

Polyethylene-Collagen Hydrolizate Thermoplastic Blends: Thermal and Mechanical Properties

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ABSTRACT: Collagen, a natural macromolecular protein from renewable resources, is widely used in many industrial applications. Mixtures of low-density polyethylene (LDPE) with collagen hydrolizate derived from the tannery industry were investigated to assess the feasibility of producing polymeric materials suitable for production of thermoplastic items for applications in packaging and agricultural segments. Different grades of polyethylenes and collagen hydrolizates characterized by different molecular weight and salinity were investigated to develop optimal blends. The physical-chemical properties of the obtained blends were assessed by thermal-mechanical, spectroscop-

ical analysis. Following the ongoing research activity, the reutilization of collagen hydrolizate derived from the leather industry for the production of environmental degradable polyethylene-based thermoplastic films appears feasible and promising. Blends of collagen hydrolizate and LDPE up to 20–30 wt % of collagen hydrolizate allow obtaining slightly opaque, cohesive and flexible films that show satisfactory thermal-mechanical responses. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3827–3834, 2009

Key words: polyethylene; collagen hydrolizate; thermal properties; mechanical properties

INTRODUCTION

Polyolefins, such as high-density polyethylene, low-density polyethylene (LDPE), and polypropylene constitute the majority of thermoplastics currently used as packaging materials.

In recent years, the development of partially or totally biodegradable materials based on inexpensive natural biopolymer (such as polysaccharides, proteins of vegetal and animal origin) in combination with synthetic thermoplastic polymers has been the subject of considerable research effort.^{1–3} Blending biodegradable and nonbiodegradable commercial polymers has become an economical and versatile route to obtain polymers with a wide range of desirable properties.

Among biobased polymers, proteins have shown to be versatile materials that combine many valuable characteristics for technical applications such as good processability in the melt, excellent processability in solution, with good film and fiber forming capability. Thus protein-based materials have been successfully blended with synthetic and natural poly-

meric matrices.^{4–9} The fairly high cost of protein and proteinaceous feedstocks when compared with some other biobased polymers, especially starch and cellulose, have somehow refrained research activity on their technical applications.^{10,11}

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 wastes of the whole district is collected and processed in a centralized plant where, through an alkaline hydrolysis, a raw collagen hydrolizate solution is obtained.

The high content of salts of the raw collagen hydrolizate, whose separation is rather expensive, represents an obstacle to recovery and reutilization.

Thus, collagen hydrolizate from the leather industry is a material easily available at low cost and its use is not in competition with food industries or other main applications, because it is a waste material and by-product of the major worldwide distributed leather industry. For these reasons collagen hydrolizate has been investigated for blending with polymeric matrices.^{11–17}

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In this work, blends of LDPE with collagen hydrolyzate have been investigated to assess the feasibility of producing a biofragmentable formulation suitable for production of thermoplastic films for applications in packaging and agriculture. Collagen hydrolyzate 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 hydrolyzate concentrated solution through alkaline hydrolysis, degreasing and concentration and a hydrolyzate in powder form upon lyophilization.

Different grades of polyethylenes and collagen hydrolyzate characterized by different molecular weight and salinity were investigated with the aim of developing blends with optimal physical-chemical and mechanical responses.

The prepared blends were characterized through infrared, thermal and mechanical testing. A specific attention was focused on the investigation of the effects of the presence of salts in the collagen hydrolyzate on the final properties of the biobased hybrid blends.

EXPERIMENTAL SECTION

Materials

Two types of LDPE were provided by Basell. Lupolen® 2426 F LDPE Film grade, as uniform granules, having the following characteristics: melting temperature T_m 111°C; density 0.924 g/cm³; tensile strength 11 MPa; elongation at break min 50% (LDPE1). Lupolen® 3020 H LDPE Film grade, as uniform granules, having the following characteristics: melting temperature T_m 118°C; density 0.927 g/cm³; melting flow index 2.0 g/10 min (under 190°C, 2.16 kg) (LDPE2).

