

Polyethylene-collagen hydrolizate thermoplastic blends: a new reutilization route to transform a waste of the leather industry into environmentally degradable plastics

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Abstract

In this work, the mixture of low density polyethylene with collagen hydrolyzate derived from the tannery industry was investigated in order to assess the feasibility of producing a biofragmentable polymeric materials suitable for production of thermoplastic items for eco-compatible applications in packaging and agricultural segments.

The present study focused on the preparation of thermoplastic blends based on low density polyethylene and collagen hydrolyzate with optimised thermo-mechanical properties and propensity to environmental degradation as promoted by biofragmentation .

Different grades of polyethylenes having and collagen hydrolyzates characterized by different molecular weight and salinity were investigated in order to develop the optimal blends.

The physical-chemical properties of the blends obtained were assessed by thermal-mechanical, spectroscopical analysis. Biodisintegration tests were started and are still in progress. At this stage of ongoing research activity, it is clear that the reutilization of collagen hydrolyzate derived from the leather industry for the production of environmental degradable polyethylene-based thermoplastic films appear feasible and promising. Blends of collagen hydrolyzate and low-density polyethylene up to a 20-30% content of collagen hydrolyzate allow to obtain transparent, cohesive and flexible films that are characterized by satisfactory thermal and mechanical responses.

Introduction

Polyolefins, such as high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP), constitute the majority of thermoplastics currently used as packaging materials. Since the production and consumption of these plastics is continuously increasing, the post-consume plastic waste has become an important issue for economic and environmental reasons. However, in contrast to glass and metals, which can be recycled into products with properties essentially similar to those of the primary materials, each time polymeric materials are reprocessed, lowering their physical and mechanical properties does occur. In addition, recycling would be neither practical nor economical for low value items such as shopping bags, agriculture mulch films and food packaging (foils and thermoformed items). For these applications, it would be better if the polyolefin-based materials degraded into safe by-products in controlled infrastructure or directly in the sites of utilization like in mulching films applications.

Other than this a mitigation of the negative environmental impact bound to littering of flexible items and light containers could be reached.

Polymeric materials that are vulnerable to microorganisms can be grouped in two major class, namely completely biodegradable systems and the biofragmentable systems that are not completely biodegradable. Biofragmentable polymers are blend materials composed of a completely degradable component and a component capable to biodegradation. Although those types of polymer blends are not completely biodegradable, they are effective for the volume reduction of plastic waste by fragmentation. In spite of this drawback they may have superior physical –mechanical properties with respect to fully biodegradable systems.

Polyolefins, as most synthetic polymers, do not decompose naturally and their resistance to biological attack is a characteristic feature which has caused negative environmental impact bound to the spreading of plastic littering. In these last years, the development of low-cost biofragmentable polymers through the blending of biodegradable polymeric components (such as polysaccharides, proteins of vegetal and animal origin) with polyolefins has assumed an increasing attention [1-17].

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. The fairly high cost of protein and proteinaceous feedstocks as compared to some other biobased polymers, especially starch and cellulose, has somehow restrained research activity on their technical applications. Films and fibers 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 hydrolyzate solution is obtained. The high content of salts of the raw collagen hydrolyzate, whose separation is rather expensive, and represents the obstacle to the recovery and reutilization.

Thus, collagen hydrolyzate from the leather industry is easily available at low cost and its use is not in competition with food industries or other main applications, since it is a waste material, a by-product of the major world-wide distributed leather industry.

In this work, blends of low density polyethylene with collagen hydrolyzate have been investigated in order to assess the feasibility of producing a biofragmentable formulation suitable for production of thermoplastic films for applications in packaging and agriculture.

Different grades of polyethylenes and collagen hydrolyzates 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 thermal, infrared, optical analyses, mechanical testing and afterwards submitted to biofragmentation evaluations.

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 procedures

Materials

Two types of low density polyethylene (LDPE):

- 1) **LDPE1**: 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%;
- 2) **LDPE2**: Basell 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 (MFI) 2.0 g/10 min (under 190°C. 2.16 kg).

