Polypropylene/Collagen Hydrolysate Thermoplastics Blends: a Waste of the Leather Industry as a Resource to Produce Innovative Materials

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Abstract: Polypropylene-based composites are prepared using collagen hydrolysate from waste of the leather industry. Blends of polypropylene and collagen hydrolysates were studied as a function of the blend composition ratio with the aim of developing a formulation with optimal physical-chemical and mechanical properties. The prepared mixtures were characterized by thermal analyses and mechanical test. Blends with content up to of 20-30% of collagen hydrolysate are susceptible to be melt processed to provide transparent, cohesive and flexible films. In front of positive results the reutilization of collagen hydrolysate derived from the tannery industry appears feasible for production of thermoplastic items for applications in packaging and agricultural segments.

Keywords: collagen hydrolysate; polypropylene; mechanical properties; thermal properties

1 Introduction

In the last decades blends of synthetic and natural polymers have been used to develop new materials. Proteins of vegetal and animal origin have been employed in blend with plastics to obtain films and other products [1, 2].

Fleshings and shavings represent one of the most important by-product of the tannery compartment. They are obtained in the fleshing/shaving phase of the hide and are mainly constituted of raw collagen. A measure of its environmental impact is given by the wastes generated by fleshing/shaving of the industrial tannery district of Santa Croce sull'Arno (Italy), whose production is close to 80.000 tons/year. Such a waste of the whole district is collected and processed in a centralized plant where, through an alkaline hydrolysis, a raw collagen hydrolysate solution is obtained. The high content of salts of the raw collagen hydrolysate, whose separation is rather expensive, represents an obstacle to recovery and reutilization.

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The present work is linked to a previous study on production of thermoplastic films based on low density polyethylene and collagen hydrolysate [3]. In order to test an alternative trade polymer, polypropylene designed for sheet extrusion was used. In this work, blends of polypropylene with collagen hydrolysate have been investigated in order to assess a formulation suitable for the production of thermoplastic films for applications in packaging and agriculture. Thermal analyses and mechanical tests were carried out in order to evaluate some properties of compression molded films.

2 Experimental

2.1 Materials

Polyepropylene (PP) Moplen RP210G was supplied by LyondellBasell Industries, as uniform granules, having the following characteristics: melting temperature 145°C; density 0.9 g/cm3; melting flow index (MFI) 1.8 g/10 min (230°C/2.16 kg). Moplen RP210G is a random copolymer with 3% of ethylene designed for blow moulding and sheet extrusion.

Collagen hydrolysate was supplied by S.G.S. S.p.A. (Santa Croce sull'Arno-Italy), a centralized plant that treats the wastes from fleshing/shaving of all Tuscany leather district, producing both a hydrolysate concentrated solution through alkaline hydrolysis, degreasing and concentration, and a hydrolysate in powder form upon lyophilization. Collagen hydrolysate in powder form derived from flashings (HC1) and from shavings (HC2) was used. The composition of the two types of hydrolysates is reported in   Table 1. Before use, the powders were dried under vacuum at 40°C for 12 hours.

2.2 Blends and films preparation

The blends were prepared by mixing the components in a Brabender (Model OHG) in the following operational conditions: temperature 155°C, rotor speed 50 rpm and a mixing time of 5 min. The content of HC in the binary blends LDPE/HC was varied between 5 and 50%, on the total blend weight. The obtained material was compression molded by a Collin hydraulic press Collin P 200E operating at 160°C and 100 bar pressure applied for 5 min and the resulting films had a thickness of 0.3 mm. Specimens to be used for mechanical tests were stamp cut from the obtained films.

