High Yield Biopolymer Systems Obtained from Leather Wastes

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Organic biopolymers are a source of raw material for agriculture, whereas the composition of protein wastes provides sufficient elements to improve the composition and remediation of degraded soils and plants by exploiting elements, such as nitrogen, calcium, magnesium, sodium, potassium etc. From processing one tone of raw hide, 75% is discarded, of which 50% could be further used as organic fertilizer. Protein biopolymers were obtained by means of an innovative enzymatic procedure for waste processing. In combination with polyacrylamide, acrylic, maleic, cellulose, starch etc. are used in the agricultural field. We characterize the protein biopolymers by specific morpho-structural analysis methods (UV-Vis, IR spectroscopy, thermal analyses, X-ray diffraction, microscopy).The novelty of this work is the biochemical combination process of synthetic polymers with organic biopolymers from tanneries with viable and interesting applications in agriculture.

Keywords: biopolymer, protein wastes, tannery, soil, structural analysis

Recent studies in Central and Eastern Europe showed that, in these regions, the main degradation processes induced by human activity result in reduced soil fertility, crust-formation, water and wind erosion, landslides and chemical pollution [1].

Many industries, including leather industry, are faced with high expenditure for solid organic waste treatment and disposal. Therefore, the tannery protein wastes must be subject to biochemical treatments in view of recycling for agricultural purposes [2].

The use of untanned wastes presents especially high interest because it provides almost total fleshing waste discharge while obtaining qualitatively and economically valuable products.

In this paper we investigate the development possibilities for various multicompound systems of biodegradable polymers and study the effects of these complex products on structural, chemical and physical characteristics of degraded or contaminated soils (having a poor level of organic matter or submitted to a strong erosion process).

Experimental part

Protein biopolymers were obtained by means of an innovative enzymatic procedure of waste processing, which in combination with other materials (polyacrylamide, acrylic, maleic, cellulose, starch etc.) can be used for crop growing.

The novelty of the promoted technology has as a starting point the obtaining of new complex products by processing tannery organic wastes which can be utilized in the agricultural field. Complex characteristics of protein wastes from the leather industry are determined by accurately investigating waste hide chemical composition and various possibilities of recovery and recycling by means of biotechnologies [3].

Processing untanned wastes from tanneries is of particular interest nowadays because of the opportunity to eliminate nearly all wastes from fleshing, while obtaining qualitatively and economically interesting and valuable products. Interactions of proteins with synthetic polyelectrolytes are involved in various chemical processes. These interactions may result in soluble complexes, complex coacervation, or the formation of amorphous precipitates. Main types of interactions between polyelectrolytes and proteins are the hydrogen bondings, hydrophobic, and electrostatic forces. The relative magnitude of each of these interactions is determined by several factors, including protein and polyelectrolyte charge densities, salt concentration, and sizes of their respective hydrophobic groups.

Polyelectrolytes are among the most important agricultural soil conditioner agents. Polyelectrolytes (PE) are polymers whose monomer units have ionized or contain ionisable groups. In aqueous solutions the PE dissociate into polyatomic macroions (polyions) and a large number of small opposite ions – counterions. In our research we used polyacids or anionic polyelectrolytes, whose functional group is the –COOH carboxyl group, $-SO_3H$ sulfonic group or $-PO_3H$ phosphonic group.

$$(-CH_2-\underset{\displaystyle COOH}{CH}-)_n \xrightarrow{\text{dissociation}} -(-CH_2-\underset{\displaystyle COO^-}{CH}-)_n + nH^+$$

Scheme1. The dissociation of a weak acid poly electrolyte poly (acryl acid)

Polymers and copolymers based on acrylate and acrylamide are the most exploited ones. Polyacrylamide determines stabilization of sandy dune soils, prevents crust formation, diminishes the intensity of elementary soil particle scattering by rain drops and hence lowers the intensity of erosion from water. Improving soil structure results in increased water infiltration rate. Hydrophilic nature of polyacrylamide increases soil capacity to retain water and reduces water loss through evaporation and infiltration in sandy soils [4].