Two types of hydrolyzate collagen (HC) in powder form:

- 1) **HC1**: derived from flashings and 2) **HC2**: derived from shavings were utilized.

The two hydrolizates were 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 the Tuscany leather district, producing both a hydrolizate concentrated solution through alkaline hydrolysis, degreasing and concentration and a hydrolizate in powder form upon lyophilization.

The composition of the two hydrolizates is reported in Table 1. Before use, the powdered hydrolizates were dried under vacuum at 40°C for 12 hours.

Blends and films preparation

The blends were prepared in a Brabender (Model OHG Duisburg) in the following operational conditions: temperature 130°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 10 and 70% HC on the total blend weigh. After mixing, the material was inserted between the plates of a heated hydraulic press where a pressure of 100 bar and a temperature of 130°C were applied for 5 min. The specimens for mechanical and dynamic mechanical tests have been cut from the obtained films.

Characterization of the blends

The properties of LDPE/HC blends were determined by the following investigation methods: mechanical tests, dynamic mechanical thermal analysis (DMTA), scanning electron microscopy (SEM), FT-IR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), respirometric biodegradation tests.

a) *Mechanical tests.* Dog-bone shaped samples, cut from the films, were used to assess the tensile properties of the studied blends by means of a an Instron mechanical tester Model 5564 according to the ASTM D638M /ASTM D882 standards for thin films. The speed of the clamp was 10 mm/min.

b) *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.

c) *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.

d) *Thermogravimetric (TGA)* curves were recorded on the film samples (20 mg), placed in a platinum crucible, by a Netzsh STA 409 thermobalance. The runs were conducted under

nitrogen flow (100 cm³/min) in the temperature range from 20°C to 700°C, at a heating rate of 10°C/min.

e) *Dynamic mechanical thermal analysis (DMTA)*. Rectangular strips of film samples were used to investigate the dynamic thermomechanical behaviour of the blends by using a Rheometric Scientific V analyser. The runs were conducted in the temperature range from -150°C to 120°C, at a heating rate of 4 °C/min. The sinusoidal excitation had a frequency of 1 Hz.

f) *FT-IR spectra* were recorded in transmittance by using a JASCO 4100 spectrometer on films obtained by pressing of the melted blends between two microscopical slides.

g) *Respirometric biodegradation tests* were carried out in cylindrical glass vessels (Biometer Flask) (500 ml capacity) containing a multilayer substrate in which defined amounts of forest sandy soil (10-15 g), sieved at 0.6 mm and mixed with 20-25 g perlite, were placed. The samples, in the form of films, were placed into the mixed soil and sandwiched between two layers of 10 g perlite wetted with 30 ml distilled water (Fig. 1). This arrangement guarantees favourable and reliable signal-to-noise ratio in the assessment of the substrate mineralization and hence an improved test accuracy, particularly when limited carbon dioxide emissions are expected from the test samples.

The vessels were kept in the dark and incubated at room temperature. For trapping the CO₂ evolved from samples, each test vessel was equipped with a beaker containing 40-50 ml of 0.05 KOH solution which was substituted every 3-14 days and back titrated with 0.1N HCl.

The biodegradation extent of each test material was calculated as a percentage (corrected for the inoculum endogenous emissions – blank flask) of the overall theoretical CO₂ production calculated on the basis of the determined carbon content of the samples. Each test was carried out in triplicate. Filter paper (Whatman 50) was used as positive control as suggested by standardization prescriptions.

Results and discussion

Properties of the hydrolized collagen

As reported in Table 1, the hydrolized collagen derived from fleshings (HC1) is characterized by a higher salt content and a lower molecular weigh with respect to the hydrolized collagen derived from shavings (HC2).

Blends and films preparation

The capability of the polyethylene matrix to incorporate the hydrolyzed collagen without compromising blend filmability from the melt was displayed up to a percentage of the hydrolyzed collagen in the blend of 50%.

At 50% HC percentage, films were successfully obtained by LDPE1 with both HC, while LDPE2 could be successfully filmed only with HC1.

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

Mechanical tests

The mechanical properties of LDPE/HC blend films decreased with increasing the concentration of the HC used, as reported in Figs. 2-4.