Tab. 1 Composition and physical-chemical characteristics of the two collagen hydrolysate samples

Properties	HC1	HC2
Dry matter (wt. %)	97-98	97-98
Ashes (800°C. wt. %)	24.68	8.36
NaCl (wt. %)	17.62	6.30
Na_2SO_4 (wt. %)	3.09	1.16
Na_2CO_3 (wt. %)	3.55	0.13
CaO (mg/kg)	0.13	0.71
Cr (mg/kg)	3.00	26.00
Pb (mg/kg)	0.51	0.19
Nitric nitrogen (wt. %)	< 0.01	< 0.01
Organic nitrogen (wt. %)	11.07	14.51
Ammonic nitrogen (wt. %)	0.26	0.21
Ureic nitrogen (wt. %)	< 0.01	< 0.01
Organic carbon (wt. %)	40.01	49.88
Organic matter (wt. %)	69.97	85.99
Density (g/cm^3)	0.40	0.38
pH	5.8-6.2	6.8-7.5
Water solubility	Total	Total
Mean molecular weigh (kDa)	1.53	4.08

2.3 Characterization

2.3.1 Scanning Electron Microscopy (SEM)

The film samples were fractured in liquid nitrogen. The fractured surfaces were observed by using a JEOL 5600LV microscope. Before the observation, the fractured surfaces were coated with Au on a SEM coating device (Edward Spotter Coater). A homogeneous layer of metal of 5-6 nm thickness coated the entire sample surface.

2.3.2 Thermogravimetric analysis (TGA)

Weight loss curves were recorded on the film samples (20 mg), placed in a platinum crucible, by a TA Instruments Q500 thermobalance. The runs were conducted under nitrogen flow (100 cm^3/min) in the temperature range from 30°C to 600°C, at a heating rate of 10°C/min.

2.3.3 Differential scanning calorimetry (DSC)

Curves were recorded by using a Perkin-Elmer Pyris 1. The samples (5-10 mg), in the form of film, were heated from 50 to 200°C, at a heating rate of 10°C/min (run I). Afterwards, the samples were cooled to 50°C (run II). Finally, a third run (run III), similar to run I. was performed.

2.3.4 Mechanical tests

Dog-bone shaped samples, stamp cut from the films, were used to assess the tensile properties of the studied blends. Tensile tests were carried on an Instron Universal 5564 tensile testing machine according to the ASTM D638M /ASTM D882 standards for thin films. The speed of the clamp was 5 mm/min.

3 Results and discussion

The capability of the polypropylene matrix to incorporate the hydrolysate collagen without compromising blend filmability from the melt was displayed up to a percentage by weight of the hydrolysates in the blend of 20% for HC1 and 30% for HC2. Mixing PP with higher quantity of HC, an incoherent material was obtained and it was not possible to produce the films. This result could be related with the melting temperature of polypropylene, higher than degradation temperature of collagen hydrolysate.

Films of pure PP are transparent, whereas the films processed from the blends appeared slightly opaque with tendency to a yellowish color. The films obtained appeared in any case cohesive and flexible.

The morphology and the phase structure of the blends are shown in the SEM micrographs of the freeze fractured transversal sections and the surfaces of PP/HCs films (Fig. 1), where the blend at 20% of collagen hydrolysate is reported for brevity. In all samples, no distinct phase segregation of the two components at micro and sub-micro scales were observed. The structure appears quite homogeneous, similarly than what obtained for similar LDPE/collagen hydrolysate blends in previous studies [3]. The present behaviour is attributed to the relatively low molecular weight of the collagen hydrolysate used that allowed a high dispersability of the natural polymer in the PP matrix.
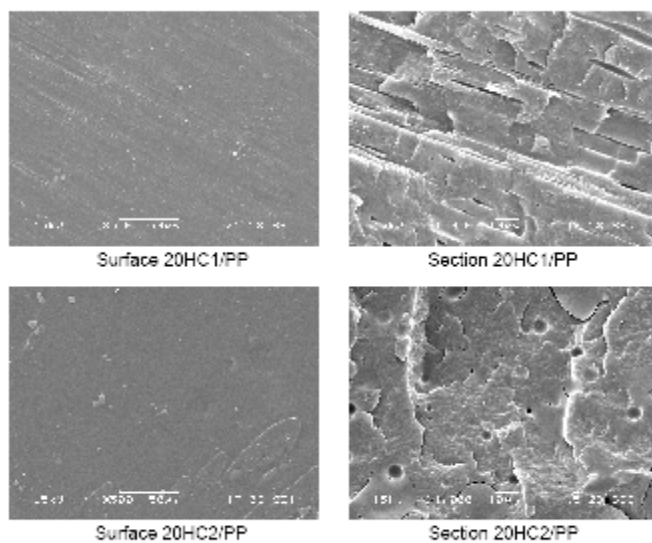

