Obtaining of Biodegradable Plastic Materials

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The paper presents the obtaining of new biodegradable plastic materials using collagen hydrolysates. As raw materials, to transform into collagen hydrolysates, untanned leathers' wastes were used. The influence of chemical structure and ratio of protein material on thermoplastic processing were investigated. The effect of protein material contents on physico – mechanical and biodegradability properties has been evidenced.

Keywords: biodegradable plastic materials, collagen hydrolysates, protein material

National / European law is pressuring the leather sector to convert wastes into added value sub-products (1). Environment protection costs of European companies represent 5% of their turnover. This has directly affected their economic competitiveness towards non-European companies that have not had to face these problems.

The application of IPPC Directive, as well as the integration in the legislation of local authorities can be accomplished by SMEs in the industrial sectors only by having a base for the development and adoption of integrated measures of prevention and control, particularly by reducing the pollutant charge from production and reducing the quantity and the costs of managing wastes and residual waters. The implementation of the project will contribute to reaching this goal in the footwear manufacturing sector by solid leather wastes recovery.

The recycling of leather wastes

At present, some solutions have been applied to finished leather scraps with a technical, but not always with commercial success. These are: Incineration in a special furnace: Bubbling fluidized bed (2); Fertilisers (3); Fibre and filler (4); Gelatine / chrome extraction (5); Non-woven (6); Paper compound (7); Absorbing material (8).

Generally the term of biodegradation refers to the biological degradation of a substance, which is induced by micro-organism (1). Most researchers dealing with biodegradability (2 – 4) degree established that the action of micro-organism may generate three different levels in the degradation of a certain substances structure: primary, partial and total biodegradation. Destruction of the polymeric wasted which infest the environment is the direct result of partial and total degradation (5 – 9).

It is generally accepted that scission of the macro-molecule chains of a given support occurs only in the presence of enzymes which, nevertheless, does not exclude concept such as cellular degradation or bacterial degradation.

The improvement of biodegradability of plastic materials used in packing up may be obtained using a natural material, like protein, as a biodegradable additive.

Experimental part

Materials and methods

Polyvynilic alcohol

Proteic hydrolysate (in powder form) were obtained from untanned bovine hides through neutral hydrolysis of 8 hours and dryed by liophilization process ($[\mu]$ = 0,15, NH_2 = 0.8766 mmol/ g).

Synthetic Polymers were obtained by polymerisation in emulsion method. The film of synthetic polymers was obtained by application on glass surface.

With respect to this principle there have been realised the films of synthetic polymers obtained from the process of polymerisation in emulsion (table 1), in which were added polyvinylic alcohol (10 %) and protein hydrolysate

No. Crt.	Latex	(%) Monomers	(%) dry substance
1.	L 1	46 % styrene; 54 % butylmetacrylate	34.1
2.	L 2	41 % styrene; 5 % glycidyl; 54 % butylmetacrylate	33.4
3.	L 3	50 % vinyl chloride; 50 % butylacylate	40
4.	L 4	50 % styrene; 50 % butylacrylate	34

Table 1
THE COMPOSITION IN MONOMERS OF LATEXES

No. Crt.	Collagen hydro-lysed	Glutar-aldehyde	g protein found in 100 ml solutie					
			0 h	1 h	2 h	3 h	6 h	24 h
1	0	0	0	0	0	0	0	0
2	2	0	0	0	0.025	0.028	0.15	0.187
3	5	0	0	0.025	0.037	0.137	0.15	0.162
4	10	0	0	0.1	0.12	0.15	0.187	0.275
5	2	1	0	0	0.025	0.025	0.025	0.125
6	5	1	0	0	0.025	0.037	0.15	0.15
7	10	1	0	0.025	0.05	0.15	0.175	0.25

Table 2
KINETICS OF ENZYMATIC TREATMENT FOR THE FILMS REALIZED WITH LATEXES L3: L4 (1:1) AND DIFFERENT RATE OF COLLAGEN HYDROLYSED IN THE PRESENCE OF GLUTARALDEHYDE

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(in powder form) in a concentration of 2; 4; 10 % related to the polymer substance.

