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Polyethylene and Hydrolyzed Collagen Blend Films Produced by Blown Extrusion

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The use of plastics packaging is widespread. For this reason, there is a growing interest in develop of novel materials by blends of synthetic and natural polymers which can help to reduce the environmental impact of plastics. Hydrolyzed collagen (HC) from leather industry is an inexpensive natural biopolymer and it is a promising material for blending with synthetic polymers (e.g., polyethylene) to produce different types of item (it is no food competition, low cost, and biodegradable-compostable). Due to the wide difference in polarity, the natural polymer does not disperse easily in nonpolar thermoplastics, therefore the structural differences between polyethylene and collagen hydrolizate make them incompatible. Thus, in this work compatibilizing agents as maleic anhydride functionalized ethylene elastomers have been used. The content of HC in polyethylene matrix varied between 10 and 50 wt%. Transparent, cohesive and flexible films, having an average thickness of 60 μm, were obtained by using the film blowing technique. Film blowing is a shaping technique used extensively to produce most plastics films and bags for packaging applications. The extruded films were characterized through mechanical testing, scanning electron microscopy, and thermal analysis. The films containing up to 20 % of collagen hydrolizate, in the presence of compatibilizing agents, are characterized by satisfactory thermal-mechanical properties. Thus HC/PE blends appear as promising candidate for the production of innovative material suitable for production of thermoplastic items for applications in packaging and agricultural segments.

1. Introduction

Plastics have become one of the most important materials in our daily life over the past four decades. However, with time, environmental pollution from consumed plastics becomes serious, particularly from package materials, disposable containers, and agriculture mulch films. With tighter environmental regulations and increasing waste disposal costs, plastic manufacturers are forced to seek solutions or alternatives. Thus, in the last years, there has been an increased interest in the production and use of fully biodegradable polymers with the main goal of replacing non-biodegradable plastics. Although many pure biodegradable polymers such as poly(lactic acid) (PLA), poly(3-hydroxybutyrate) (PHB), polyhydroxyalkanoates, and poly(vinyl alcohol) possess the required properties and can be used for the production of blown film and injection-molded materials, they are not widely used because of their high costs. Therefore, multicomponent materials have gained an increased importance (Abarca et al., 2013), in particular blends of synthetic and natural polymers (Rogovina et al., 2013), through object-oriented synthesis, blends, and modification that produce tailor-made characteristics in the areas where these materials are to be used (Fréderix et al., 2011). Due to the wide difference in polarity, the natural polymer does not disperse easily in nonpolar thermoplastics. Moreover, due to the strong intermolecular hydrogen bonding, the natural polymer tends to agglomerate during mixing with plastics (Puccini et al., 2014a). As a result, poor compatibility and dispersability of the natural polymer with nonpolar thermoplastics are serious drawbacks for obtaining composite materials with improved mechanical properties. To improve their compatibility, various attempts have been made to modify either natural polymer or synthetic polymer. More recently, an increased interest has appeared in the use of polymers containing reactive groups (e.g., maleic anhydride) as compatibilizers (Liu et al., 2003).

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The hydrolyzed collagen is an inexpensive natural biopolymer obtained from the solid wastes of the fleshing/shaving phase of the hide during tannery process and it is mainly constituted of raw collagen. Through alkaline or enzymatic hydrolysis, degreasing, concentration and liophilization of fleshings and shavings, a collagen hydrolizate in powder form is obtained. As hydrolyzed collagen has shown to be a versatile materials that combine many valuable characteristics for technical applications such as good processability in the melt with good film forming capability (Castiello et al., 2009), in this work the industrial applications of collagen hydrolyzate as filler for thermoplastic materials have been investigate by using the film blowing technique. Film blowing is one of the most significant polymer processing operations: the majority of products manufactured on blown film equipment are used in commodity applications with low profit margins (carrier bags, garbage bags, flexible packaging and films for agricultural purposes). In the film blowing process, the molten polymer is extruded through an annular die and the air is forwarded from the center of die to form a bubble. The molten tube leaving the die is stretched upwards by the nip rolls, at the same time cooling is performed through an air ring which directs air to the outside surface of the bubble and thus will affect closely molecular relaxation and crystallinity. The properties of blown films are determined by a complex relationship involving materials properties, the structure developed after the polymer exits the die where the bubble undergoes orientation, and crystallization and morphology development.