Two types of hydrolyzed collagen (HC) were supplied by S.G.S. S.p.A. (Santa Croce sull'Arno-Italy), in powder form by lyophilization: derived from flashings (HC1) and from shavings (HC2). The composition of the two hydrolyzates is reported in Table I. Before use, the powdered hydrolyzate were dried under vacuum at 40°C for 12 h.

Blends and films preparation

The blends were prepared by melt-mixing the ingredients with a Brabender Plastograph OHG (Germany) in the following operational conditions: temperature 130°C, rotor speed 50 rpm, and mixing time 5 min. The content of HC in the binary blends HC/LDPE was varied between 10 and 70 wt % HC, on the total blend weight. The symbols of the blends indicate the composition in HCs.

TABLE I
Properties of the HC Samples Used in the Preparation of the LDPE/HC Blends

Properties	HC1	HC2
Water solubility	Total	Total
Dry matter (wt %)	97–98	97–98
Ashes (800°C, wt %)	24.68	8.36
NaCl (wt %)	17.62	6.30
Na ₂ SO ₄ (wt %)	3.09	1.16
Na ₂ CO 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
Mean molecular weight (kDa)	1.53	4.08
Free amino acids (wt %)	12.95	6.90
Total amino acids (wt %)	72.09	92.25

The obtained material was compression molded by a Collin hydraulic press Collin P 200E operating at 130°C and 100 bar pressure applied for 5 min and the resulting films had a thickness of 0.3 mm. The specimens used for mechanical and thermal dynamic mechanical tests were stamp cut from the obtained films.

Investigation methods

Infrared spectroscopy

FTIR spectra were recorded in transmittance by using a JASCO 4100 Spectrometer (Japan) on films obtained by pressing of the melted blends between two microscopic slides.

Scanning electron microscopy (SEM)

The film samples were fractured in liquid nitrogen. The fractured surfaces were observed by using a JEOL 5600LV (Japan) SEM. 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. Magnification was 1000×.

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 (England) according to the ASTM D638M/ASTM D882

standards for thin films. The speed of the clamp was 10 mm/min.

Thermogravimetric analysis

Weight loss curves were recorded on the film samples (20 mg), placed in a platinum crucible, by a Netzsch STA 409 (Germany) thermobalance. The runs were conducted under nitrogen flow (100 mL/min) in the temperature range from 30 to 600°C, at a heating rate of 10°C/min.

Differential scanning calorimetry (DSC)

Curves were recorded by using a PerkinElmer Pyris 1 (UK) DSC. 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). Afterward, the samples were cooled to 50°C (run II). Finally, a third run (run III), similar to run I was performed.

Dynamic mechanical thermal analysis (DMTA)

The dynamic thermomechanical behavior of the film samples, in the form of rectangular strips, was investigated using a Rheometric Scientific dynamic mechanical analyzer DMTA V (US) (equipped with Rheometric Scientific Plus V software). The runs were conducted from –150 to 120°C with a heating rate of 4°C/min. The sinusoidal excitation had a frequency of 1 Hz.

RESULTS AND DISCUSSION

The capability of the polyethylene matrix to incorporate the hydrolyzed collagen (HC1 and HC2) without compromising blend filmability from the melt was displayed up to a percentage by weight of the hydrolyzed collagen in the blend of 50%. At 50% HC, films were successfully obtained by LDPE1 with both HC, whereas LDPE2 could be successfully filmed only with HC1.

As reported in Table I, the hydrolyzed collagen derived from fleshing (HC1) is characterized by a higher salt content and a lower molecular weight with respect to the hydrolyzed collagen derived from shavings (HC2).

Films of pure LDPE are transparent, whereas the films processed from the blends appeared slightly opaque with tendency to a yellowish color that was more intense in the blend comprising HC1 hydrolyzate. The films obtained appeared in any case cohesive and flexible.