In order to observe the influence of protein when it is reticulated, some experiments have been performed, where glutaraldehyde was added with a concentration of 1 % related to the protein weight. The films have been obtained through depositing on anti-adherent paper of the solutions and drying for 3 min at 120 °C.

The biodegradability of the films has been tested using a method that simulates the natural phenomenon of biodegradation, by immersion of the films for 8 - 48 h into an enzyme solution (trypsin) of 2 % concentration, *p*H = 8; T = 36° C.

The kinetics of enzymatic treatment on the films has been observed by the quantity of dissolved protein. The biodegradability degree has been evaluated by loosing of weight of the films (table 2).

Results and discussions

The following results have been obtained:

-the quantity of dissolved proteins during enzymatic treatment is more when the quantity of collagen hydrolysate contained in the films is higher;

-the speed of the enzymatic reaction is higher in the first six hours, after that it remains constant;

-in all the cases, the reticulation of the protein with glutaraldehyde leads to the increasing of their biodegradability;

-the using of a latex mixture of poly-butyl-acrylate – poly-vinyl-chloride inhibits the enzymatic activity.

The biodegradability of the films has been investigated also by the loosing of physico – mechanical properties after enzymatic treatment.

The modification of some properties of the films like: the permeability to water vapours, the permeability to air, the tensile strength, the elongation and the morphological aspects as radius and number of the pores were investigated.

The modification by biodegradation of the chemical – morphological structure of the films obtained from synthetic polymers has been evidenced by modification of some properties, such as:

- permeability to air increased for all types of tested films;
- permeability to water vapours increased when the collagen hydrolysate was added to composition of the films, before, or after enzymatic treatment (fig. 1 and fig. 2):

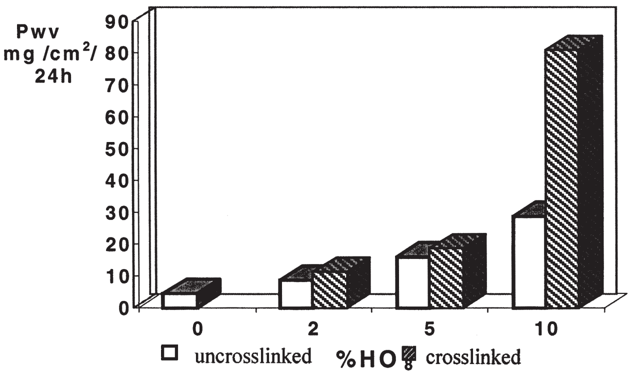


Fig. 1. Permeability to water vapours of sheets made of latex blend L3: L4 (1:1), before biodegradation

- the number of pores increases at the same time with the increasing of the protein rate in the film composition. By biodegradation (enzymatic treatment), their porosity increases (increases the pore radius), the phenomenon which can be explained by extraction of the protein from polymeric composite (fig. 3 and 4);

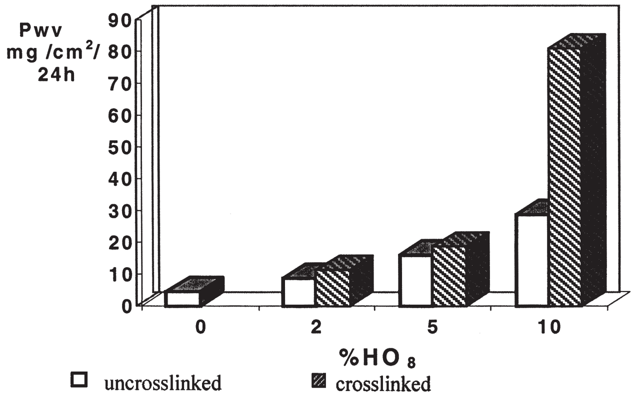
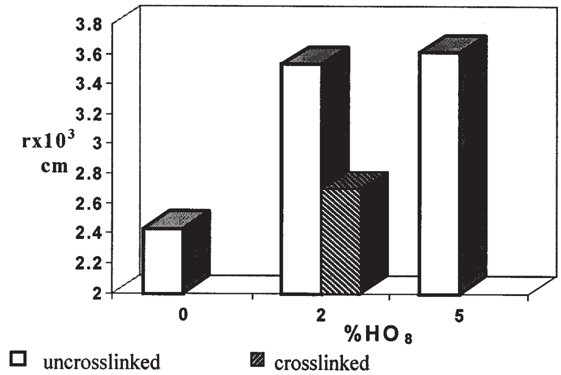


