ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

STUDY CONCERNING THE INFLUENCE OF CERTAIN HYDROPHILIC AUXILIARIES ON THE PROPERTIES OF THE PLASTICIZED POLYVINYL CHLORIDE POROUS FILMS PART 1 - MOISTURE SORPTION

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Abstract: *Plasticized PVC films are cheaper but their hydrophilic properties are still a problem. Sustained research in this respect is carried out. This research work refers to either poromeric films containing reactive hydrophilic groups linked to PVC or the utilization of hydrophilic auxiliaries in aqueous media. The present paper has the purpose of obtaining plasticized PVC porous films with an enhanced capacity of moisture sorption, by inducing the porosity with the help of the high frequency electric field (H.F.E.F.) simultaneously with the utilization of certain hydrophilic auxiliaries such as: collagen hydrolysates (CH), hydroxyl-terminated polydimethylsiloxane (HTPDMS), and nonylphenol ethoxylate (NPE). The collagen hydrolysates were obtained by the recovery of the Chamois leather waste resulted from the buffing operation, using a new method of electrolytic hydrolysis on an own design installation. The resulting product was analyzed in terms of the hydrolysis yield and of the structural changes, highlighted by the IR analysis. The resulting hydrolysis product was used as such or in different mixture varieties as hydrophilic agent for the obtaining of plasticized PVC porous films. The films were analyzed in terms of moisture sorption in correlation with the version of the recipe used. The obtained results highlighted the efficiency of using CH as such or in some binary and ternary mixtures as regards the enhancement of the moisture sorption of the plasticized PVC films, effect which is also amplified by the utilization of H.F.E.F.*

Key words: *sheepskin wastes, electrolytic hydrolysis, H.F.E.F generator, spectral analysis, collagen hydrolysates.*

1. INTRODUCTION

Leather industry provides a large amount of solid wastes; in this category, are included the wastes produced during the processing of Chamois leather which is used in the auto industry, and the wastes resulted in the leather goods industry. Generically the hides and skins waste material consists mainly of proteins and lipids. The most important is the collagen component which is a fibrous protein that is found abundantly in all animals and is the main leather making protein [1,2].

Leather waste hydrolysates prove to be a valuable protein resource possible to be converted to added value commercial products as: soil fertilizers, biodegradable polymers and additives for cosmetic industry, building materials, composite fabrics, surface-active agents and hydrophilic auxiliaries, nutritional supplements for the food-processing industry [3-8].

The research in the present paper targeted aspects with an applicative character regarding the possibility of recovery of certain by-products with a protein component such as collagen hydrolysates. They were obtained by electrolytic hydrolysis starting from Chamois leather powder resulted from the dry finishing operation (buffing), according to a methodology described in a previous paper [9].

In the field of artificial leather, there occurred old and recent concerns for the obtaining of plasticized PVC porous films used to create leather substitutes for different branches: footwear,

clothing, leather goods etc. Plasticized PVC films are cheaper but their hydrophilic properties are still a problem, sustained research in this respect being carried out. This research work refers to either poromeric films containing reactive hydrophilic groups linked to PVC or to the utilization of hydrophilic auxiliaries in aqueous media.

The chemical structure of the hydrophilic auxiliaries, with the existence of certain free chemical functions such as: -NH_2, -OH, -COOH (collagen hydrolysates), -OH (hydroxyl-terminated polydimethylsiloxane and nonylphenol ethoxylate), allows an enhanced absorption of water vapour by generating certain additional hydrogen bonds [10].

The present paper has the purpose of obtaining plasticized PVC films with an enhanced capacity of moisture sorption, by inducing the porosity with the help of the high frequency electric field simultaneously with the utilization of certain hydrophilic auxiliaries. The presence of the exterior electric field can also determine possible grafting processes between the vinyl group in PVC and the reagent groups in the hydrophilic auxiliaries (OH, NH_2, COOH, alkyl radicals etc), ultimately resulting in a porous structure with an enhanced moisture sorption.[11]

The use of the auxiliary components to obtain new types of porous structures allows the attainment of cellular structures where the walls of the cells obtained from the expanding process display an enhanced humidity absorption.