The IR-spectra of pure HC1 and HC1/LDPE2 (20/80) blend are reported in Figure 1. They show that no major reaction seemed to take place between the polyethylene and the collagen hydrolyzate reactive

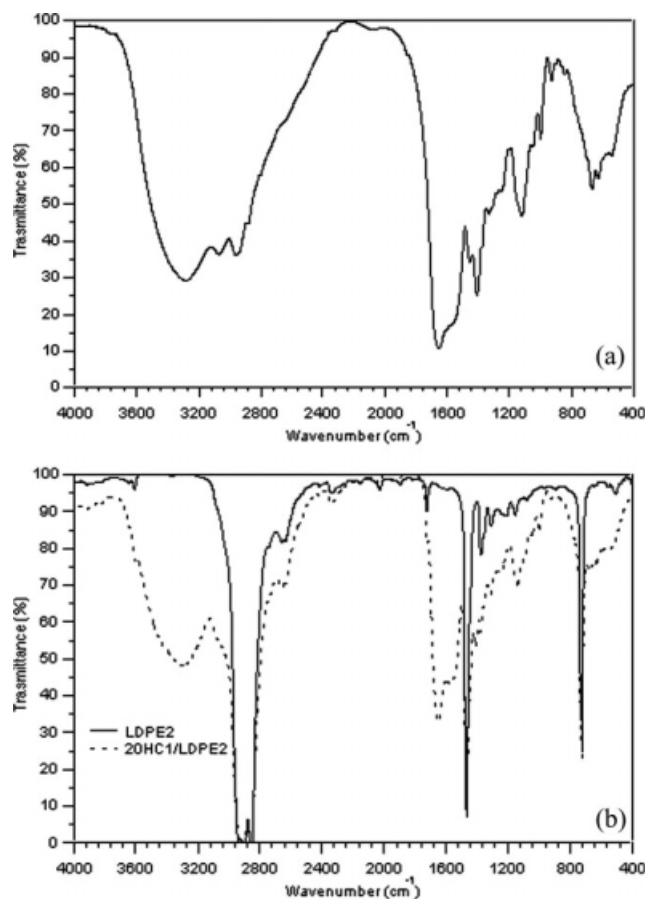


Figure 1 FTIR spectra of (a) the pure HC1, and (b) the pure LDPE2 and HC1/LDPE2 (20/80) blend.

groups, because the spectra of the blend result as an overlapping of the pure components typical peaks.

The morphology of the blends is shown in the SEM images of the freeze fractured transversal sections and the surfaces of HCs/LDPEs films (Fig. 2), where just the blend at 20% of collagen hydrolyzate is reported for brevity. In both blends at 10 and 20% HC, no distinct phase segregation of the two components was observed at micro- and submicro scales. The structure appears quite homogeneous, differently than what observed by Dascalu et al.¹² for HC/LDPE blends. The present behavior can be attributed to the lower molecular weight of the collagen hydrolyzate used in this work that allowed to improve the dispersability of the natural polymer in the LDPE matrix. Irregularities and cavities can be observed on the surface, whereas pores formed on the transversal section of the samples. The porosity occurrence can be attributed to the presence of residual water (despite the vacuum drying before use) in the hydrolyzed collagen samples, highly hydrophilic, that evaporates from the bulk during the blend melt processing.

Mechanical properties of the HC/LDPE films decreased with increasing content of the HC