Pure LDPE2 showed a higher Young modulus, and thus a higher rigidity, than LDPE1 (Fig. 2). When the collagen hydrolyzate is added, the Young modulus shows a gradual decrease with the increasing percentage of HC. This behaviour may be related to a decrease of the LDPE crystallinity by effect of the introduction of the HC amorphous component. For both LDPEs, the blends with HC1 produced a more rigid structure with respect to the blends with HC2. This result may be attributed both to the higher salt content of HC1 and to its lower molecular weight. The less rigid LDPE1 showed a more marked decrease of the tensile strength than LDPE2 when blended with collagen hydrolyzate (Fig. 3). According to the increase of rigidity induced by the addition of the collagen hydrolyzate, the strain at break of the blended films showed a rapid decrease when the HC percentage is increased above 20% (Fig. 4). The LDPE2/HC1 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 the results of the mechanical tests, the subsequent characterizations were focused on the blends with 10 and 20% of HC, that guarantee an optimal trade-off between percentage of HC reutilized and mechanical performances.

Scanning electron microscopy (SEM)

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 LDPEs/HCs films (Fig. 5), where 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 at micro and submicro scales were observed. The structure appears quite homogeneous, differently from similar LDPE/collagen hydrolyzate blends [1]. This behaviour is most likely due to the relatively low molecular

weight of the collagen hydrolyzate used, that allowed a higher compatibility between the two components. Rugosity and cavities could be observed on the surface whereas pores formed on the transversal section of the samples. These are due to the presence of residual water (despite the vacuum drying) of the powdered hydrolyzates, that evaporates from the bulk during the blend melt processing.

Differential scanning calorimetry (DSC)

DSC results are given in Tables 2 and 3, including the melting temperature (T_m), crystallization temperature (T_c), melting heat (ΔH_m), crystallization heat (ΔH_c), and crystallinity index (I_c). It can be observed that, for both LDPE samples, the melting temperatures and the crystallization temperatures are insignificantly changed by the amount and type of HC incorporated. The melting and the crystallization heats decreased when HC is incorporated in the blend, due to the decrease of the crystallinity of the LDPE when added with an amorphous component. For both LDPE samples, the melting temperatures and the crystallization temperatures of the blends are insignificantly changed by the type of HC incorporated. The crystallinity index of each blend was determined as the ratio $\Delta H_{m \text{ blend}}/\Delta H_{m \text{ reference}}$, where the reference assumed was ΔH_m of pure LDPE2 (the most crystalline between the two LDPE samples used). For each LDPE, the crystallinity index decreased when HC is incorporated in the blend. It can be observed that, for each LDPE, the crystallinity index of the blends are insignificantly changed by the type of HC incorporated.

Thermogravimetric (TGA) analyses

The thermogravimetric analysis was conducted in order to assess the thermal stability of the LDPE samples when the HCs are incorporated in the blend. As reported in the TG and DTG curves of Fig. 6, the collagen hydrolyzates, after a minor weight loss peak close to 150°C, related to the loss of the lighter components, showed the major weight loss peak at a temperature close to 300°C. The TG and DTG curves of LDPEs showed a thermal stability of the polymers up to 400°C and the thermal degradation peak close to 480°C (Fig. 7). No significant variation of the thermal stability was observed when the HCs were incorporated to the LDPE samples. As reported in Fig. 8 (where the blends LDPE1/HC2 are reported for brevity), the major thermal degradation peak remained close to 480°C. A minor weight loss was observed in the temperature region around 300°C, typical of the thermal degradation of the HCs. It must be observed that this minor weight loss is about 5% for the blends at 10% HC and about 10% for the blends at 20% HC. This indicates that, roughly, only half of the collagen hydrolyzate was degraded at 300°C, thus proving that the protein fraction incorporated in the polymer matrix improves by far its thermal resistance.

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical thermal analysis (DMTA), through dynamic strains and dynamic temperature sweeps performed on the sample, is a valid method to investigate the 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 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 solicitation). This investigation method provides further substantiation to the information gained by DSC analysis and evidences secondary transitions (characterized by very low heats) that the DSC analysis is not able to appreciate.

