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Biodegradable Hybrid Polymer Films Based on Poly(Vinyl Alcohol) and Collagen Hydrolyzate

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Summary: Hybrid blends of poly(vinyl alcohol) (PVA) and collagen hydrolyzate (CH), an added value waste from leather indutry, have been converted by blown molding extrusion, to environmentally degradable films.
Blown extruded films comprising 5-15% of CH, were tested as sel fertilizing mulching films and analyzed for their propensity to enviromental degradation.
PVA/CH films rapidly disintegrate when buried in soil, and resulted promising for application such as transplanting films, with additional fertilizing action of CH.

Keywords: biodegradability; blown extrusion; films; polymer blends; poly(vinyl alcohol); protein; renewable resources

Introduction

In the leather industry the tanning process generates a huge amount of protein waste, thus it has been estimated that one metric ton of wet salted hides yields 200 Kg of leather and over 600 Kg of solid waste [1]. Approximately 600,000 metric tons of chromium-containing solid wastes are generated worldwide. The problems associated with this mass of collected waste are compounded by the nature of the leaching medium. The majority of dispersed and dissolved organic and inorganic substances are removed from liquid waste (sewage water) by applying a combination of precipitation and filtering techniques and the resulting slurry is been utilized as an agrotechnical fertilizer or component of composite boards [2]. Nowadays the tannery pays for transportation and reprocess of these wastes and for disposal [3]. Interest for alternative applications comprising the promotion of of collagen hydrolyzate (CH) is high, since ultimately a compensation on the waste disposal cost can be attained by the CH intrinsic value and abatement of environmental impact.

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As a part of a research program aimed at the preparation and evaluation of environmentally degradable polymers for various applications in agricultural practices, with specific reference to the in situ formulation of self-fertilizing mulching and seedling pots, we reported on the preparation of blends based on poly (vinyl alcohol) (PVA) and animal gelatin [4,5]. PVA has been used in blends and composite with proteic materials [6,7] since PVA hydrophilic character allow for some grade of compatibility. In the present study we started to consider the possibility of utilizing PVA and CH for the production of degradable films by melt blow extrusion. Collagen hydrolyzate utilized in the present study has been produced by enzymatic hydrolysis of solid wastes derived from chrome tanning process of leather [8-10].

Materials

Poly(vinyl alcohol) (PVA) was Sloviol, P08/88, from Novaky (Slovakia) with 88% hydrolysis degree and 8 mPas viscosity (4% at 20 °C) grade.

Collagen hydrolyzate (CH) was a slightly yellow powder from enzymatic hydrolysis process from leather industry, chromium compounds-free, by Kortan (Czech Republic). N 13,2%, C 39,3%, H 6,1%. Particle size of the PVA and CH powders, was measured by sieving 50 g of each component with ASTM sieves for about 1h. The relevant results are reported in Table 1.

Table 1. Particles Size for PVA Sloviol 08/88 and Collagen Hydrolyzate (CH).

Mesh	mm	%PVA	%CH
$\phi>50$	$\phi>0.425$	15.1	0.5
$50<\phi<70$	$0.425<\phi<0.212$	16.3	0.5
$70<\phi<100$	$0.212<\phi<0.150$	18.1	17.0
$\phi<100$	$\phi<0.150$	50.5	82.0

Sample Preparation

PVA Sloviol P08/88 was tested in Idroplast (Italy), on the major ingredients of their proprietary PVA formulation grade suited to melt blow extrusion. Subsequently mixtures of same grade PVA and CH were prepared with 5-15% by weight of the proteic compound.

SEM Analysis

SEM inspection was carried out on a Jeol T300 scanning electron microscope. The film samples were prepared by critical point drying followed by sputtering with gold and observation at 10 KeV.

Mechanical Analysis

Tensile tests were performed by mean of an Instron Model 4201 Universal testing Machine. ASTM D-638 specimen, 0.03 mm thickness, were stamp cut from blown films based on PVA and PVA/CH. Tensile tests were performed after specimen conditioning at 23 °C and 50% RH, crosshead speed was 50 mm/min.

Water Solubility

Water solubility was assessed by introducing 3x3 cm square sample, 0.03 mm thickness, in 150 ml water at 20 °C. Time for disintegration was recorded.

Soil Burial Respirometric Test

Respirometric soil burial test was performed by buring 350 mg of dry films in 10g of forest soil collected at S.Rossore Park (Pisa). CO_2 developed within the time fromt the test sample, the blank and filter paper as positive control, was recorded by absorption on KOH (0.05N) solutions and retrotitration with HCl 1N, after addition of $BaCl_2$. Mineralization was expressed as percent of evolved CO_2 (corrected for the CO_2 produced in the blank experiment) with respect to the theoretical CO_2.