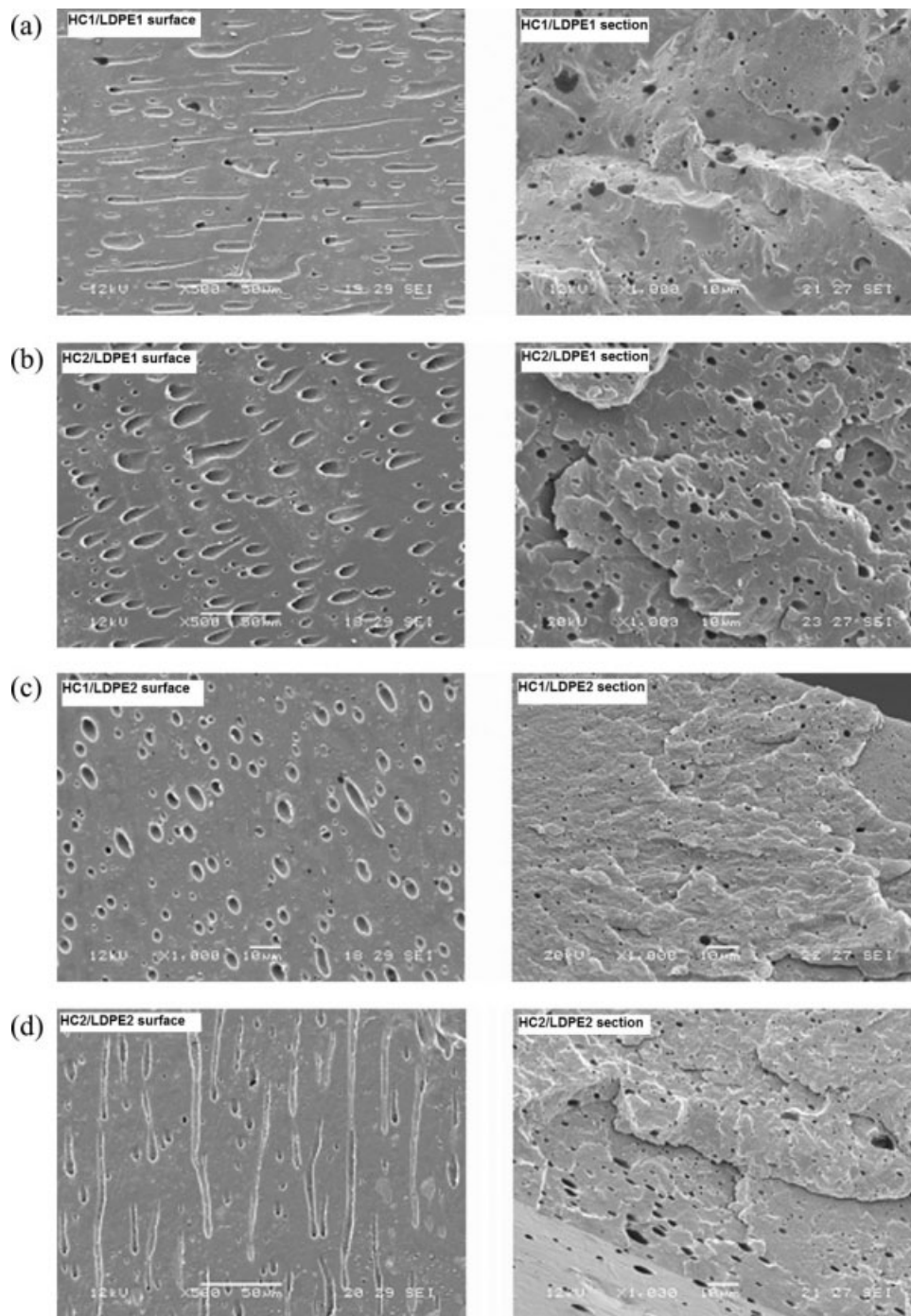


Figure 2 SEM images of surface and transversal sections of the HCs/LDPEs blends at 20 wt % HCs.

(Figs. 3–5) in accordance with the results obtained by Dascalu et al.¹² because of poor adhesion between LDPE and HC. Pure LDPE2 showed a higher Young's modulus, and thus a higher rigidity than LDPE1 (Fig. 3). It can be observed that the continuous decrease of Young's modulus with the increase of HC content for the four series of HCs/LDPEs blends are under study. This behavior is related to the decrease of the LDPE crystallinity by effect of the HC introduction as reported in Table II.

For both LDPEs, the blends with HC1 produced a more rigid structure with respect to the blends with HC2. This result can be attributed to both higher salt content of HC1 and its lower molecular weight. The less rigid LDPE1 showed a more marked decrease of the tensile strength than LDPE2 when blended with HC (Fig. 4). According to the increase of rigidity induced by the addition of the HC, the strain at break of the blend films showed generally a rapid decrease when the HC percentage was increased

