Smart Hydrogels with Collagen Structure Made of Pelt Waste

GABRIEL ZAINESCU[1], RODICA ROXANA CONSTANTINESCU[1], CARMEN SIRBU[2]*

[1]National R&D Institute for Textiles and Leather – Division: Leather and Footwear Research Institute, 16 Lucretiu Patrascanu Str., 030508, Bucharest, Romania

[2]National R&D Institute for Pedology, Agrochemistry and Environmental Protection, 61 Marasti Blvd., 011464, Bucharest, Romania

The area of interest is the synthesis and study of properties of new types of hydrogels made from pelt waste, in order to recover waste from tanneries. Leather processing in tanneries results in about 500-600 kg of pelt waste from a ton of raw hides. These hydrogels are made using smart processes in order to then be applied in agriculture, for preservation of water in the soil or for controlled release of fertilizers, pesticides but also for the development of additivated agricultural film biodegradable over time (between 1 month and 6 months). Hydrogels that are based on biopolymers, compared with hydrogels based on synthetic polymers, have the advantage of biodegradability, biocompatibility, and a low level of toxicity. The paper presents the production of biodegradable polymer mixtures obtained from hydrolysis and enrichment of the resulting hydrolysate with phosphorus and potassium. Hydrogels with collagenous structure are tested using a high-performance instrumental analysis system (FT-IR-ATR, UV-Vis-NIR, SEM, EDAX, etc). The paper presents an experimental model for obtaining hydrogels with collagenous structure from pelt waste resulting from the liming process.

Keywords: hydrogels, pelt waste, tannery, soil

Biopolymers of organic nature are a source of raw materials for agriculture, as protein waste composition provides sufficient elements to improve the composition of degraded soils and plants can harness some elements: nitrogen, calcium, magnesium, sodium, potassium, etc.

This paper presents exploratory research as a starting point to obtain new polymeric complex products - multicomponent - called hydrogels, by processing organic waste with applications in agriculture.

The paper contributes both to the reuse of poor and degraded soils in agriculture and to the recovery of protein waste which is currently disposed of in landfills (processing 1 ton of raw hide results in 75% waste, of which about 50% - approximately 600 Kg - is protein waste that can be used in agriculture) [1-3].

Obtaining hydrogels with collagen structure by pelt waste hydrolysis with applications in agriculture is a novelty, given that collagen is used only in medicine.

Multicomponent absorbent hydrogel-type networks are next generation materials, with three-dimensional structure and high swelling capacity. The applications of these materials are diversifying, in recent years entering the fields of agriculture, food, pharmaceuticals, electrical devices and electronics, environmental protection and biomaterials [4]. Hydrogels have a distinct three-dimensional structure [5-7], and although they have a high water content, hydrogels are water-insoluble due to the crosslinked (physical or chemical) structure of the steric or crystalline linkages. When the hydrogel is in contact with the aqueous solution, there is a swelling thereof.

Hydrogels can be obtained by two major mechanisms: hydrogels with covalent or irreversible links and hydrogels with reversible or physical links [8,9]. The second category includes various subclasses such as ionic interactions (ionic hydrogels or cross-linked polyelectrolyte complexes) and secondary interactions (*entangled* hydrogels, grafted or complexed hydrogels, etc.) [10-12].

Experimental part

In the past decade, interest in different types of gels in areas such as pharmaceuticals, food chemistry, medicine and biotechnology has increased.

The numerous applications of hydrogels are due to their outstanding properties [9], of which the most important are:

- The water content and elasticity that make them similar to natural tissue, in terms of biological interactions at the molecular level;
- The mechanical properties and the degree of swelling in water (amount of water retained) of the hydrogels may be adjusted relatively easily, for instance by changing the cross-linking density;
- Hydrogels may be designed to alter their properties under the action of external stimuli, such as temperature, *p*H, etc.

The applications of hydrogels in agriculture aim at water retention in the soil or controlled release of pesticides or fertilizers. In the first case, the application is based on hydrogels' ability to quickly absorb large amounts of water and then release it gradually, supplying plants with water for longer periods after watering the field (rain or irrigation) has ceased.

Currently, most hydrogels are based on synthetic polymers, so this research proposes the use of collagen hydrolysate obtained from pelt waste (HA) and a synthetic copolymer based on polyacrylamide (CAAm).