Our previous studies dealt with the polyethelene/hydrolyzed collagen blends processing by injection moulding (Puccini et al., 2014b). Due their incompatibility, in this work compatibilizing agents as maleic anhydride functionalized ethylene elastomers have been used. The content of HC in polyethylene matrix varied between 10 and 50 wt%. The extruded films were characterized through mechanical testing, scanning electron microscopy, and thermal analysis.

2. Experimental section

2.1 Materials

The low density polyethylene (PE) Riblene FF 30 was supplied by Eni-Versalis (Milan, Italy), as uniform granules, having the following characteristics: melting temperature 113 °C; density 0.923 g/cm^3; melting flow index (MFI) 0.80 g/10 min (190°C/2.16 kg). Riblene FF 30 is a high molecular weight low density polyethylene resin suitable for blown film extrusion, characterized by a good melt strength leading to a good bubble stability during extrusion. The hydrolyzed collagen (HC) was supplied by S.G.S. S.p.A. (Santa Croce sull'Arno, Italy). The sample in powder form derives from shavings by alkali hydrolysis, with the following elemental composition: 42.21 % C; 6.37 % H; 15.71 % N; 35.71 % O. The average molecular weight is 4.08 kDa; other characteristics are: dry matter 96.6 wt%; ashes 5.7 wt%; organic matter 92.4 wt%. The composition in amino acids of the protein phase (84.17 wt% of the hydrolyzed collagen) is reported in Table 1. Polyethylene-grafted maleic anhydride (PE-*g*-MA) was used as compatibilizer agent. PE-*g*-MA was supplied by Auserpolimeri (Lucca, Italy), having the following characteristics: melting temperature 120 °C; density 0.924 g/cm^3; melting flow index (MFI) 1.6 g/10 min (190°C/2.16 kg).

2.2 Blends and blown film preparation

Blends preparation. The blends were prepared in a double screw extruder Thermo PRISM TSE 16/28 TC using the following temperature profile: 120/130/140/150 °C. The content of HC in the ternary blends PE/HC/PE-*g*-MA varies between 10 and 50 wt% in respect with the total blend weight. The content of the compatibilizing agents was constant, namely 5 wt% on the total blend weight. Before use, the powdered hydrolizate were dried under vacuum at 40 °C for 12 h and manually premixed with polyethylene.

Blown film. Blown films of obtained blends were manufactured using a blow film line Thermo Scientific Rheomex 19/25 QC equipped with a single screw extruder and a blown film take-off. The extrusion and blowing parameters are shown in Table 2. The specimens used for thermal and mechanical tests were stump cut from the extruded films.

Table 1. Composition in aminoacids of the protein phase (wt%)

Glycine	15.70	Histidine	5.90
Proline	11.69	Aspartic acid	5.39
Glutamic acid	9.96	Arginine	5.07
Hydroxyproline	9.53	Lysine	3.56
Methionine	7.51	Others	9.86

Table 2. Extrusion and blowing parameters.

Die diameter	24 mm
Die gap	0.8 mm
Screw diameter	19 mm
Screw length/diameter ratio	25
Screw speed	30 rpm
Temperature profile	130/140/150/150

2.3 Investigation methods

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) to induce electro conductivity. A homogeneous layer of metal of 5-6 nm thickness coated the entire sample surface.

Mechanical tests. Tensile properties (tensile strength, elastic modulus and elongation at break) of the blown films were measured along the machine direction (MD) and transverse direction (TD). The tests were carried out using 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. For each film sample a minimum of ten specimens were tested to obtain an average value.