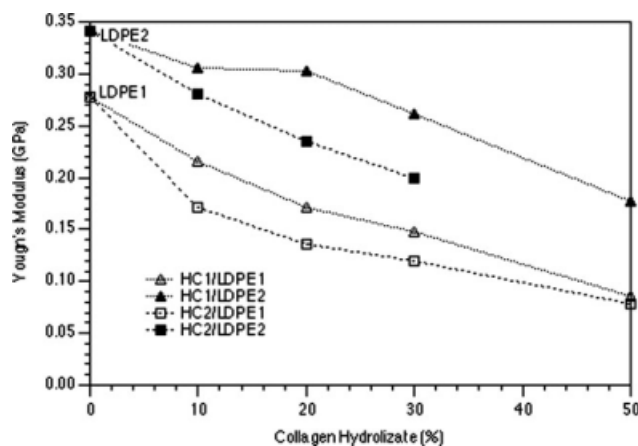


Figure 3 Young's modulus of the HC/LDPE films versus HC content.

above 20% (Fig. 5). The HC1/LDPE2 blend showed the higher rigidity also at low percentages of HC. This is due to the combination of the higher rigidity of LDPE2 and the more pronounced stiffening effect of HC1. On the basis of mechanical test results, the subsequent characterizations were focused on the blends with 10 and 20 wt % of HC that guarantee an optimal trade-off between content of HC and mechanical performances.

Thermogravimetric analysis under nitrogen was conducted to assess the thermal stability of the LDPE samples when the HCs are incorporated in the blend. As reported in the weight loss (TG) and derivative weight loss (DTG) curves of Figure 6, 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 weight 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.

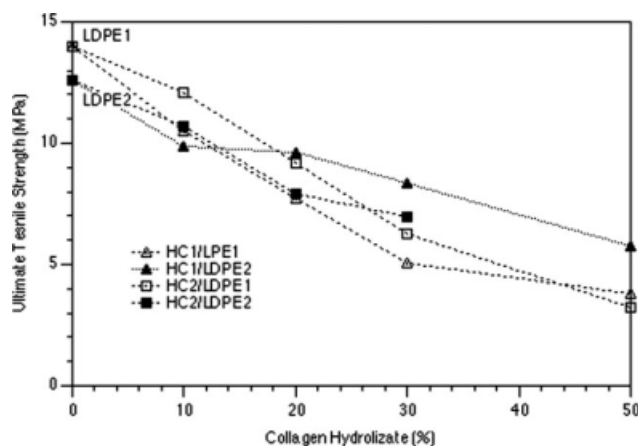


Figure 4 Tensile strength of the HC/LDPE films versus HC content.

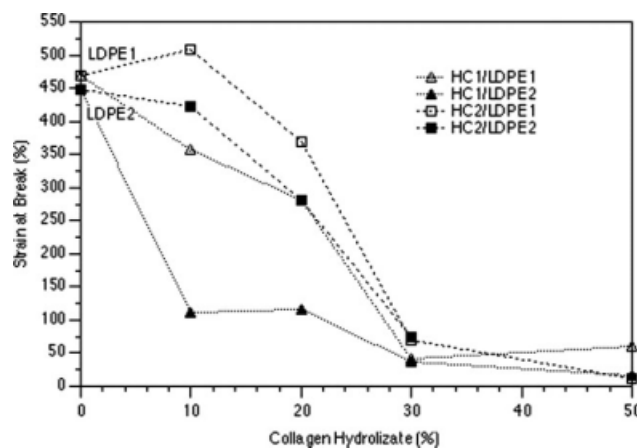


Figure 5 Strain at break of the HC/LDPE blended films versus HC content.

The TG and DTG curves of LDPEs showed thermal stability of the polymers up to 400°C and a single thermal degradation peak close to 480°C (Fig. 7) in accordance with the TG/DTG data obtained by McNeill and Mohammed¹⁸ for LDPE using the same operating conditions. No significant variation of the LDPE thermal stability was observed when the HCs were incorporated according to thermogravimetric data of HC/LDPE blends reported by Dascalu et al.¹² As reported in Figure 8, where the blend 50HC2/LDPE1 is reported for brevity, the major thermal degradation peak imputable to the LDPE remained close to 480°C. The theoretical curve of weight loss for 50HC2/LDPE1, as evaluated by addition of the weight loss of single component (HC2 and LDPE1) in the proportion present in the blend (50%) is compared with the experimental curve. It can be clearly observed that the calculated curve is placed under the experimental curve indicating a major thermal stability in the HC/LDPE blend respect to a mechanical mixing of the components. Indeed, for blends based on LDPE1 and containing 10 and 20 wt % of HC2, a minor weight loss was observed in the temperature range around