Surface 20HC1/PP   Section 20HC1/PP

Surface 20HC2/PP   Section 20HC2/PP

Fig. 1 SEM micrographs of surface and transversal section of the HCs/PP blends at 20% HCs

Thermogravimetric analysis was conducted in order to assess the thermal stability of the PP samples when the HCs are incorporated in the blend. As reported in the weight loss (TG) and derivative weight loss (DTG) curves of Fig. 2, HC, after moisture loss, presented a weight loss peak close to 150°C, related to the loss of the lighter component, and then showed the major weigh loss peak at a temperature close to 300°C. HC1 presented a higher residual weight at 600°C (43%) than HC2 (25%) as expected because of the higher content of salts in HC1.

The TG and DTG curves of PP showed a thermal stability of the polymer up to 350°C and a thermal degradation peak close to 460°C (Fig. 3). No significant variation of the thermal stability

of the polypropylene was observed when the HCs were incorporated to the PP samples (Fig.4). It was observed that the blends containing HC1 and the blends containing 10% of HC2 showed a single-stage degradation close to 460°C. Instead, for blends containing 20 and 30% of HC2 a weight loss was observed in the temperature region around 300°C, typical of the thermal degradation of the collagen hydrolysate. It must be observed that this minor weight loss is about 10% for the blends at 20% HC and about 20% for the blends at 30% HC.
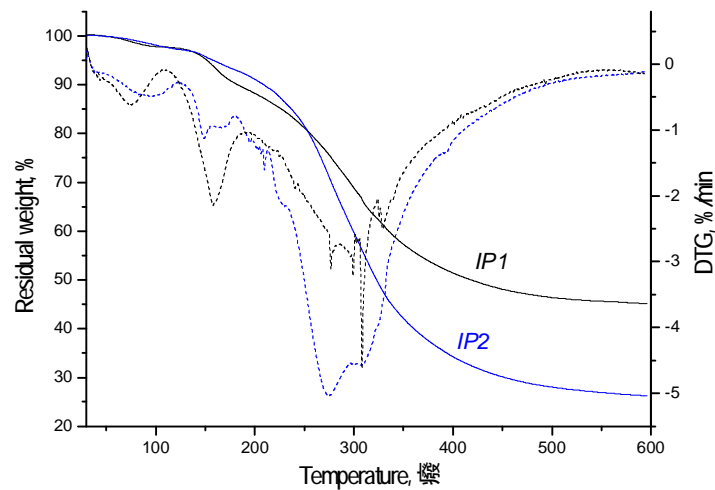
Fig.2 Weight loss and derivative weight loss of the collagen hydrolizates

This indicates that, roughly, only half of the collagen hydrolizate was degraded at 300°C, thus confirming that the protein fraction incorporated in the polymer matrix improves by far its thermal resistance. Besides the outcomes of thermal analysis indicate a higher dispersability of the collagen hydrolysate from flashing in the PP matrix. The present behaviour is attributed to the lower molecular weight of HC1 than HC2.
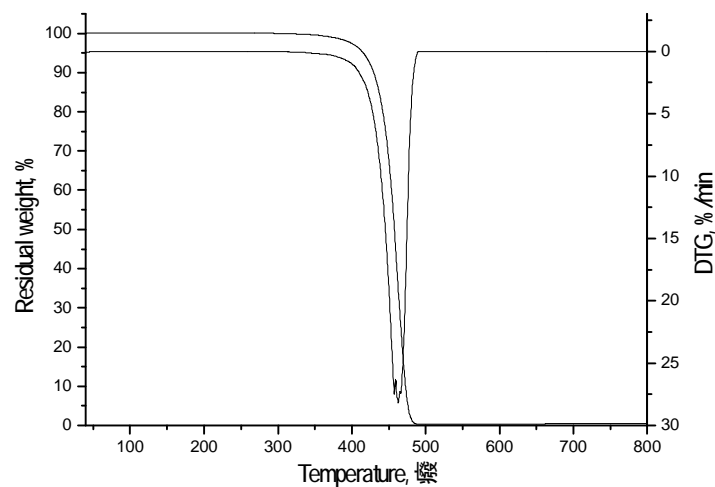