The behaviour of both pure LDPEs and of their blends resulted similar, hence the $\tan \delta$ DMTA curves of HC1/LDPE1 blend is reported for conciseness in Fig. 9. Pure LDPE1 showed two transitions, α and γ . The α -transition, observed in all semi-crystalline polymers, is attributed to interface processes at the boundary between crystalline and amorphous phase before melting. The γ -transition has its origin in the amorphous phase and is associated to the rotation of four carbon chain segments. The introduction of the collagen hydrolyzate was evidenced by the occurring of the β -transition, that is often associated to the glass-rubber transition in the amorphous phase. The β -transition temperature was quite constant or slightly decreasing with the increase of the HCs content in the blends (Fig. 10). Due to its higher crystallinity, LDPE2 showed a decrease of the β -transition temperature when the amount of HC was increased, indicating a higher impact of the amount of amorphous hydrolyzate on the crystalline regions.

FT-IR spectra

The IR-spectra of pure HC1 and HC1/LDPE2 blend are reported in Fig. 11. They show that no major reaction seemed to take place between the polyethylene and the collagen hydrolyzate reactive groups, since the spectra of the blend result as a mathematical overlapping of the pure components typical peaks.

Respirometric biodegradation tests

Table 4 reports the results of the biodegradation test in the first 60 days of experiments, that are currently in progress. The role of perlite, a chemically inert (heat expanded naturally occurring aluminium silicate), is to reduce the amount of soil and hence the carbon dioxide production from the blanks. Perlite is widely used in horticultural applications as a component of soil-less growing mixes, where it provides aeration and optimum moisture

conditions for the plant growth. Accordingly, perlite was used to ensure satisfactory incubation conditions, whereas the soil was used mainly as microbial inoculum. The cumulative CO₂ emissions of samples are still very low but are consistent with incubation times close to five months reported in literature for LDPE containing pro-oxidant additives [18].

Conclusions

At this stage of ongoing research activity, it is clear that the reutilization of collagen hydrolyzate derived from the leather industry for the production of biofragmentable polyethylene-based thermoplastic films appear feasible and promising. Blends of collagen hydrolyzate and low-density polyethylene up to a content of 20-30% of collagen hydrolyzate are susceptible to be melt processed to provide transparent, cohesive and flexible films that are characterized by satisfactory thermal and mechanical resistance. The ongoing biodegradation respirometric tests are clearly showing that the blends tend to be biofragmented by digestion of the protein component. It will be interesting to determine if the LDPE matrix may be oxidized during aerobic degradation tests and become vulnerable to micro organisms. Research is in progress on hybrid blends based on oxo biodegradable polyethylene samples and collagen hydrolyzate as aimed at assessing any synergistic effect in the oxo biodegradation of LDPE matrix by the organic component present in the blends.

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Table 1. Composition and physical-chemical characteristics of the two utilized collagen hydrolizate powder samples.

Properties	Collagen hydrolizate samples	
	Fleshing-derived (HC1)	Shaving-derived (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	26
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 weigh (kDa)	1.53	4.08
Free amino acids (wt.%)	12.95	6.9
Total amino acids (wt.%)	72.09	92.25

Table 2. Melting (T_m) and crystallization (T_c) temperatures, melting (ΔH_m) and crystallization (ΔH_c) temperatures of the blends.

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

Table 3. Crystallinity index of the blends.

Sample	Crystallinity index
LDPE2	1
LDPE1	0.82
10HC1/LDPE1	0.77
20HC1/LDPE1	0.70
10HC2/LDPE1	0.77
20HC2/LDPE1	0.72
10HC1/LDPE2	0.90
20HC1/LDPE2	0.87
10HC2/LDPE2	0.94
20HC2/LDPE2	0.82

Table 4. Respirometric biodegradation tests results.

