# STUDY CONCERNING THE INFLUENCE OF CERTAIN HYDROPHILIC AUXILIARIES ON THE PROPERTIES OF THE PLASTICIZED POLYVINYL CHLORIDE POROUS FILMS PART II - HYGIENIC PROPERTIES

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***Abstract:*** *The purpose of this paper was to obtain certain PVC films with improved hygienic properties, with applications both in the artificial leather industry and in other domains. This was done by introducing certain hydrophilic auxiliaries with free chemical functions into the chemical structure of the PVC films, such as: collagen hydrolysates (CH), hydroxyl-terminated polydimethylsiloxane (HTPDMS) and nonylphenol ethoxylate (NPE). The use of these hydrophilic auxiliaries combined with the action of the high frequency electric fields (H.F.E.F.) allows the attainment of cellular structures where the walls of the cells obtained from the expanding process display an enhanced humidity absorption. The collagen hydrolysates used to obtain the plasticized PVC porous films was obtained by electrolytic hydrolysis starting from Chamois leather powder waste resulting from buffing operation, according to a methodology described in a previous paper. The first part of this study was concerned with the influence of the addition of hydrophilic agents upon the moisture sorption of the plasticized PVC porous films. In this paper, there was investigated the water vapour and air permeability as well as the water vapour absorption of the porous films expanded in the H.F.E.F. in correlation with the nature and the recipe variant of the hydrophilic auxiliaries. The results highlighted the fact that the use of certain combinations of hydrophilic agents led to obtaining materials with adequate hygienic properties.*

***Key words:*** *collagen hydrolysates, electrolytic hydrolysis, H.F.E.F generator, vapour permeability, air permeability, humidity absorption.*

## 1. INTRODUCTION

The set of characteristics that allow assessing the extent to which, at the contact between the human organism and some material, the normal activity of the skin is ensured, defines the concept of hygienic properties, including: water vapour and air permeability, water vapour absorption/desorbtion, and antimicrobial ability. In this respect, there are numerous signals in the specialized literature which point to the concern about the enhancement of the PVC films' hydrophilicity. If in the case of polyurethane films, this challenge was achieved, for plasticized PVC films, the problem has not been fully solved; there are still concerns due to lower cost price offered by this type of materials. The latest efforts of the specialists in the domain of leather substitutes indicate a constant concern to obtain poromeric films with remarkable hygienic properties.

This was done either by the direct synthesis of certain vinyl polymers containing hydrophilic groups, or by using additions of collagen hydrolysates-based aqueous solutions, polyvinyl alcohol, or by coupling collagen materials with polyvinyl alcohol in the presence of reagent auxiliaries, or by using acrylic copolymer blends and composite materials [1-6].

Besides the contributions brought to the induction of porosity with the help of the high frequency electric fields, the purpose of this paper was also to obtain certain polymer films with improved hygienic properties, with applications both in the artificial leather industry and in other domains. This was done by introducing certain hydrophilic auxiliaries with free chemical functions into the chemical structure of the PVC films, such as: collagen hydrolysates (HC), hydroxyl-terminated polydimethylsiloxane (HTPDMS) and nonylphenol ethoxylate (NPE). The polar character of the used mixtures, as well as the changes appeared in the chemical structure of the films expanded due to the action of the high frequency electric fields can constitute a supplementary factor for the improvement of the hygienic properties of these new types of films [7].

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.

The humidity transfer through the expanded films which contain these components is made by diffusion mechanism, by absorption through the pore walls and/or by movement the water molecules along the pore walls by adsorption (chemisorption). At the same time, certain constituents such as: HC and NPE also have the character of surface-active agent, representing a supplementary effect of the water vapour retention in the resulting porous structures.

The collagen hydrolysates used to obtain the plasticized PVC porous films was obtained by electrolytic hydrolysis starting from Chamois leather powder waste resulting from buffing operation, according to a methodology described in a previous paper [8].

The first part of this study was concerned with the influence of the addition of hydrophilic agents upon the moisture sorption of the plasticized PVC porous films. In this paper, there was investigated some hygienic properties as: the water vapour and air permeability as well as the water vapour absorption in correlation with the nature and the recipe variant of hydrophilic auxiliaries.