Fig. 3 Weight loss and derivative weight loss of the polypropylene

DSC results are given in Table 2, including the melting temperature (T_m), the crystallisation temperature (T_c), the melting (ΔH_m) and crystallisation (ΔH_c) heat normalized to PP content, and the crystallinity index (I_c). The degree of crystallinity of the PP blends was evaluated by the ratio between the enthalpy of fusion of the blend and the enthalpy of fusion of the perfectly crystalline PP [4]. It can be observed that the amount and the type of HC incorporated insignificantly change the melting and crystallisation temperatures of the blends. The melting and the crystallisation heat decreased when collagen hydrolysate is incorporated in the blend, and this can be explained by the decrease of the degree of the crystallinity of the polypropylene with amorphous component addition. It was observed that the type of collagen hydrolysate incorporated insignificantly changes the crystallinity index of the blends.

Mechanical properties of the HC/PP films are reported in Fig. 5-7. No significant variation of the Young's modulus and tensile strength of the polypropylene was observed with the collagen hydrolysate addition. This result can be related to low degree of crystallinity of the polypropylene that allowed to effective dispersability of the amorphous component in the PP matrix, in accordance with thermal stability verify by thermogravimetric analyses.
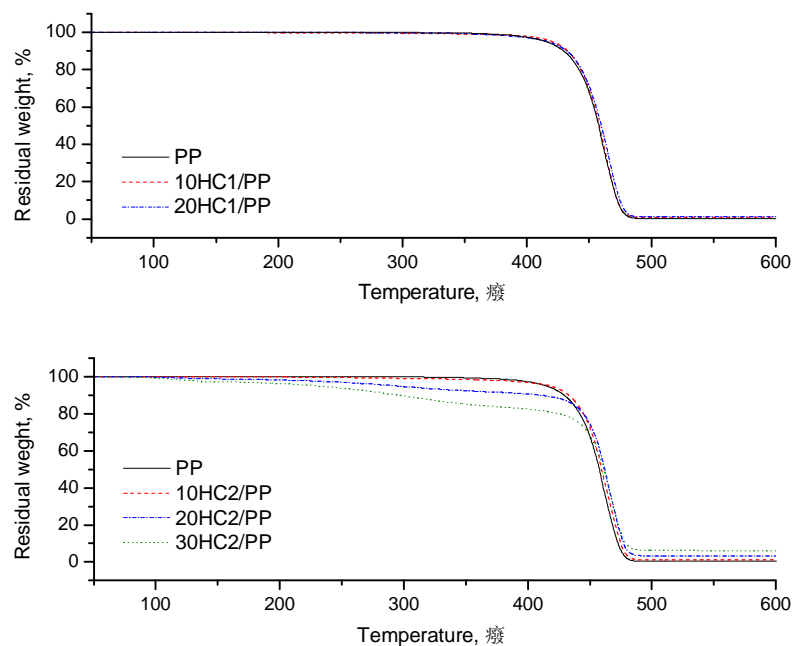