TABLE II
Thermal Parameters and Crystallinity Index of the LDPEs and Their Blends with HCs

Sample	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)	Crystallinity index
LDPE1	116.2	97.5	102.2	80.1	0.82
10HC1/LDPE1	115.1	98.2	96.8	74.3	0.78
20HC1/LDPE1	114.4	99.1	87.0	67.7	0.70
10HC2/LDPE1	115.8	97.8	95.7	76.9	0.77
20HC2/LDPE1	114.5	98.4	89.7	68.9	0.72
LDPE2	118.2	104.1	124.8	98.2	1.00
10HC1/LDPE2	118.2	104.7	112.9	86.8	0.90
20HC1/LDPE2	117.6	104.0	108.7	87.0	0.87
10HC2/LDPE2	118.5	102.9	117.1	90.4	0.94
20HC2/LDPE2	117.6	104.0	102.1	81.2	0.82

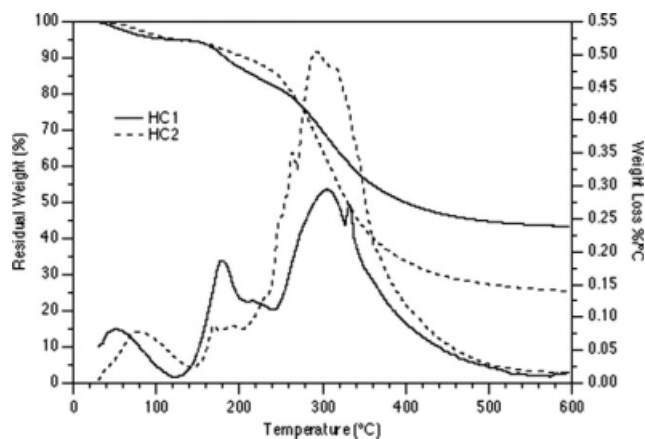


Figure 6 TG and DTG curves of the collagen hydrolyzates.

300°C [Fig. 9(a)], typical of the thermal degradation of the HCs. It must be observed that this minor weight loss is about 5% for the blends, which contain 10 wt % HC and about 10% for the blends at 20 wt % HC. This indicates that, roughly, only half of the collagen hydrolyzate was degraded at 300°C, showing that the natural polymer fraction incorporated in the synthetic polymer matrix improves by far its thermal resistance. This was also observed by Dascalu et al.¹² and imputed to the reciprocal influence of the components.

DSC results are given in Table II, including the melting temperature (T_m), the crystallization temperature (T_c), the melting (ΔH_m), and crystallization (ΔH_c) heat normalized to LDPE content, and the crystallinity index. The crystallinity index of each blend was determined as the ratio ΔH_m blend/ ΔH_m reference,¹⁹ where the reference assumed was ΔH_m of pure LDPE2 (the most crystalline between the two LDPE samples used).

It can be observed that, for both LDPE samples, the amount and the type of HC incorporated insignificantly change T_m and T_c of the blends, in accord-

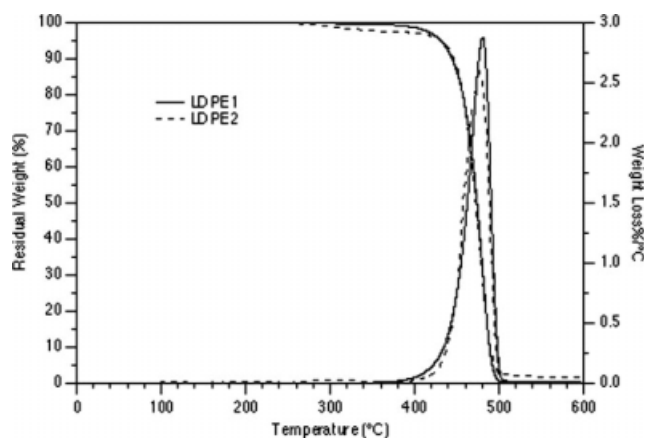


Figure 7 TG and DTG of the polyethylenes.