It is known that polyacrylamide is a crosslinked polymer that retains its hydrophilic nature and can absorb a large amount of water and increase its volume. Some of the advantages of hydrogels based on acrylamide include being chemically inert, transparent and stable in a wide range of *p*H, temperature and ionic strength. CAAm copolymer based on polyacrylamide is a granular anionic polyelectrolyte with high molecular mass produced in Germany.

In this research, synthesis of hydrogels is reported to CAAm and HA by chemical crosslinking using different concentrations and crosslinking agents, polymers of different ratios to determine the effect of variations in the hydrogel and establish the optimal reaction conditions. Then characterization techniques were performed to determine the thermal, structural, morphological and swelling capacity of the hydrogels.

**email: carmene_sirbu@yahoo.ro*

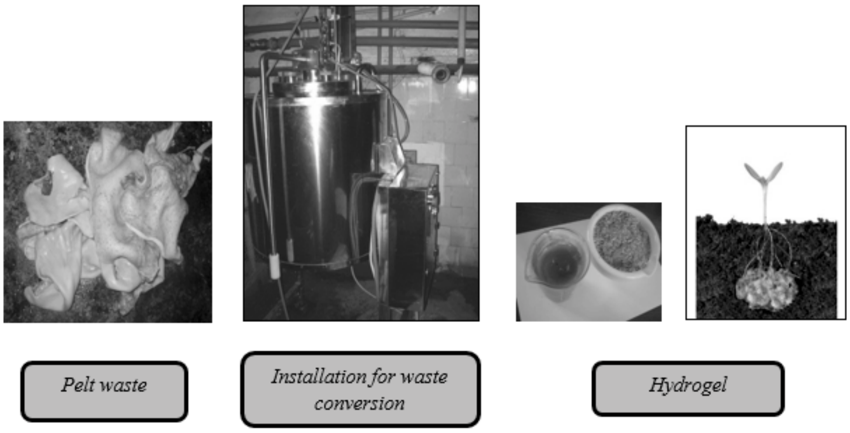

Fig 1. The technological process for obtaining hydrogel by pelt waste hydrolysis

In this study, limed hide waste (treated with 1.2% sodium sulfide, sodium hydrosulfide and 1.5% 3% calcium hydroxide) was used. Raw hide contains (based on dry weight) 50-68% protein, 0.6 to 9% fat, 15-50% ash and less than 5% water.

The waste came from fleshing and trimming cattle hides (weight category 35 kg) from SC Pielorex tannery in Jilava, Ilfov County, Romania.

An innovative process is proposed for treating rawhide waste by protein waste hydrolysis in acid or alkaline medium, to obtain a proteinaceous biopolymer which, in combination with other polymers (polyacrylamide, acrylic acid, maleic acid, cellulose, starch, etc.) can be used in agriculture as hydrogels with controlled release of nutrients.

The proposed technological process for obtaining protein hydrogel includes the following:

- aquantity of 4.5 to 6.0 kg of pelt waste is washed with water at a temperature of 20-25 ^{0} C in a drum for 20-30 min (as it is strongly alkaline);
- hide waste is then ground using a special grinder (with double knives), yielding a pasty homogenous mass - protein biopolymer;
- the protein biopolymer is introduced together with 5 to 6.5 % dipotassium hydrogen phosphate (which helps to improve the nutritional properties by the addition of phosphorus and potassium) in an autoclave equipped with heating jacket and agitator. The mixture is stirred for 60-120 min at 85-96 ^{0} C;
- then to this mixture an amount of 18 to 25% of a synthetic polymer based on Praestol polyacrylamide is introduced and stirring is continued for 120-180 min.
- 0.5-1% boric acid is added and the mixture is removed from the autoclave in plastic drums;

Depending on the fertilizer particle structure, the resulting hydrogel may form the matrix where the fertilizer is embedded or the coating for the solid fertilizer (mono- or multi-layered particles).

Results and discussions

A hydrogel is defined as a polymer network which has the property of absorbing large amounts of solvent causing macroscopic changes in the dimensions of the polymer. The most important property of hydrogels is their degree of swelling as well as dissolution and gradual release of water and nutrients needed for plant growth.

Hydrogels reduce water consumption and irrigation allotted time by 70 %. The hydrogel is an organic soil conditioning substance, which retains the water and diluted nutrients necessary to these plants. Hydrogel in an optimum amount helps plant growth by releasing the necessary water and nutrients.