## 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), expeanding 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, Digital Balance KERN 474, D72336 (Kern&Sohn – Balingen Germany). For Chamois powder waste degreasing a classic Soxhlet installation was used, and for electrolytic hydrolysis an own design device was used [8].

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, desiccator, Textest FX 3300-CK (Switzerland) air permeability tester, STM 473 apparatus for the vapour permeability determination, and STD 478 water vapour absorbtion test apparatus.

### 2.2. Working method

The electrolytic hydrolysis of the leather waste (Chamois powder from the dry finishing of leather) was achieved under the conditions described in the first part of this paper.

The plasticized PVC porous films were made with the same variants of hydrophilic agent mixtures and under similar conditions to those described in the first part of this paper.

Before all tests, the specimens were conditioned for 72 h at a standard atmosphere (t = 20 $^0$C ±2 °C, φ = 65 ±5 %, i. e. 20/65), according to SR EN 20139: 1999.

Water vapour permeability and absorption of the investigated PVC films were determined according to the requirements of standard methods.

Water vapour permeability was measured according to LST EN ISO 14268 using a STM 473 test machine, at the same constant temperature (t = 20 $^0$C ±2 °C) and relative humidity (φ = 65 ±5 %). Circular specimens of films were placed over pots, which contain a solid desiccant, i.e. silica gel. The samples were placed over the opening of the pot and secured with a screw top, which leaves the surface of the material exposed. The pots containing the silica gel and sample were weighed and located into a test station in the rotary support. The test stations are rotated for the duration of the test, and a controlled airflow passes over the surface of the test materials secured to the test pots; the test is run in a temperature and humidity conditioned atmosphere (i.e. 20/65). At the conclusion of the test (after 8, and 24 h respectively), the test jars are re-weighed. The increase in weight due to moisture passing through the sample materials and combining with the desiccant is used to determine the test samples' permeability. The obtained results are presented in table 1 and figure 1.

Air permeability of the samples was measured via standard TS 391 EN ISO 9237 method, using a Textest FX 3300 air permeability tester. The measurements performed at a constant pressure drop of 100 Pa. All tests were performed under standard atmospheric conditions (20ºC, 65 %RH). The obtained results are presented in table 1 and figure 2.

Water vapour absorption was measured according to LST EN ISO 17229. The tests were conducted using a STD 478 water vapour absorption test apparatus. Each test specimen was clamped between the open end of a test pot containing a specified volume of water (50 ml) and an impermeable seal. The pots were stored at 20 $^0$C for a set time (3 ÷ 24 h) and, on conclusion of the test the specimens were removed and reweighed. The increase in weight of the sample was used to determine the water absorption capacity of the material. The results are presented in table 2 and figure 3.

## 3. RESULTS AND DISCUSSIONS

The results obtained for the water vapour and air permeability and for water vapour absorption, depending on the working variant and time are presented in Tables 1-2 and in Figures 1-3.

***Table 1.*** *Water vapour permeability and air permeability depending on the recipe variant*

| No. | Sample | Water vapour permeability | | Air permeability AP (Nl/100 cm$^2$/h) |
|---|---|---|---|---|
| | | WVP (mg/dm$^2$/8h) | WVP (mg/dm$^2$/24h) | |
| 1 | 100% HTPDMS | 232 | 621 | 67 |
| 2 | 100% CH | 211 | 607 | 62 |
| 3 | 100% NPE | 181 | 560 | 53 |
| 4 | 50% CH + 50% HTPDMS | 214 | 595 | 95 |
| 5 | 50% PHDMS + 50% NPE | 175 | 535 | 87 |
| 6 | 50% CH + NPE | 270 | 671 | 112 |
| 7 | 33,3% HTPDMS+ 33,3% CH + 33,3% NPE | 252 | 662 | 98 |

***Table 2****. Water vapour absorption depending on the recipe variant and time*

| No. | Sample | Water vapour absorption WVA (%) | | | | |
|---|---|---|---|---|---|---|
| | | 3h | 6h | 9h | 12h | 24h |
| 1 | 100% HTPDMS | 0,82 | 1,21 | 1,34 | 1,47 | 1,88 |
| 2 | 100% CH | 0,95 | 1,18 | 1,37 | 1,52 | 2,57 |
| 3 | 100% NPE | 1,09 | 1,25 | 1,45 | 1,64 | 2,83 |
| 4 | 50% CH + 50% HTPDMS | 1,25 | 1,37 | 1,62 | 1,71 | 3,35 |
| 5 | 50% HTPDMS + 50% NPE | 1,21 | 1,36 | 1,63 | 1,68 | 3,29 |
| 6 | 50% CH + NPE | 1,28 | 1,42 | 1,71 | 1,78 | 3,49 |
| 7 | 33,3% HTPDMS+ 33,3% CH + 33,3% NPE | 1,35 | 1,78 | 2,42 | 2,56 | 3,85 |