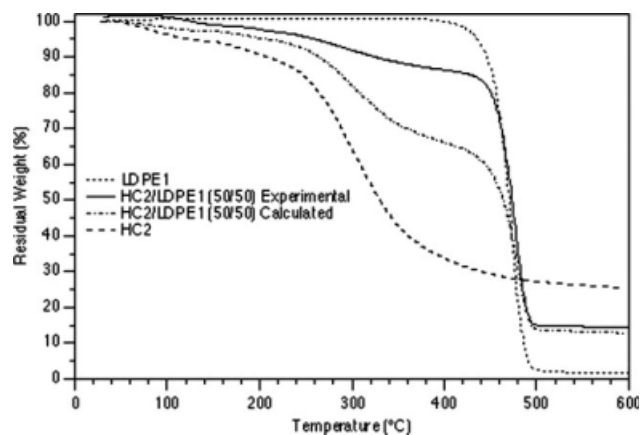


Figure 8 Weight loss of LDPE1, HC2, experimental and calculated for the HC2/LDPE1 (50/50) blend.

ance with the data reported by Dascalu et al.¹² The melting and crystallization heats decreased when HC is incorporated in the blend, and this can be explained by the decrease of the crystallinity degree of the LDPE¹² (see Table II) with the amorphous component addition, supporting the results of the mechanical tests. It can be observed that, for each

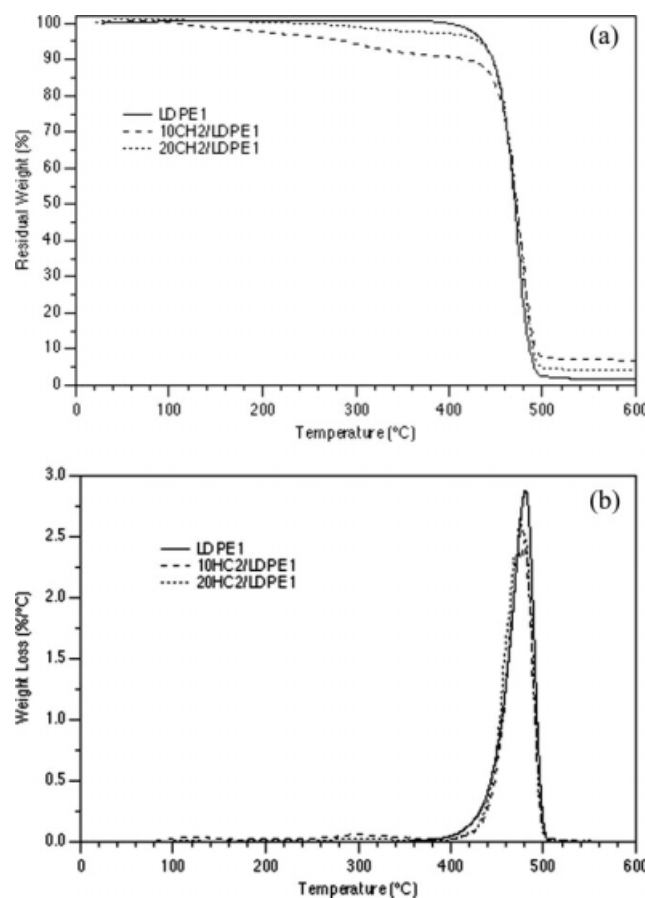


Figure 9 Weight loss (a) and derivative weight loss (b) of the LDPE1 and HC2/LDPE1 blends containing 10 and 20 wt % HC2.