	Cumulative CO₂ (mg) evolved from the samples								
	4 days	9 days	15 days	21 days	28 days	35 days	42 days	50 days	60 days
LDPE1	12.9	23.5	33.4	40.8	50.2	59.3	68.6	81.8	97.2
LDPE2	13.2	24.6	34.6	43.1	53.1	62.5	72.6	86.2	103.0
10HC1/LDPE1	11.7	23.2	32.6	40.2	49.9	59.6	69.5	82.7	98.6
20HC1/LDPE1	15.0	29.0	39.6	49.9	60.7	71.9	82.7	97.2	114.4
10HC2/LDPE1	12.3	22.9	31.4	39.9	49.9	59.8	70.1	84.2	98.7
20HC2/LDPE1/	13.2	24.1	34.9	45.8	57.8	69.2	81.5	98.7	119.8
10HC1/LDPE2	13.2	23.8	34.0	43.1	52.5	62.5	73.0	87.1	101.6
20HC1/LDPE2	12.6	24.1	34.3	43.4	52.8	63.1	72.7	86.4	105.3
10HC2/LDPE2	12.0	24.3	33.4	43.4	52.5	62.5	71.9	85.5	101.3
20HC2/LDPE2	12.6	25.5	38.1	50.2	61.9	73.6	86.2	101.6	120.1
Blank	12.3	23.8	32.6	40.9	49.7	58.5	68.6	80.7	95.3
Filter paper	12.6	25.8	38.4	49.9	63.1	75.4	92.1	111.8	137.6

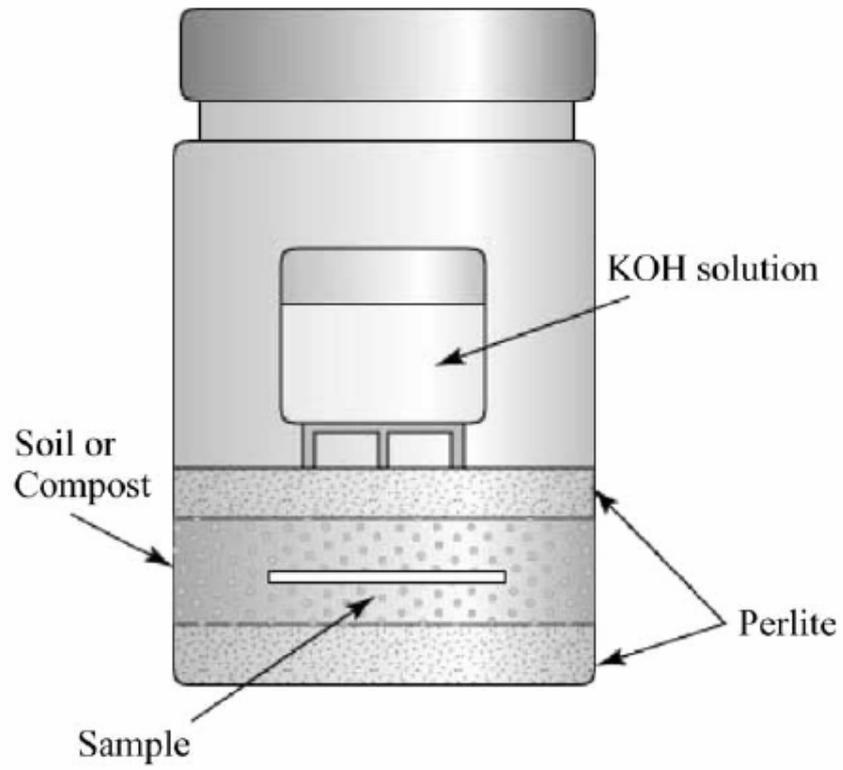


Fig. 1. Biometer flask for simulated soil burial biodegradation tests.