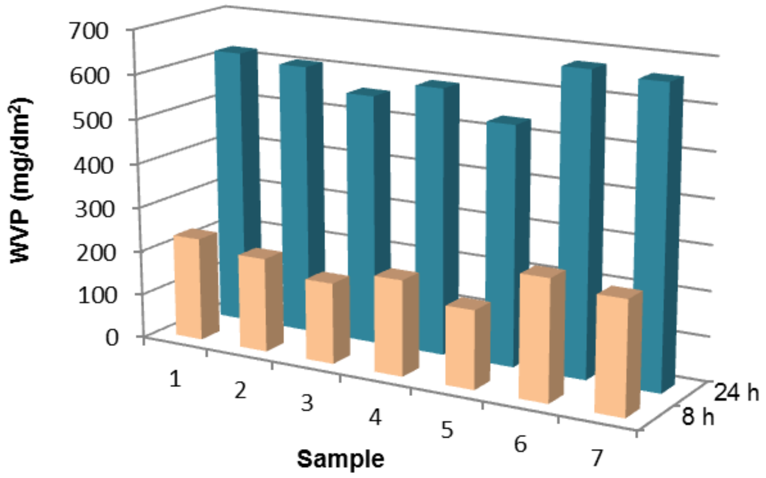


***Fig. 1:*** *Water vapour permeability depending on time and the working variant*

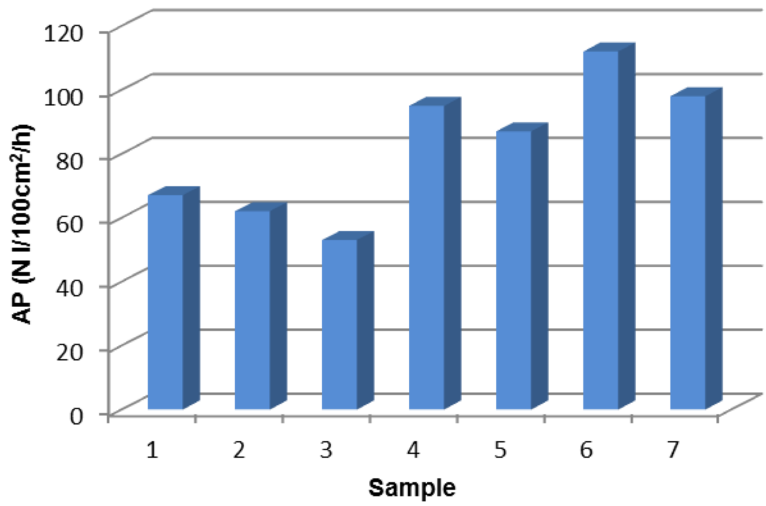


***Fig. 2:*** *Air permeability depending on the working variant*

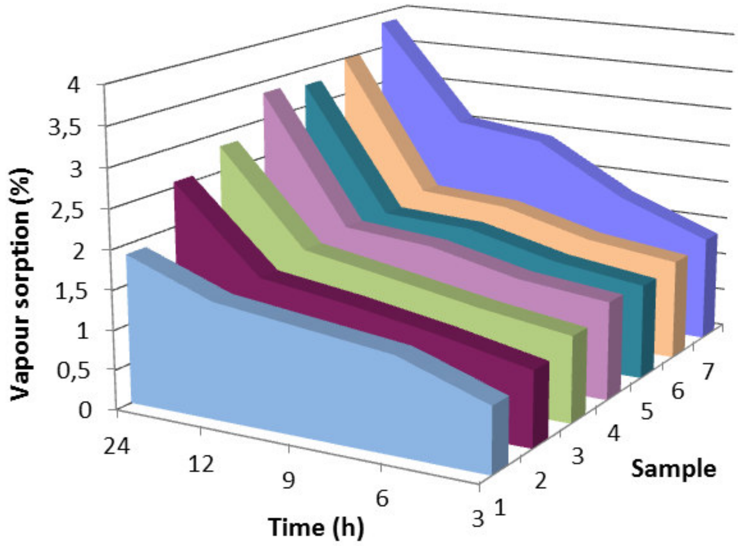


***Fig. 3:*** *Water vapour absorption depending on time and the working variant*

The analysis of the experimental data on the amount of transferred water vapour (Table 1, Figure 1) shows:

The amount of transferred water vapour increases with increasing the duration of maintaining the sample in a humid atmosphere, being dependent on the composition of the expanded films.