Hydrogel binds the water and nutrients in the water and continuously provides them to the roots of the plants. The life cycle of the hydrogel can be up to 7 years, after this time it decomposes naturally, without environmental pollution.

Chemical analysis of collagen structure hydrogel for field experiments resulted in $N_{12}P_9K_{12}$ composition (12.74% total nitrogen, phosphorus, 3.64% P_2O_5, potassium K_2O_5 6.18%).

To highlight the structural changes in the process of hydrolysis and interaction with various synthetic polymers, attenuated total reflectance spectrophotometer FT / IR-ATR, Perkin Elmer, USA, was used. By knowing the main spectral characteristics of protein biopolymers in the fields of IR and UV / Vis, some significant bands for the amide structure were selected.

Table 1
TOTAL CHEMICAL ELEMENT CONTENT OF HYDROG

Lot 2			
No.	Specification of components	UM	Values reported to relative humidity upon release
1	Total nitrogen (Nt)	%	12.74
2	Phosphorus (P_2O_5)	%	3.64
3	Potassium (K_2O)	%	6.18
4	Sodium (Na_2O)	%	0.37

Total phosphorus (P_2O_5), total potassium (K_2O) and total sodium (Na_2O) - were analyzed by extraction through wet mineralization with sulfonated per chloric mixture

- K_2O and Na_2O were determined by atomic emission spectrophotometry
- P2O5 was determined by molecular absorption spectrophotometry
- Nt -mineralization and distillation by the Kjeldahl method

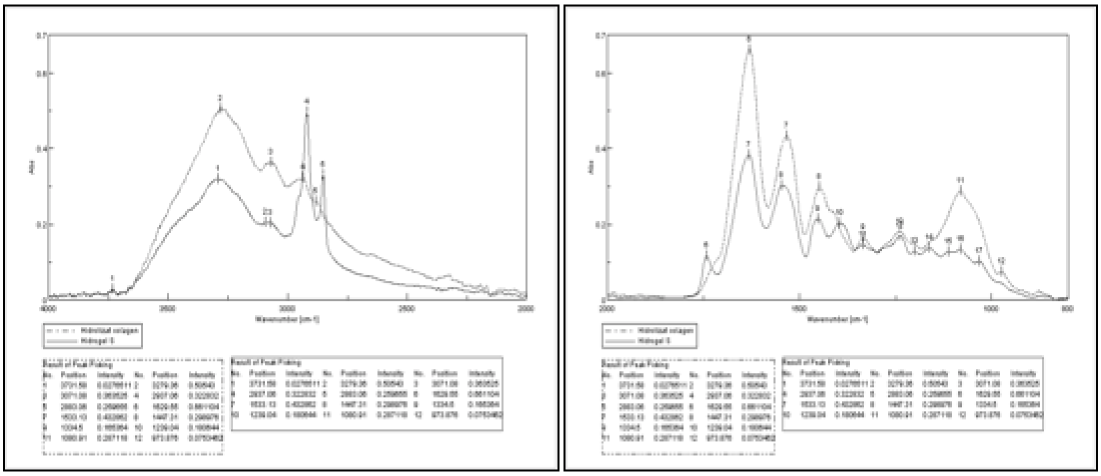

Fig. 2. IR spectrum of the hydrogel, collagen / acrylamide

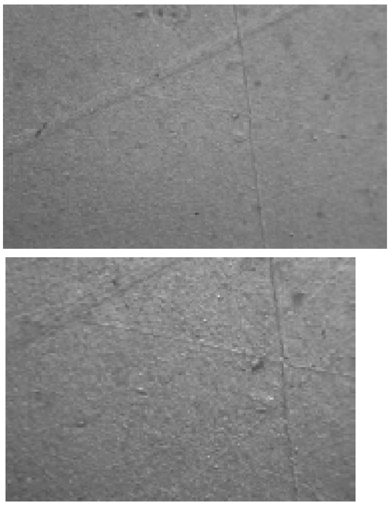

Fig. 3. Micrograph of the hydrogel film (40x)

Molecular absorption spectrometry in the infrared IR is based on vibration-rotation transitions that occur at the molecular level by absorbing infrared radiation. From IR spectra chemical bonds and the molecular structure of organic compounds may be identified. The bands specific for collagen are similar to those of other proteins. The IR spectrum shows bands of the amide I, II and III at about 1660, 1550 and 1240 cm^{-1}, respectively.