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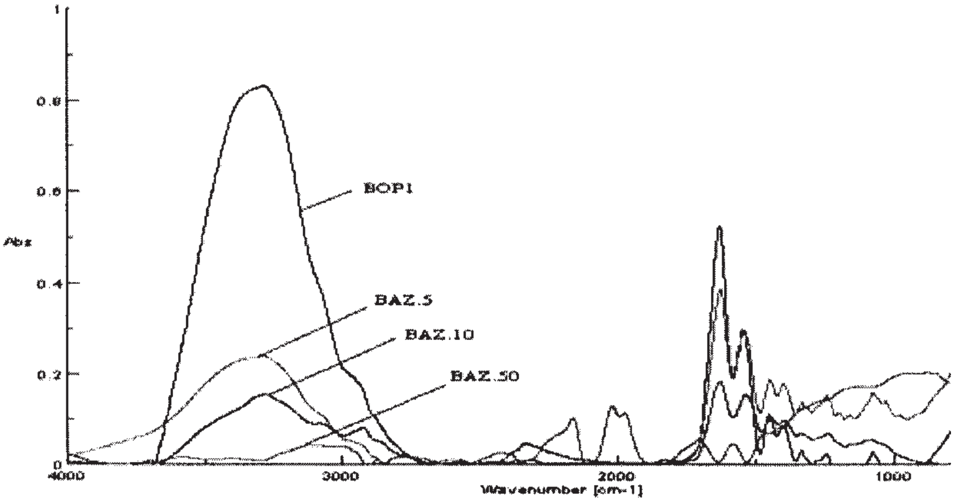

Fig. 1. FT/IR-ATR spectra of biopolymer samples (BOP1- hydrolyzed leather waste, BAZ- protein biopolymers 5, 10, 50% synthetic polymer)

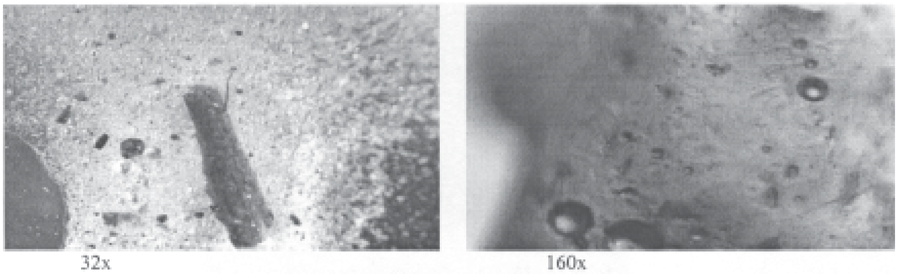

Fig. 2. Optical microscope images for biopolymer samples (32X and 160X)