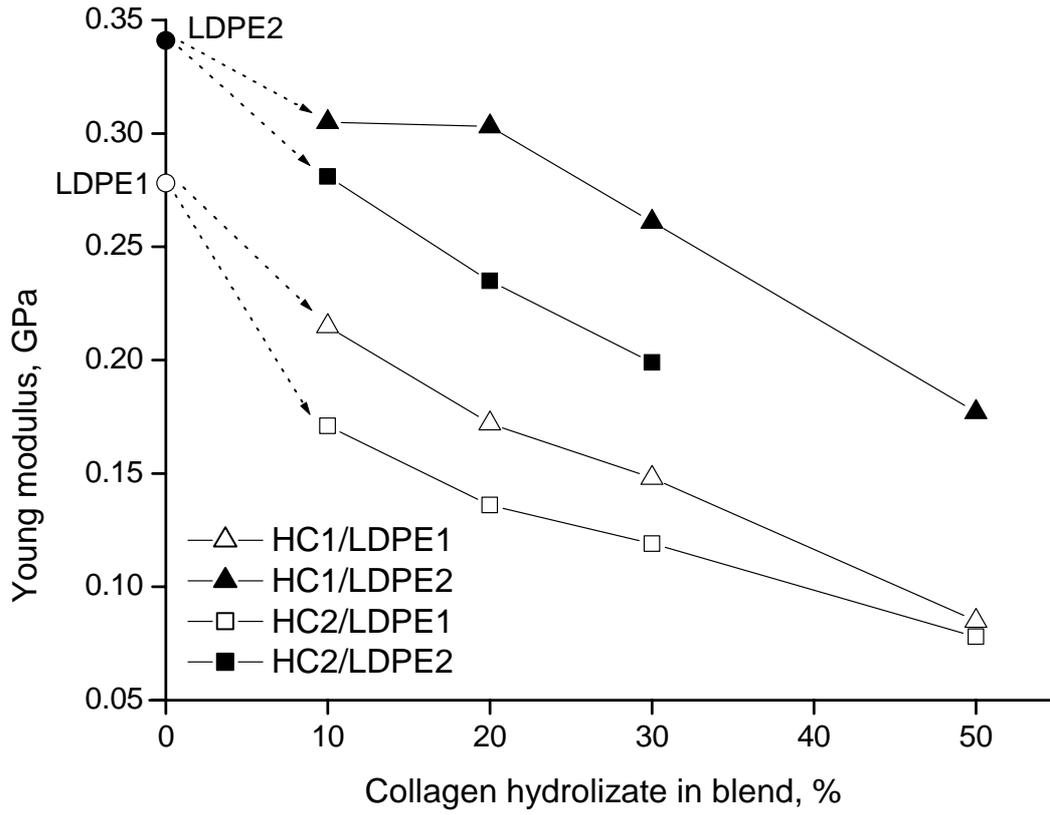


Fig. 2. Young modulus of the HC/LDPE blended films.