Hydroxyl groups and the hydrogen bonds are recorded between 3600 and 3100 cm^{-1}. According to the spectral assignments, in the case of collagen hydrolysate, bands were observed corresponding to amide groups ($\nu_{C = 0}$ 1645cm^{-1} to δ_{NH} and ν_{C-N} 1556cm^{-1}). Also, the characteristic signals of NH groups are present at 1338 cm^{-1}. OH groups in units of hydroxyproline, are signalled at 1082 cm^{-1}. Therefore, the bands at 1660 to 1550 cm^{-1}, by their position and absorbance, give information on the degree of degradation. If movements and changes in their transmittance are found, it is clear that structural changes have taken place. If the band at 1550 cm^{-1} moves to 1530 cm^{-1}, the movement is considered a marker of distortion. Hydrolysis of the chain is marked by changes in the band from 3450-3200 cm^{-1} region that tends to broaden and change its transmittance; at the same time, the band at 1660 cm^{-1} increases in intensity, because its structure includes a -OH component, and the band at 1550 cm^{-1} decreases in intensity. In the collagen hydrolysates, some of the OH groups are replaced with methoxide groups, (CH_3), which attenuate the hydrogen bonds and decrease the crystallinity of the collagen while increasing the water solubility.

Thus, the presence of collagen and acrylamide is confirmed in the molecular structure of the hydrogel.

Figure 3 shows the micrograph of the hydrogel film (40x), where agglomerations can be noticed on the surface due to the acrylamide copolymer and collagen hydrolysates.

Conclusions

Hydrogels as controlled fertilizer release systems in agriculture have major advantages in that they combine water absorption and its slow release with nutrients (N, M, P, Fe, Zn, B, etc.) necessary for plant growth.

The hydrogels synthesized from compounding acrylamide and collagen simultaneously yield a complex with a high degree of swelling, around 72 %, with a value of 798 %.

A framework technology was established for obtaining hydrogels with collagen structure from pelt waste.

Optimal parameters were set for obtaining collagen / acrylamide hydrogel with controlled release of nutrients (nitrogen, phosphorus, potassium, boron, iron, etc.) necessary for plant growth.

Optical microscopy and IR analysis confirmed the presence of cross-linked collagen (HA) and polyacrylamide CAAm in the molecular structure of hydrogel.

Acknowledgements: PN 16 34 01 06 project: "Polymer hydrogels with collagen structure for obtaining multifunctional products SMART supported by National Authority for Scientific Research and Innovation (ANCSI).

References

1. ZAINESCU G., ALBU L., DESELNICU D., CONSTANTINESCU R. R., VASILESCU A. M., NICHITA P., SIRBU C., Mat. Plast., **51** , no. 1, 2014, p. 90

2. ZAINESCU G., CONSTANTINESCU R. R.,.PETRE V., DESELNICU C.D., Rev. Chim. (Bucharest) **67**, no.1, 2016, p. 48

3. CONSTANTINESCU R. R, CRUDU M., ZAINESCU G., COARA G. Rev. Chim. (Bucharest) **66**, no. 8, 2015, p. 1244

4. CONSTATINESCU R. R., CRUDU M., ZĂINESCU G. A., CRUDU A., VOICU P., , 15th SGEM**,** Albena Bulgaria 19-21, 2015 pp 747.

.5 POOLEY S. A., RIVAS B. L., LILLO F. E., PIZARRO G. DEL C., J. Chil. Chem. Soc., 55, pp 19–24, 2010.

6. ABD EL-REHIM H. A., HEGAZY E-S. A., ABD EL-MOHDY H. L., J. of Applied Polymer Science, 101, 3955-3962, 2006.

7. PEPPAS N. A., Academic Press, New York, 2004, p 100.

8. HENNINK W. E., VAN NOSTRUM C. F., Advanced Drug Delivery Reviews, 54, pp 13–36, 2002.

9. HO E., LOWMAN A., MARCOLONGO M., Biomacromolecules *7/* 2006, p 3223.

10. PEPPAS N. A., 2-nd ed., New York, p. 100, 2004.

11. BELCHEVA N., STAMENOVA R., TSVETANOV C., Macromol. Symp**.** 103, p 193, 1996.

12. DADSETAN M., SZATKOWSKI J. P., YASZEMSKI M. J., LU L., Biomacromolecules 8/2007, p 1702.

Manuscript received: 31.05.2016