Differential scanning calorimetry (DSC). Differential scanning calorimetry measurements were performed by a PerkinElmer Pyris 1 DSC. The samples (5–10 mg), under nitrogen flow of 20 mL/min, were heated from 50 to 200 °C at a heating rate of 20 °C/min (run I). Afterward, they were cooled to 50 °C at the same rate (run II) and then reheated to 200 °C at 10 °C/min (run III).

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 mL/min) in the temperature range from 30 °C to 600 °C, at a heating rate of 10 °C/min.

3. Results and discussion

The capability of the polyethylene matrix to incorporate the hydrolyzed collagen without compromising extrusion from the melt to produce pellets was displayed up to a percentage by weight of the HC in the blend of 50 %. However, the mixtures were easily processed by injection moulding up to 20 wt% of HC without compatibilizer agent and up to 40 % of HC by adding the PE-*g*-MA compatibilizer.

To process HC/PE blends by film blowing technique it was need to find the processing conditions for obtaining a stable bubble during manufacturing. Bubble stability plays a very important role in evaluating the processability of a material. A stable bubble is a requirement not only for the continuous operation of the process but also for the production of an acceptable film. As the shape of the bubble depends on the combined influence of process parameters, blends films were prepared by varying temperature and screw rpm. The film forming characteristics of composites were optimized to obtain the shape and the thickness of the bubble constant with time. From these studies, for HC/PE/PE-*g*-MA blends processing the temperature profile of the extruder barrel, the die temperature and the screw speed were 130/140/150 °C, 150 °C and 30 rpm, respectively. The extruded films of pure PE are transparent, whereas the films processed from the blends appeared slightly opaque with tendency to a yellowish colour that was more intense increasing the HC content. A stable bubble, and satisfactory films, cohesive and flexible having an average thickness of 60 microns, were obtained for the blends with a content of HC up to 20 wt% without the PE-*g*-MA and up to 30 wt% with the compatibilizer.

The morphology structure of polymer blends is a very important characteristic because it ultimately determines most of its properties, such as mechanical properties. In most cases, the major component of the blend forms the continuous phase, whereas the minor component is the dispersed phase. In the present study, the hydrolyzed collagen functioned as filler because the granular structure of HC was retained after extrusion, but agglomerates were noted in the structure, which was indicatives of heterogeneous dispersion of HC in the polyethylene matrix (Figure 1).

The smooth surface of HC, and the distinct interfacial appearance between collagen hydrolizate and polyethylene suggest that there was lacking interaction between them. Therefore, their interfacial tension was large and their interfacial adhesion was low, which agreed with results of Dascalu et al. (2004).

The morphology of ternary blends HC/PE/PE-*g*-MA with different HC contents is shown in Figure 2. In comparison with Figure 1, the dispersion of hydrolizate in the PE matrix was greatly improved after the addition of compatibilizer, and few HC agglomerates were observed, indicating that PE-*g*-MA improved the interfacial adhesion between PE and HC. This improved interfacial adhesion resulted in increased miscibility. The improved interfacial adhesion was attributed to the chemical interaction between hydrolyzed collagen and PE-*g*-MA, and the strong physical interaction between PE and PE-*g*-MA. The chemical interaction presumably resulted from reaction of amino groups in HC with anhydride groups in PE-*g*-MA under the extrusion conditions of high temperature and high shear, with some minor interaction from their hydrophilic interaction. When PE-*g*-MA was situated at the interface between hydrolizate and polyethylene and interacted with both, the interfacial tension was reduced and compatibility was increased.

Differential scanning calorimetry (DSC) was used to investigate the crystallization behavior of PE/HCs systems under non-isothermal experimental conditions. All thermograms for the neat polymer as well as for the composites have similar one step crystallization between 80 and 100 °C, indicating a similar crystallization behavior. The crystallization temperature (T_c) and melting temperature (T_m) of HC/PE blends with and without PE-*g*-MA are reported in Table 3. The crystallization peak temperature (Tc) shifted toward higher values with increase in HC content, which indicates that the crystallization starts at higher temperatures, due possibly to the nucleating effect of hydrolyzed collagen that acts as nucleating agents. The melting temperature (T_m) also shifted toward higher for the blends with HC. When PE-*g*-MA was added to HC/PE blends, the T_m showed a trend similar to that for blends without PE-g-MA. Hence, hydrolyzed collagen not only affected crystallization but also the melting behaviour of PE.