At the same time, certain constituents such as: the collagen hydrolysates and/or the nonylphenol ethoxylate also have the character of surfactant agent, representing a supplementary effect of the water vapour retention in the resulting porous structures.

2. EXPERIMENTAL

2.1. Materials and apparatus

In order to carry out the laboratory experiments, the following substances were used:

- to obtain the collagen hydrolysates: NaOH, NaCl, Na_2CO_3, alcohol, acetone, HCl, trichlorethylene, Chamois powder;
- to obtain the plasticized PVC films: PVC emulsion (Kw 68-70 index) plasticizer dioctylterephthalate (DOTP), thermal stabilizer (KZII), expanding agent (Genitron AC4), and as hydrophilic agents: collagen hydrolysates (CH), hydroxyl-terminated polydimethylsiloxane (HTPDMS), and nonylphenol ethoxylate (NPE).

The equipment used for the experiments was: an electric stove with a magnetic stirrer, thermoregulated oven, centrifuge, IR-ATR spectroscopy using a DIGILAB – SCIMITAR Series FTS 2000 spectrometer with ZnSe crystal, 750 - 4000 cm^{-1} range, 4 cm^{-1} resolution, Digital Balance KERN 474, D72336 (Kern&Sohn – Balingen Germany), desiccator.

For Chamois powder waste degreasing a classic Soxhlet installation was used, and for electrolytic hydrolysis an own design device was used [9].

For PVC expanded films and tests were used: a laboratory blender, 3-roll calender, vacuum oven, Werner-Mathise laminating device, H.F.E.F generator, KPV-Hungary climatic chamber.

2.2. Working method

a) Electrolytic hydrolysis

Chamois leather waste was first subjected to the process of soaking using a solution of Na_2CO_3 5% and then were dried in the thermoregulated oven at 60ºC, for 24 h, and next degreased in a Soxhlet type laboratory installation, for 8 h, using the trichloroethylene as degreasing agent.

For electrolytic hydrolysis a paste with a concentration of 10% degreased powder in 16 % NaOH was prepared. This paste was allowed to swell at room temperature, for 24h and then, the mixture was introduced in the tank of the electrolytic hydrolysis installation [9].

The working parameters were: time - 2h, voltage - 10 V, current intensity - 9 A, the distance between the electrodes – 3 cm, the nature of the electrodes – stainless steel. The anode area was separated from the cathode area by some semi-permeable fluoropolymer-based membranes which covered the 2 electrodes, in order to avoid gases from being released in the mixture and in order to direct the protein components through electrodeposition.

After the electrolytic process, the resulting mixture was introduced in a glass column and then it was allowed to decant in order to separate the components. The liquid phase was treated with a NaCl 30% solution for salting out effect and the solid fraction was then collected. Then these components were introduced in a glass, diluted with distilled water and treated with HCl 0,5N. The resulting precipitate was resuspended, and it was brought to a neutral pH and centrifuged at 8000 rpm, for 20

min. The solid component was then mixed with alcohol/acetone and dried at 25ºC for 24h and then introduced in a desiccator with $CaCO_3$.

For the dry powder resulting from experiments yield extraction was determined (table 1), and IR analysis (figure 1) was also performed in order to detect structural changes induced by the hydrolysis.

b) PVC plasticized film obtaining

Plastisols with the following composition were prepared: PVC - 100 parts, plasticizer - 60p, thermal stabilizer - 3p, expanding agent - 2p, hydrophilic agents - 8 p.

The hydrophilic agents were used as such or in different varieties of mixtures according to Table 2.

Each plastisol was prepared in a blender, refined on a laboratory 3-roll calendar, deaerated in a vacuum oven and left at rest for 2 hours; 0.5 mm thick-films were then laid on anti-adherent paper, in a Werner-Mathise laminating device. Then, 2x10 cm samples were cut and expanded in a 13.56 MHz H.F.E.F. at 190°C for 1 min.