Among the monocomponent mixtures, those based on HTPDMS and CH have the highest values of permeability to water vapours; multi-component mixtures have both synergistic and anergetic effects, depending on their composition. Thus, in the case of the binary mixtures a prevalent anergetic tendency can be noticed especially for the HTPDMS+NPE variant, while a strong synergy can be noticed in the case of the CH+NPE binary mixture as well as in the case of a ternary mixture.

In regard to the air permeability (Table 1, Figure 2), among the monocomponent mixtures, the highest values are registered for those based on HTPDMS. The binary mixtures have a synergistic character, which is stronger in the case of the CH+NPE combination; the ternary mixture also has a synergistic effect.

The results obtained both in the case of the water vapour permeability and that of the air permeability indicate the fact that both the CH+NPE binary mixtures and the ternary mixtures have the best values, pointing out that the resulting porous structures offer the possibility of an adequate water vapour and air transfer.

On the other hand, the porous structure characteristics represent another important factor in these processes, aspect to be investigated in a future study.

In regard to the results for the humidity absorption (Table 2, Figure 3), an increasing over time accumulation can be distinguished for all types of films. The obtained values explain their tendency to bond with water, due to the hydrophilic groups the components have, but also due to the surface-active character of the collagen hydrolysates and of the nonylphenol ethoxylate in the mixtures.

Higher values of humidity absorption are noticed for the multicomponent mixtures, having a synergistic effect in all cases, but strongest for the CH+NPE binary combination and for the ternary one; a possible explanation, besides the existence of mutual physico-chemical interactions of the components, could be the influence of the type of the created porous structure.

It would be expected that lower values of absorption correspond to high values of water vapour permeability. Nevertheless, the hydrophilic character of the components in the mixture, correlated to the surface-active character of some of those, the possibility of multiple interactions that may occur between them, as well as with the other components in the plastisols mixture in the presence of H.F.E.F., as well as the characteristics of the created porous structures, can increase the amount of humidity that can bond with the porous structures that result under these conditions.

The comparative data about the water vapour permeability and humidity absorption as shown in Table 3 indicate good response of the new obtained porous structures.

***Table 3.*** *Comparative data regarding some hygienic properties of certain representative types of leather substitutes and of the PVC film obtained according to the no. 7 recipe variant [ 9]*

| No. | Sample | Water vapour permeability ($mg/dm^2/24h$) | Absorption on 24 h (%) | Destination |
|---|---|---|---|---|
| 1 | Coaleda | 623 | 1,65 | Lining materials |
| 2 | Ceeregas | 456 | 0,38 | |
| 3 | Porokord Kid | 269 | 2,63 | |
| 4 | Dermosin 200 | 200 | 2,1 | |
| 5 | Loricel 38 | 770 | 6,6 | Insole materials |
| 6 | Texon | 611 | 5,9 | |
| 7 | Konit | 466 | 5,6 | |
| 8 | Berflax | 409 | 5,5 | |
| 9 | PVC films – no.7 recipe variant | 662 | 3,85 | |

## 4. CONCLUSIONS

1. The use of hydrophilic agents to obtain plasticized PVC porous films expanded in H.F.E.F. lead to poromeric films with high hygienic properties.
2. Certain binary and ternary mixtures based on collagen hydrolysates have a stronger synergistic effect as compared to the others.
3. An important factor in the adjustment of hygienic properties is represented by the porous structure characteristics, aspect to be investigated in a future study.
4. There can be noticed an improvement to some hygienic characteristics as compared to other similar materials.
5. The current study adds novelty both in terms of the method used to obtain collagen hydrolysates and of its valorisation to obtain certain materials with improved properties which makes them ideal for the footwear industry.

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