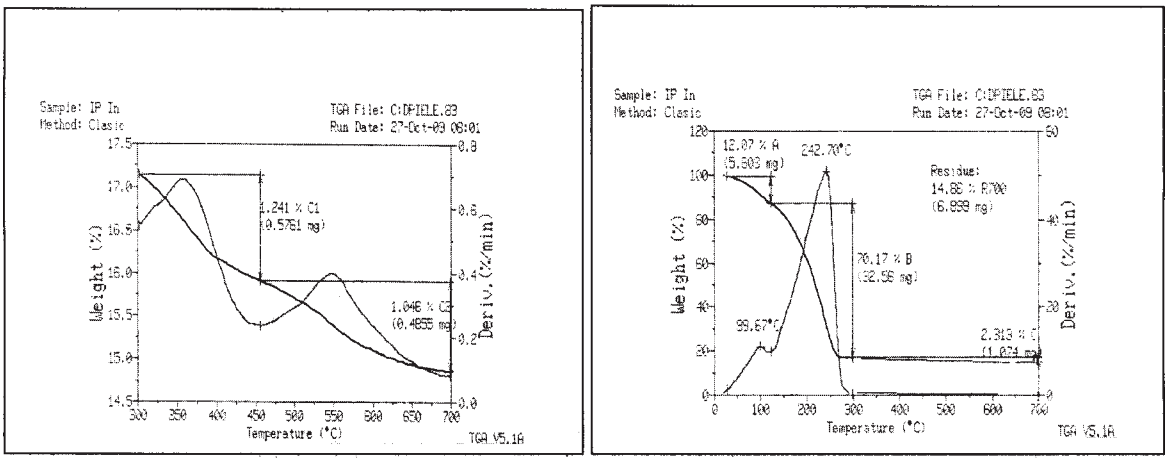

Fig. 3. TG/DSC derivatographic curve for DPP10 synthesized biopolymer

By knowing the main spectral characteristics of protein biopolymers (in IR and UV/Vis domains), a few significant bands for the amidic structure have been selected. These can enhance structural modifications taking place in the hydrolysis process and in the interaction with various synthetic polymers, in the presence of enzymatic "enhancers".

Characteristic bands of collagen are similar to those of other proteins. IR spectrum presents amide I, II and III bands around 1660, 1550 and 1240 cm^{-1} respectively. Hydroxyl groups and hydrogen bonds are recorded between 3600 and 3100 cm^{-1}.The 2500–2000 cm^{-1} domain indicates the presence of stretching vibrations given by groups $X \equiv Y$, X=Y=Z (where X, Y, Z can be: C, N, O, S and X can be replaced as well with: Cl, Br, I), being present in all samples (also confirmed by the technological process of obtaining protein biopolymers).

Polarized light optical microscopy images (fig. 2) show synthetic polymers in the shape of filiform needles (left) and skin fibers (right).

By various thermal analysis methods (Differential Thermal Analysis - DTA, Thermogravimetry - TG), the temperature range for which the polymer decomposition process occurs was investigated. In the first part, the crystallization water is evaporated up to temperatures of about 200°C (fig. 3).

Subsequently, in the range 200-300°C, burning (decomposition) and elimination of gaseous products CO and CO_2 take place, with strong exothermic effect on the DTA curve of polysaccharides. Between 300-500°C the resulted oxide mass is practically constant. The presence of poly(methyl methacrylate) - PMMA determines an order at close range in the case of protein biopolymers, resulting in the increase of the Glass Transition Temperature (Tg).

Thus, by increasing the amount of synthetic polymer in the biopolymer structure we expect an increase for the Tg values. This behavior can be equally expected due to potential reticulations between protein and the synthetic polymer, and to the relative order level generated by the presence of enzymes in the hydrolysis process.

The process of biochemical combination of synthetic polymers with organic biopolymers from tanneries has innovative applications in pedology. Gelatin hide wastes

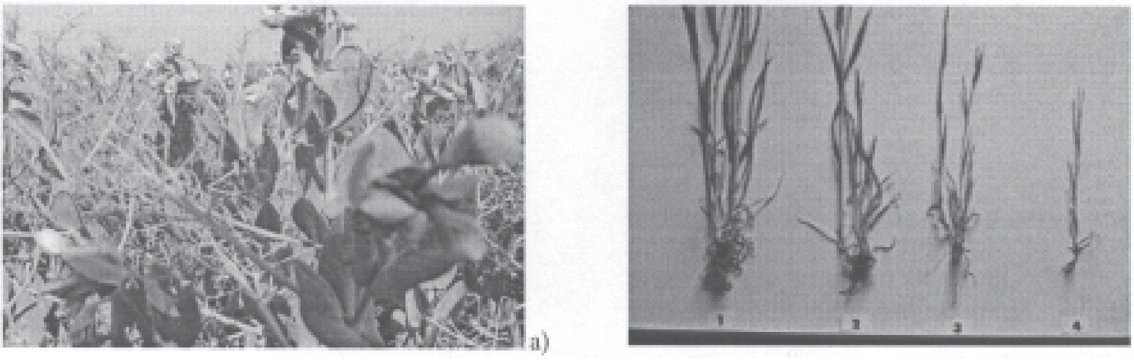

Fig. 4. a)Phenophase of pea culture (Diana type 2010) when nodosities were counted; b)Treated barley plants categories (1, 2, 3) compared to untreated specimen (4).

were obtained from SC Pielorex Jilava (Ilfov county) tannery. The study involved treating by chemical and enzymatic process the wastes from bovine hide shavings and trimmings.