Water sorption of the PVC films was determined using the method of discontinuous registration of weight changes in a static system by placing the samples into a controlled humidity environment at a constant temperature until an equilibrium state was obtained.

The expanded films were pre-dried for 72 hours in a desiccator with $CaCl_2$ ($t = 23^0C$ şi $\varphi <$ 0,5%), and then introduced in a KPV-Hungary climatic chamber at a temperature of 23ºC, with different values of the relative humidity of the air ranging between 40 – 90 %. They were then dried in the oven at a temperature of 105ºC to a constant mass. The amount of humidity taken by the samples was determined by weighing and the obtained results were presented in Table 2 and Figure 2.

3. RESULTS AND DISCUSSIONS

For the collagen hydrolysates resulting from hydrolysis yield extraction (table 1) shows an optimum value.

Table 1. *Characteristics of hydrolysate product*

Analysis	Values
Sample used (g)	10
Solubilised matter (g)	8,5
Yield (%)	85
Insoluble residue (g)	1,5
Time (h)	2

In figure 1 the spectra of leather samples treated by electrolytic hydrolysis shows changes of the characteristic band peaks especially in the area of the Amide A, Amide B, amide I, amide II, amide III, as compared to the initial sample, which indicates the formation of hydrolysis products (the fragmentation of the amino acid chains in collagen). These bands corresponding to amide A, amide B, amide I and III are very intensive, compared with the same bands of initial sample, which is due to the decrease of intermolecular interactions associated with a higher number of free functional groups.

The spectrum of initial sample shows a shift to lower frequencies of amide A band (at ~ 3300 cm^{-1}), suggesting that more NH groups were involved in the hydrogen bonding, in contrast to the hydrolysed sample where this band occurs at ~ 3400 cm^{-1}. This increase of intermolecular interactions is associated with broadening of the amide A band.

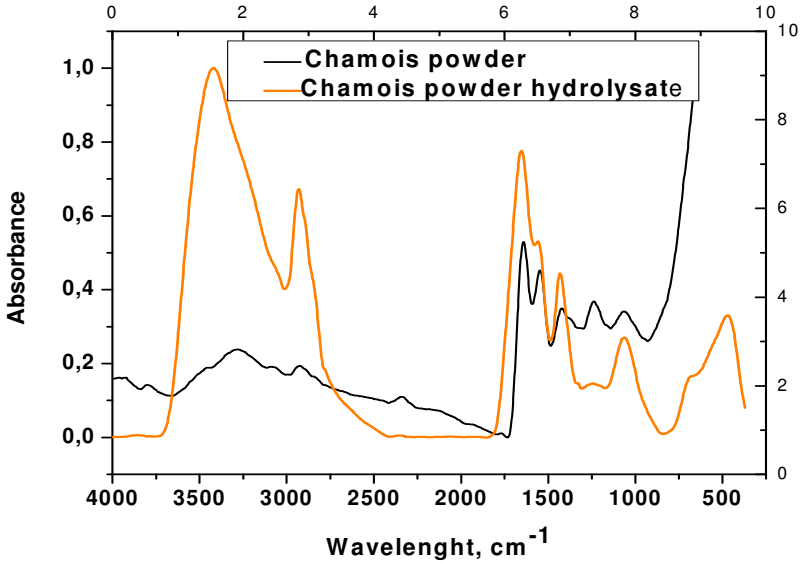

Fig. 1: *IR spectra of Chamois powder waste*

The results obtained for the sorption capacity of the films depending on the hydrophilic auxiliaries used in the recipe are presented in Table 2 and Figure 2.