Results and Discussion

PVA Sloviol 08/88 from Novaky was tested in Idroplast according to Idroplast formulation for melt blow film extrusion. The PVA was premixed with the Idroplast additives and processed pellets by a twin screw extruder. These were processed at 170-190 °C, to give a film. Clear flexible blow extruded films was produced with a relatively minimal fish eyes that were attributed to the fairly broad particle size distribution of the PVA sample.

Thus for the applied technology a PVA with a fairly narrower particles size distribution would be recommended. A part this aspect the PVA resulted suitable for this technical application. PVA and CH with 5-15% of CH by weight were prepared and submitted to the processing steps applied to the PVA formulation.

This mixture was processed with the twin screw extruder to produce pellets. The resulting pellets appeared pale yellow colored, uniform and homogeneous.

During the processing of PVA and CH blend formulations a very minimal smell of degraded protein was recorded, especially in comparison with what previously experienced during processing of protein hydrolyzate derived by direct chemical dechromatization [11]. PVA/CH pellets were blow molded to produce thin films.

SEM micrographs of PVA and PVA/CH films evidenced an extremely good compatibility of the two materials, since PVA/CH surface presented little irregularities due to protein aggregates in the PVA matrix (Figure 1b) and PVA/CH fracture was indistinguable form PVA fracture (Figure 2).

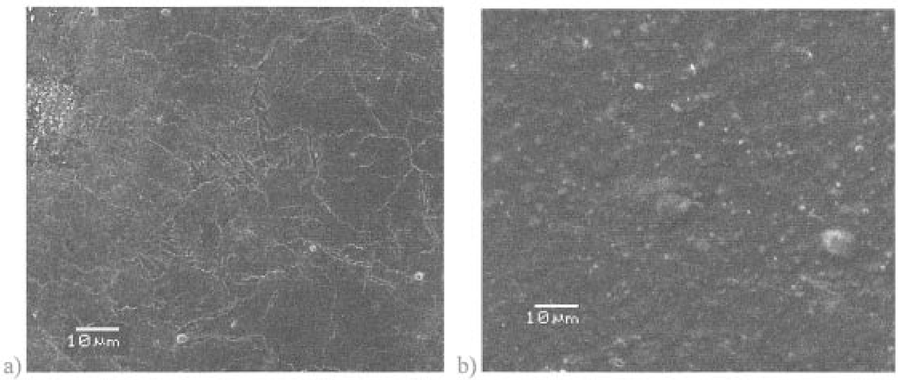

Figure 1. SEM Micrographs (1000X) of PVA (a) and PVA/CH (b) Blown Film Surface

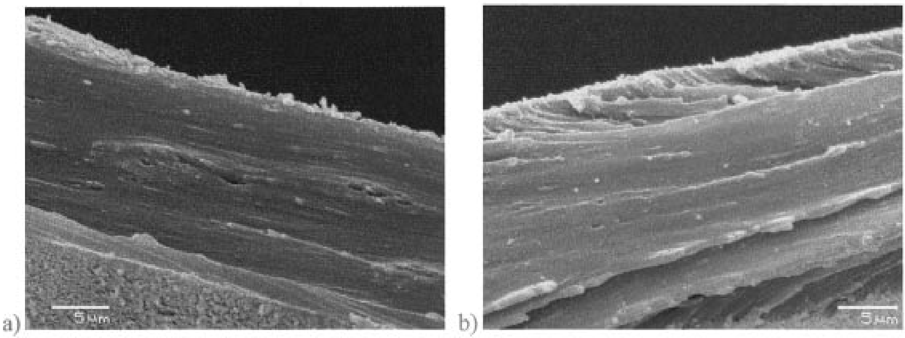

Figure 2. SEM Micrographs (3000X) of PVA (a) and PVA/CH (b) Blow Film Fracture

In previous studies on PVA/gelatin films, prepared by of casting aqueous solutions/disperisons, SEM micrographs of fracture evidenced PVA-gelatin distinguished phases [4].

Stamp cut dog bones of the prepared film containing 10% by melt of CH were tested for mechanical properties and the results are reported in Table 2.

Table 2. Mechanical properties (machine direction) of PVA and PVA/CH (10% CH) blown films.

Sample	El (%)	StDv (MPa)	UTS (MPa)	StDv	YM	StDv
PVA	154	11	16	1	86	15
PVA/CH	93	15	19	2	110	20

El=Elongation at break, UTS= Ultimate Tensile Strength, YM= Young's Modulus, StDv= Standard Deviation

The addition of CH in the film induced a reduction in the elongation at break with a concomitant increase in ultimate tensile strength and Young's modulus.

