------|----------------------------------|---------------------------|--------------------------|---------------------------------------------|
| 1     | 0.5                                  | 3.0                     | 65.0                          | 6.6                             | 111.0                     | 238.9                    | 80.0                                        |
| 2     | 0.5                                  | 3.0                     | 70.0                          | 6.5                             | 106.5                     | 207.2                    | 50.1                                        |
| 4     | 1.0                                  | 4.0                     | 70.0                          | 7.4                             | 113.0                     | 257.9                    | 88.7                                        |
| 3     | 1.0                                  | 4.0                     | 66.6                          | 6.4                             | 107.0                     | 233.7                    | 76.7                                        |
| 5     | 1.0                                  | 3.0                     | 62.9                          | 5.2                             | 108.5                     | 258.6                    | 108.8                                       |
| 6     | 0.5                                  | 3.0                     | 64.3                          | 5.1                             | 111.0                     | 278.5                    | 77.4                                        |
| 7     | 1.0                                  | 4.0                     | 78.6                          | 6.4                             | 111.0                     | 239.2                    | 61.2                                        |
| 8     | 1.0                                  | 4.0                     | 88.6                          | 5.1                             | 106.5                     | 236.6                    | 66.0                                        |
| 9     | 1.0                                  | 3.0                     | 70.0                          | 7.3                             | 110.5                     | 255.8                    | 128.3                                       |
| 10    | 0.5                                  | 2.0                     | 71.9                          | 6.3                             | 111.0                     | 244.0                    | 115.1                                       |
| 11    | 1.0                                  | 4.0                     | 79.2                          | 6.7                             | 106.0                     | 229.0                    | 106.3                                       |
| 12    | 1.0                                  | 4.0                     | 69.2                          | 6.4                             | 113.5                     | 248.2                    | 98.3                                        |
| 13    | 1.0                                  | 4.0                     | 77.1                          | 6.2                             | 108.5                     | 225.0                    | 91.1                                        |
| 14c   | 1.5                                  | 10.0                    | 54.4                          | 3.1                             | 97.5                      | 237.0                    | 93.0                                        |
The visuals construct the optimal area and conditionally optimal values of NPCPT leather was intended using mathematical equations and presented on figure 1.

Figure 1 show that optimal parameters of NPCPT process by following ranges of coded units $(x_1 = -0.8; x_2 = +0.7; x_3 = -0.4)$, represent the following functions report: volume yield $Y_1 = 241.7 \text{ cm}^3/100\text{g}$, shrinkage temperature $Y_2 = 109.6^\circ\text{C}$; the mass part of chrome oxide $Y_3 = 6.1\%$.

Subsequently, on the set of all parameters that describe the processing efficiency 10 group was chosen, in which the processing parameters (consumption of PMAA in amount 1.0% and chrome tanning agent in amount 1.6%, polymeric processing at 1.5h) provide appropriate level of exhaustion tanning agent from working solution, high mass part of chrome oxide in tanned leather, high shrinkage temperature, thickness and volume yield.

![Figure 1. Diagram of optimal area of NPCPT process.](image)

As compared with the known technology garment leather production that provides chrome-pickling tanning, new technology excludes pickling process and decrease the environmental and energy impact on the environment as a result decrease the content compounds of chrome (III) in waste solutions in 2.0 times, sulphates in 1.5 times, chlorides in 1.2 times, index of BOD in 2.0 times (table 4) and significantly shorten duration of tanning in 5.0 times (table 3).

| Index          | Exhaustion of tanning agent (%) | BOD (g O$_2$/l) | COD (g O$_2$/l) | Content in the waste solutions (g/l) |
|----------------|---------------------------------|-----------------|-----------------|-------------------------------------|
|                | Technology                      |                 |                 | chrome oxide | sulphates | chlorides |
| known          | 54.4                            | 4.7             | 8.2             | 7.3         | 10.1      | 19.4      |
| new            | 71.9                            | 2.3             | 7.0             | 3.7         | 6.8       | 16.7      |

4. Conclusions

To improve the technology of leather production the possibility of using a polymeric material based on acrylic acid to processing the battered pelt of sheep skin before chrome tanning and replace the pickling was investigated. It was found experimental the increasing of penetration and fixation of chrome tanning agent in structure of derma.

Using mathematical planning of the experiment, the optimal processing parameters were determined: consumption of polymeric material 1.0%; chrome tanning agent 1.6%; duration of polymeric processing 1.5h.
New pickling-free chrome tanning technology of garment leather production promotes the intensification of tanning in 5 times, increases the thermostability of leather on 13.5 °C, yield of thickness to 22.1%, exhaustion of tanning agent to 17.5%.

This improves the composition of waste solutions: index of BOD decreases in 2.0 times, content of chrome oxide in 1.9 times, sulphates in 1.5 times, chlorides in 1.2 times.

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