Table 2. *The moisture content depending on the working variant*

No.	Sample	Relative humidity (%)					
		90%	80%	70%	60%	50%	40%
1	100% HTPDMS	11,58	7,95	5,2	4,3	3,35	2,43
2	100% CH	12,7	8,15	6,31	5,2	4,39	3,68
3	100% NPE	11,29	7,11	4,98	4,08	2,94	2,36
4	50% CH + 50% HTPDMS	12,41	7,39	5,74	4,84	4,38	3,26
5	50% PHDMS + 50% NPE	11,27	6,92	5,17	4,3	3,42	2,61
6	50% CH + NPE	14,87	9,14	7,28	6,4	5,38	4,33
7	33,3% HTPDMS + 33,3% CH + 33,3% NPE	14,94	8,41	6,7	5,7	5,04	4,11

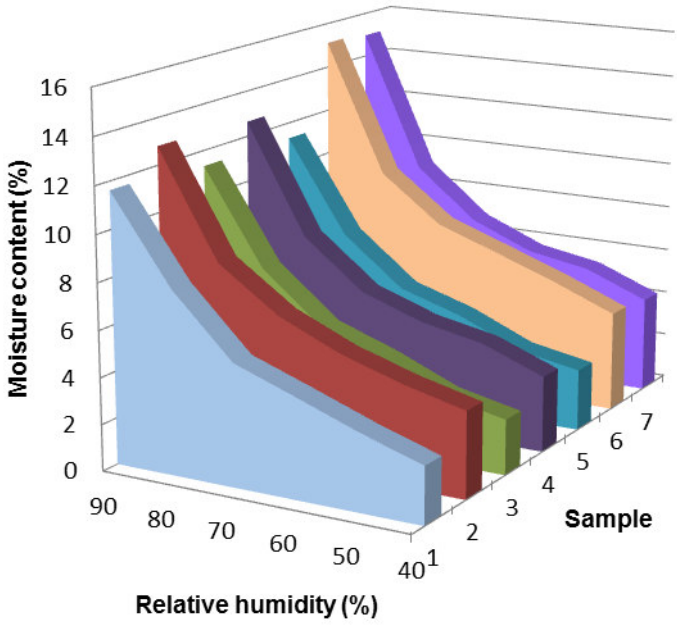

Fig. 2: *Moisture content depending on the relative humidity and the recipe variant*

The analysis of the experimental data in Table 2 highlights the following aspects:

- the monocomponent mixtures have sorption values correlated mainly with the chemical structure but also with the porous structure characteristics of the films. The highest values are noted for the hydrolysed collagen auxiliary (CH) followed by the hydroxyl-terminated polydimethylsiloxane (HTPDMS) and the nonylphenol ethoxylate (NPE), with almost similar values;
- the presence of a stronger synergistic effect for the ternary and HC/NPE binary mixtures.
- the THPDMS/NPE binary mixture presents an anergetic effect.

The synergistic effect could be owed to the surface-active character of the components in these mixtures correlated with a stronger internal plasticizing effect; at the same time, these effects are highly influenced by the H.F.E.F. The enhancement of the gelling-expanding processes under the influence of H.F.E.F. is accompanied at the same time by a supplementary internal plasticizing due to a strong stirring of the dipoles in the mixture at a frequency equal to that of the external electric field. This leads to the occurrence of a so-called "dielectric viscosity" which decreases during the film formation and increases at the end of the process. This contributes to the formation of a porous structure with an enhanced humidity sorption capacity.

There are, however, other interactions between the components of the mixture, intensified by the exterior electric field, but the multitude of the factors involved complicates very much the physico-chemical processes taking place. On the other hand, the porous structure characteristics represent another important factor in these processes, aspect to be investigated in a future study

4. CONCLUSIONS

1. Starting from the leather waste, there can be obtained valuable by-products like collagen hydrolysates by electrolytic hydrolysis, using an own design installation and method, and getting a good extraction yield.
2. The structural changes during hydrolysis materialized in a higher number of free functional groups were revealed by infrared analysis.
3. Of all the hydrophilic agents used to obtain plasticized PVC films, the collagen hydrolysates determined a higher enhancement of the moisture sorption.
4. Certain collagen hydrolysates binary and ternary combinations have stronger synergistic effects.
5. Supplementary plasticizing effect can occur under the action of H.F.E.F. by a permanent reorientation of the dipoles correlated with the decrease of the dielectric viscosity of the mixture during the process of gelling-expanding which contributes to an enhanced moisture sorption capacity.

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