In previous studies on PVA/CH blow extrusion a crosslinking between PVA and CH was hypotized, thus CH is reach of free NH_2 groups, available for interaction with the residual acetate groups of PVA[12]. The strengthening effect detected for the PVA/CH analyzed film appear to confirm this hypothesis.

When introduced in water PVA films dissolved in 10 min, PVA/CH films dissolved in less than 5 min. Thus films appear suitable for applications such as laundry bags, self-fertilizing packaging and seedling pots.

PVA/CH was tested as transplanting film on lettuce sprouts (*lactuca sativa*). 30 lettuce sprouts were packed in a 30x100 mm PVA/CH film and planted in soil (Figure 3).

Films disappeared in 5-10 days and lettuce showed a regular grow in comparison with unpacked sprouts.

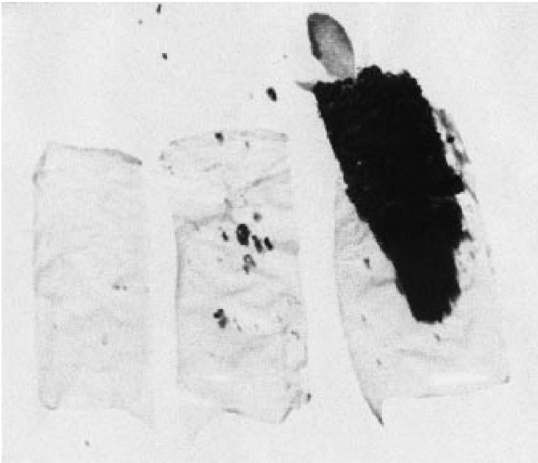

Figure 3. PVA/CH film tested as as transplanting sack on lettuce sprouts

In soil burial biodegradation test, a limited mineralization was recorded for both PVA and PVA/CH. After 60 days the mineralization of the hybrid films was in any case higher than that of PVA alone. However at the present state of the investigation no correlation can be drawn on any beneficial or detrimental effect played by the presence of CH in the hybrid films.

Thus probably only the plasticizers and proteic component are mineralized in the experiment condition (Figure 4).

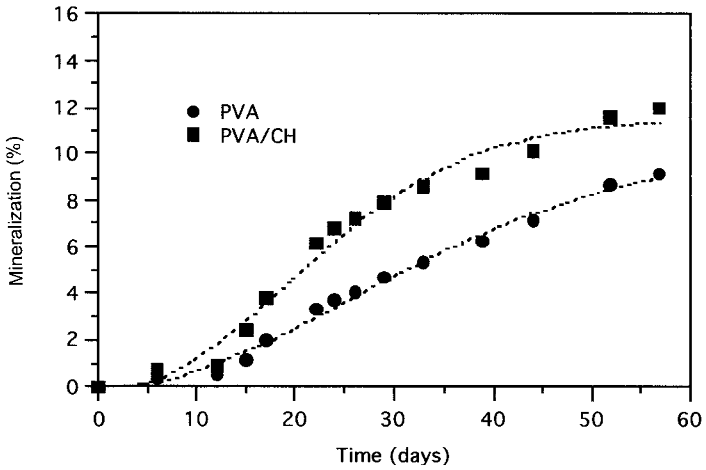

Figure 4. Mineralization rate of PVA and PVA/CH films

PVA slow degradation in soil has been amply documented [13-17] and atributed to the concomitant absence of PVA degrading microorganism in unpolluted soil and PVA adsoprtion by soil [18].

PVA based films are prone to be degraded in acclimatated envrionment such as waste waters from paper industry [19]. In this of PVA/CH hybrdi films an increase in rate and extent of degradation was detected.

Conclusions

Polymeric films based on hibrid blends of poly(vinyl alcohol) (PVA) and collagen hydrolizate(CH) from tannery proteic waste, can be prepared by melt blow extrusion under conditions analogous to those used in the PVA formualte melt blow extrusion.

PVA/CH formulation resulted suitable for processing by melt blow extrusion for a 5-15% CH on PVA.

PVA/CH films rapidly disintegrate when buried in soil, and resulted promising for application such as transplanting films, with additional fertilizing action of CH.

Slow PVA mineralization in soil is already documented in literature. The addition of CH increase the overall degree of biodegradation. Studies are in progress to identify any potential effect of CH on PVA biodegradation both in soil burial and aqueous environmental beds.

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