The distribution of a dispersed phase in the matrix phase and the interfacial adhesion between a dispersed phase, and the matrix are key factors determining the mechanical properties of polymer blends (Jang et al., 1985). A dispersed phase with a small particle size, and a homogenous distribution will improve the ability of the resulting blend to tolerate external force, resulting in a more homogenous distribution of stress and better mechanical properties of the blend. The tensile properties of different polyethylene and HC/PE blown films, with and without PE-*g*-MA, were tested both in the machine (MD, along the long axis of the bubble) than in the transversal (TD, around the hoop direction of the bubble) blow direction. Results are shown in Figure 3.

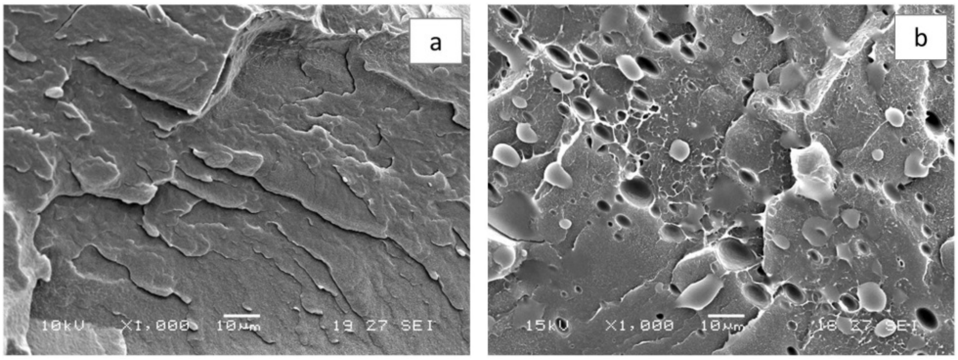

Figure 1: SEM micrographs of fracture surface of PE (a) and HC/PE blend at 20 wt% HC (b).

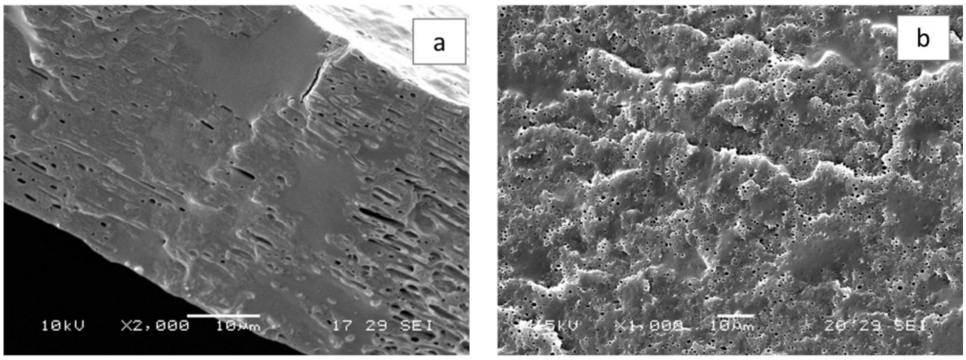

*Figure 2: SEM micrographs of fracture surface of HC/PE/PE-*g*-MA blends at 20 wt% (a) and 30 wt% (b) of hydrolyzed collagen.*

Table 3. Thermal properties of HC/PE blends

HC (%)	Crystallization temperature (T_c)		Melting temperature (T_m)	
	Without PE-*g*-MA	With PE-*g*-MA	Without PE-*g*-MA	With PE-*g*-MA
0	90.9		114.4	
20	92.3	93.6	119.5	119.1
30	92.4	94.3	119.0	118.5

The increase of the tensile strength of blends with 20 wt% of hydrolyzed collagen, compared to polyethylene, can apparently be attributed to the reinforcing effect of the HC component (Matzinos et al. 2000). It would appear that the morphology obtained allows the successful stress-transfer from the polymeric matrix to the HC particles resulting in a material with increased mechanical properties.