Fig. 4 Weight loss of the HC1/PP blends

Tab. 2 Thermal parameters and crystallinity index of HCs/PP blends

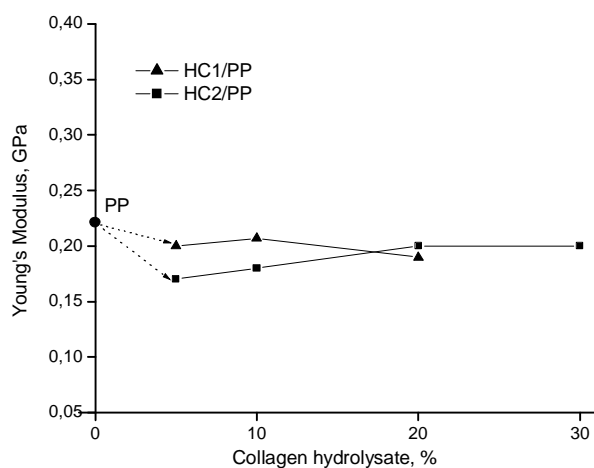| Sample	Tm (°C)	Tc (°C)	ΔHm (J/g)	ΔHc (J/g)	Crystallinity index
PP	143.7	100.3	62.5	62.5	0.30
5HC1/PP	143.6	98.8	52.7	61.8	0.25
10HC1/PP	143.1	100.1	48.4	60.7	0.23
20HC1/PP	143.5	99.6	47.1	62.4	0.22
5HC2/PP	143.6	101.5	51.5	62.3	0.25
10HC2/PP	144.3	101.5	49.6	60.1	0.24
20HC2/PP	143.9	102.6	49.3	59.8	0.23
30HC2/PP	144.3	102.2	38.7	47.3	0.19

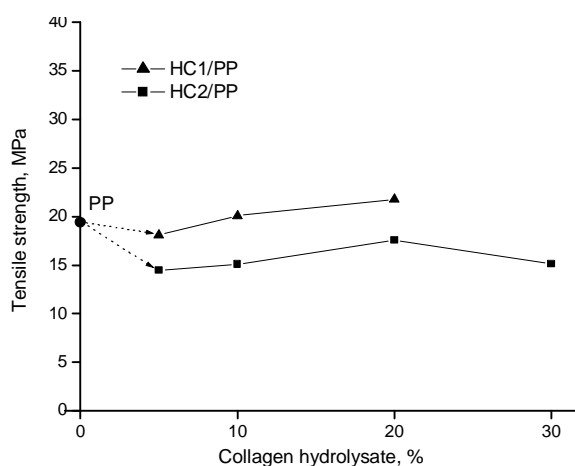**Fig. 5 Young's modulus of the HC/PP films as a function of HC content**

Fig. 6 Tensile strength of the HC/PP films as a function of HC content

According to higher rigidity of the blends with HC1 respect to the blends with HC2, the strain at break of the films showed a rapid decrease with addition of the hydrolysate from shaving, but this value keep constant up to 20% content (Fig. 7). For the blends with HC2 the strain at break showed a rapid decrease when the collagen hydrolysate percentage was increased above 10%.
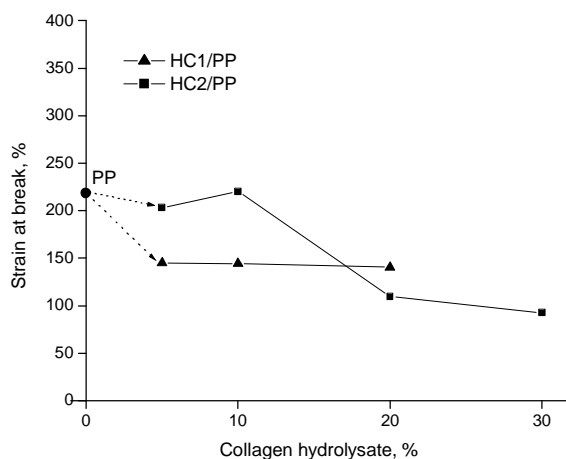

Fig. 7 Strain at break of the HC/PP films as a function of HC content

4 Conclusions

Polypropylene matrix showed a capability to incorporate the investigated collagen hydrolysate (HC) without compromising blend filmability from the melt up to a percentage by weight of 30%. The films obtained were transparent, cohesive and flexible. The relatively low molecular weight of the collagen hydrolysate used allowed a high compatibility with LDPE as shown by SEM analysis.

HC thermal stability was compatible with melt processing with polypropylene and the protein fraction incorporated in the PP matrix improves by far its thermal resistance.

On the basis of mechanical tests results, blends of collagen hydrolysate and polypropylene up to 20 wt% of HC guarantee an optimal trade-off between percentage of HC and mechanical performances.

The obtaining of positive results in blending PP and collagen hydrolysate from waste of the leather industry in absence of crosslinking agent or compatibilizing agents allows for low cost and simple processing procedure.

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