Soil conditioning consists in improving the physical properties by means of substances with varied origins, known in literature as “soil conditioners”. Soil contamination represents a moderate increase in the concentration of certain substances which are not harmful for plant growth and development, but can represent the initial phase in the pollution process. Decreasing the effects of soil weathering/ contamination/ pollution involves the use of certain methods which lower the negative consequences of the soil fertility degradation and contamination or pollution.

ICPI together with the National Research & Development Institute for Pedology, Agrochemistry and Environment Protection Bucharest and the R&D Institute for Plant Culture and Protection Bucharest have recently tested protein biopolymer systems for use on degraded soils and for greenhouse and field plant growth [5,6].

Usually, polyelectrolytes and other polymer classes contribute to the improvement of soil properties, through one or more of the following effects:

- an increase in the aggregation of soil structural elements in weathered soils;
- prevention of crust formation in the period between sowing and spring, especially for plants with small seeds, which are very vulnerable;
- an increase in resistance to water and wind erosion of soils located on slopes and coarse grained soils (less than 12% clay).

Micromorphology analyses were conducted on a glazed, loamy-clayish chernozem, on leossoide deposits in the north area of Bucharest, where the protein biopolymer (BAZ. 50) was applied. Micromorphology analyses for thin sections on the distribution behaviour of the soil bioenhancer (BAZ.50) and its relationship with different components of soils was made possible by using a new technique (marking the conditioner with three types of dyes - hematoxylin, fluorescein, isothiocyanate).

The bioenhancer (BAZ.50) was experimented on a culture of peas (annual vegetable) for improving the land through soil enrichment with biologically fixed nitrogen and to allow the early release of land. The land was then prepared for sowing barley. Beside the nutrients in the soil, it has been shown that peas need nitrogenous fertilizers, especially during the first stages of development. Subsequently, it grows at the expense of the fixed nitrogen in the air by bacteria that form nodosities on the roots. The most suitable soil type for pea cultivation is neutral or slightly alkaline, meaning that it can be moderately amended with limestone, but only by predecessor plants (not directly). In the blooming phenophase, the nodosities on the pea roots were considered from the treatment before sowing with bioenhancer (BAZ.50) (0.5 kg/m^2).

The bioenhancer (0.25-0.5 kg/m^2) soil treatment significantly influenced the number of nodules developed on the plant roots. Roots and organic remainders gathered in the soil by the pea plants are an important source of nutrients and energy for soil microorganisms. Additionally, their decomposition results in a significant amount of necessary elements (especially nitrogen) for the nutrition of superior plants.

These studies contribute both to the recovery of poor and degraded soils in agriculture and to the reduction of environmental pollution by exploiting protein wastes.

Conclusions

Biopolymers have been obtained by an innovative enzymatic procedure of processing protein waste resulted from leather processing. In combination with other polymers (polyacrylamide, acrylic polymer, maleic polymer, cellulose, starch, etc.) they can be used for improvement of degraded/eroded soils and growth of greenhouse and field plants.

All instrumental analyses (UV-Vis, IR spectroscopy, thermal analyses, X-ray diffraction, microscopy etc) have highlighted both reticulations between the protein polymer and the synthetic one, and the high order of the polymeric structure, which is due to the enzymatic hydrolysis process.

For an efficient crop growth, it is not enough to add only the missing element, but also to satisfy, as much as possible, all the needs of the plants. This implies acting simultaneously on various factors in the complex condition determining agricultural production.

The obtained experimental results demonstrate that the protein biofertilizer materials produced an interesting outcome both in terms of improving the soil quality and growing large-scale crop plants, showing highly potential applications in agriculture and environmental sciences.

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