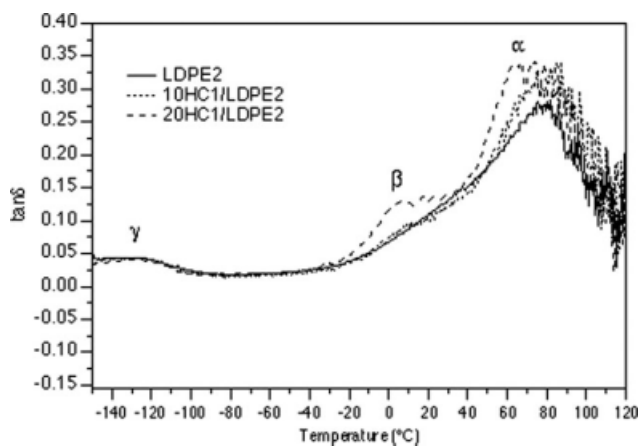


Figure 10 Tan δ versus temperature for HC1/LDPE2 blends containing 10 and 20 wt % HC1.

LDPE, the type of HC added insignificantly changes the crystallinity index of the blends.

DMTA, through dynamic strains and dynamic temperature sweeps performed on the sample is a valid method to investigate the possible changes induced in the LDPE sample by the incorporation of the HCs. The response of the sample to the dynamic sweeps may be expressed through the typical parameters: E' , storage modulus that accounts for the elastic component of the material and it is a measure of its rigidity, E'' , loss modulus that accounts for the dissipated energy as heat, and $\tan \delta (=E''/E')$ that accounts for the ratio between dissipated and stored energy in a complete cycle of sollicitation. The relaxation spectra in terms of $\tan \delta$ versus temperature of the both series of HCs/LDPEs blends resulted similar; in Figure 10 $\tan \delta$ curves for LDPE2, the more crystalline LDPEs used in this work, and HC1/LDPE2 blends are reported for conciseness. At the frequency of 1 Hz, pure LDPE2 showed two transitions, α and γ . The α -transition is a complex process, due to combined relaxations in the crystallites and in the amorphous regions; this is primarily caused by the longitudinal chain transport through the crystallites of semicrystalline polymer, which facilitates the reorganization in the adjacent amorphous regions.^{20–22} The β -transition has its origin in the amorphous phase and is attributed to the glass-rubber transition in the amorphous phase.²⁰ The γ -transition is also related to the amorphous phase but involved in more localized motion than β process.¹² It can be observed that the β -transition began to appear with the progressive addition of collagen hydrolizate and the β -transition temperature slightly decreased with the increase of the HCs content in the blend. Also, the α -transition was shifted to lower temperatures with HC addition. Considering that the relaxation is related to the onset of movement in the amorphous phase, these results show a signifi-

cant impact of the amorphous collagen hydrolizate on the crystalline regions of the LDPEs as supported also by the crystallinity index decrease with increasing HC content (see Table II). The amorphous HC addition effect was more pronounced for the blends based on LDPE2 and this is attributable to its higher crystallinity degree.

CONCLUSIONS

Polyethylene matrix showed a capability to incorporate the investigated hydrolyzed collagen (HC) without compromising blend filmability from the melt up to a percentage by weight of 50%. No major reaction seemed to take place between the polyethylene and the collagen hydrolizate reactive groups as evidenced in FTIR spectra. The relatively low-molecular weight of the collagen hydrolizate used allowed a high compatibility with LDPE as shown by SEM analysis differently than what reported for similar HC/LDPE blends by other authors.

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

Mechanical properties of HC/LDPE blend films decreased with increasing the concentration of the HC. A decrease of the LDPE crystallinity by effect of the introduction of the HC amorphous component was observed by mechanical tests (Young's modulus) and confirmed by DSC and DMTA results.

At this stage of ongoing research activity, it is clear that the reutilization of collagen hydrolizate derived from the leather industry for the production of biofragmentable polyethylene-based thermoplastic films appears feasible and promising. Blends of collagen hydrolizate and LDPE up to a content of 20–30 wt % of collagen hydrolizate are susceptible to be processed by the melt and provide transparent, cohesive and flexible films that are characterized by satisfactory thermal and mechanical resistance. The positive results obtained in blending LDPE and collagen hydrolizate in the absence of crosslinking agent or compatibilizing agents allows for low cost and simple processing procedure.

Research is in progress on hybrid blends based on oxo-biodegradable polyethylene samples and collagen hydrolizate as aimed at realizing biodegradable low-cost films.

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