When PE-*g*-MA was added to the blends, the tensile strength and elongation at break of the blends were improved. It is believed that PE-*g*-MA increased adhesion between the PE matrix and the HC filler, by locating between them and interacting with them, which is in agreement with DSC and SEM results. The improved interfacial adhesion played an important role in the process of stress transfer, thus reducing the chance of interfacial debonding and leading to improved tensile properties. In addition, these results also support the assumption that the HC and PE-*g*-MA interaction was between hydroxyl and amino groups in collagen hydrolizate and anhydride groups in PE-*g*-MA.

Thermogravimetric analysis (TGA) curves of collagen hydrolizate and HC/PE films are presented in Figure 4. The HC thermogram displays, after moisture loss, a weight loss peak close to 150 °C, related to the loss of the lighter component, and a second shift started at 300 °C, where the thermal decomposition of hydrolyzed collagen occurred. Three well-defined shifts were observed in the TG curve of the blown films. The first shift, at around 100 °C, produced by water evaporation is weaker than the HC sample, indicating that a small quantity of water was adsorbed in their structures. A minor weight loss (about 5 %) was observed in the temperature region around 300 °C, associated to the thermal degradation of the hydrolyzed collagen. This indicates that, roughly, that the protein fraction incorporated in the polymer matrix improves by far its thermal resistance, attributable to the reciprocal influence of the components. The third mass-loss zone is centered around 480°C, related to thermal decomposition of polyethylene. Comparing with HC curve, the starting decomposition temperature of HC/PE blends increased, which led to the stability of collagen hydrolizate.

4. Conclusions

Polyethylene matrix showed a capability to incorporate the investigated hydrolyzed collagen without compromising blend filmability up to a percentage by weight of 20 wt% HC. The miscibility between collagen hydrolizate and polyethylene was improved by the addition of a commercially available compatibilizer (PE-*g*-MA), producing transparent, cohesive and flexible blown films. Results from DSC, SEM, and tensile analysis suggest that the improved compatibility could be attributed to the chemical interaction between hydrolysed collagen and PE-*g*-MA (through a reaction of amino groups in HC with anhydride groups in PE-*g*-MA), and the strong physical interaction between PE and PE-*g*-MA.

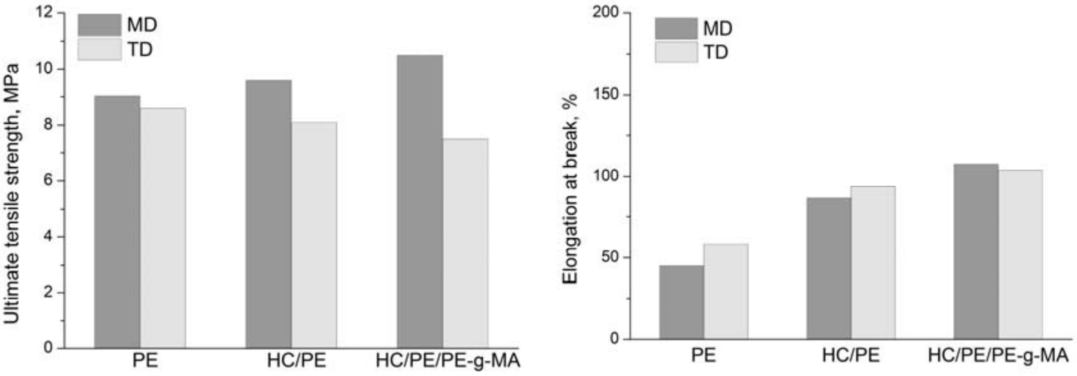

Figure 3: Mechanical properties of PE and HC/PE films at 20 wt% of hydrolyzed collagen.