Fig. 2. Permeability to water vapours of sheets made of latex blend L3: L4 (1:1), after biodegradation



Figu. 3. Radius of pores for sheets made using latex L1, before biodegradation

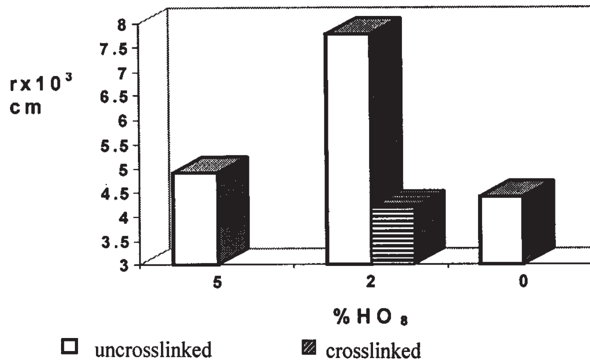


Fig. 4. Radius of pores for sheets made using latex L1 after biodegradation

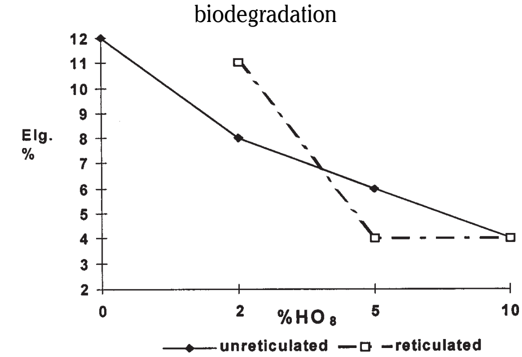


Fig. 5. Elongation at break of sheets made using blend L3 : L4 (1:1), before biodegradation treatment

-tensile strength and elongation decrease when protein additive was introduced in a high rate (fig. 5 and 6):

A quantity of 2% collagen hydrolysate added to composite has the result of keeping the physico -

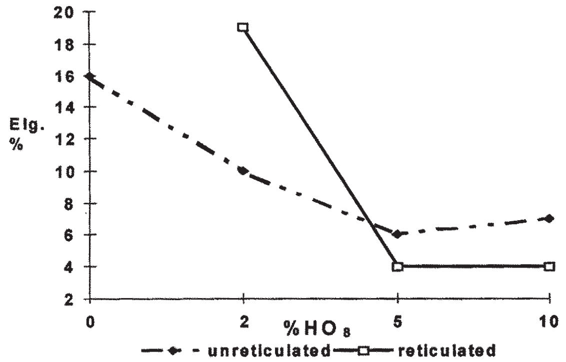


Fig. 6. Elongation at break of sheets made using blend L3 : L4 (1:1), after biodegradation treatment

mechanical properties at a high level. The reticulation of protein with glutaraldehyde leads also to a high level of physico – mechanical properties of the films.

Conclusions

The addition of the collagen hydrolysates to synthetic polymers represents a suitable solution for improving the biodegradability of plastic materials used for packing up. The rate of 2 % collagen hydrolysates keeps the physico – mechanical properties of plastic material unmodified.

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