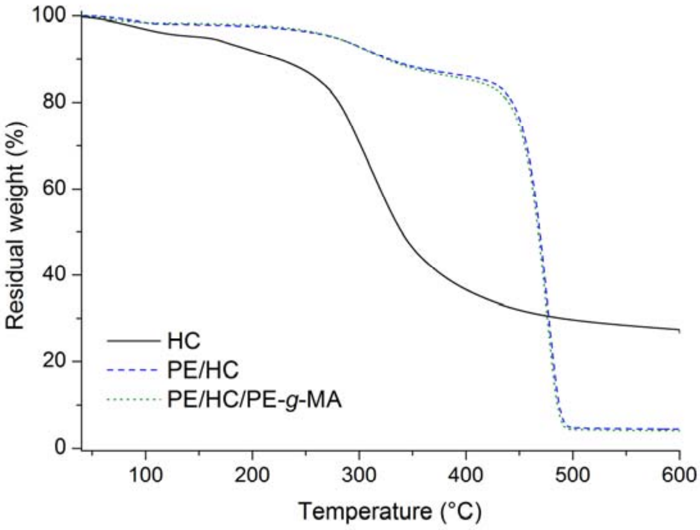

Figure 4: Weight loss of collagen hydrolizate and HC/PE blown films at 20 wt% of hydrolyzed collagen.

Collagen hydrolizate thermal stability was compatible with melt processing with PE, and the protein fraction incorporated in the PE matrix improves by far its thermal resistance. The HC/PE/PE-g-MA blown films showed good morphological and mechanical properties. Therefore this blend appears as promising candidate for the production of innovative material suitable for production of thermoplastic items by film blowing technique for applications in packaging and agricultural segments.

References

Abarca S.A.C., Flores O., Prette A.L.G., Barroso G.S., Coan T., Motz G., Machado R.A.F., 2013, Synthesis and thermal characterization of silicon-based hybrid polymer, Chemical Engineering Transactions, 32, 1621-1626.

Fréderix C., Talon O., Lewillion F., 2011, In situ compatibilization of thermoplastic starch and poly(butylene adipate-co-terephtalate) by reactive melt blending in presence of maleic anhydride, Chemical Engineering Transactions, 24, 865-870.

Castiello D., Chiellini E., Cinelli P., D'Antone S., Puccini M., Salvadori M., Seggiani M., 2009, Polyethylene-collagen hydrolizate thermoplastic blends: thermal and mechanical properties, Journal of Applied Polymer Science, 114(6), 3827-3834.

Dascalu M.C., Silvestre C., Pascu M.C., Fekete E., Vasile C., 2004, On the compatibility of low-density polyethylene/hydrolyzed collagen blends, Chemical Reactions, Nova Science Publ., New York, USA, 21-47

Jang B.Z., Uhmann D.R., Sande J.B.V., 1985, Rubber particle size dependence of crazing in polypropylene, Polymer Engineering and Science, 25(10), 643-651.

Liu W., Wang Y.-J., Sun Z., 2003, Effects of polyethylene-grafted maleic anhydride (PE-g-MA) on thermal properties, morphology, and tensile properties of low-density polyethylene (LDPE) and corn starch blends, 88, 2904-2911.

Matzinos P., Bikiaris D., Kokkou S., Panayiotou C., 2000, Processing and characterization of LDPE/starch products, Journal of Applied Polymer Science, 79, 2548-2557.

Puccini M., Castiello D., Seggiani M., Vitolo S., 2014a, Properties of thermoplastic blends with polypropylene and collagen hydrolizate, Advanced Materials Research, 893, 235-240.

Puccini M., Seggiani M., Castiello D., Calvanese G., Vitolo S., 2014b, Novel thermoplastic materials from wastes of the leather industry, Applied Mechanics and Materials, 467, 41-48.

Rogovina S., Aleksanyan K., Prut E., Gorenberg A., 2013, Biodegradable blends of cellulose with synthetic polymers and some other polysaccharides, European Polymer Journal, 49(1), 194-202.