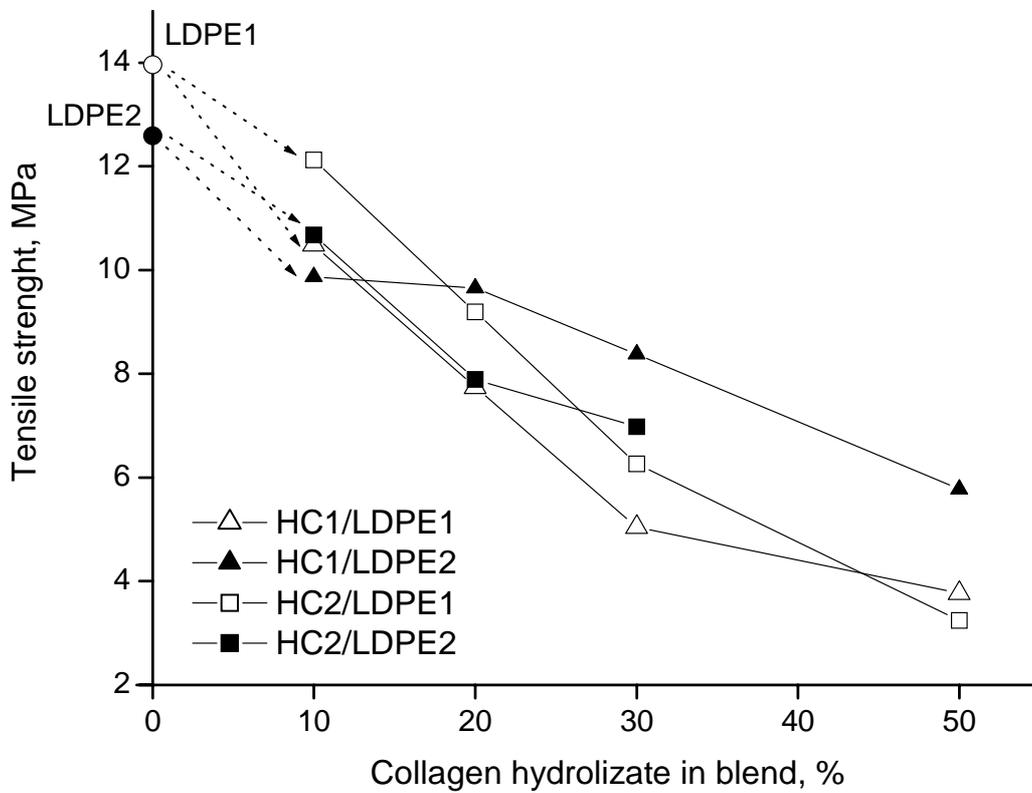


Fig. 3. Tensile strength of the HC/LDPE blended films.

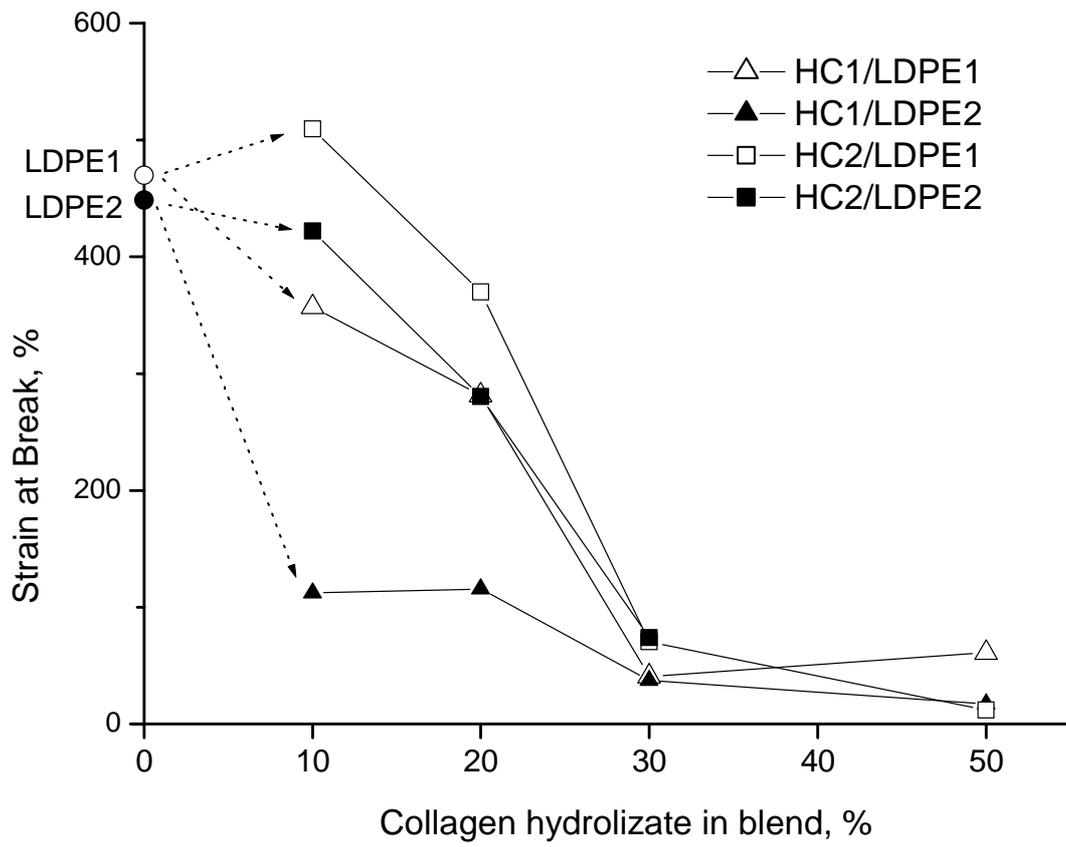
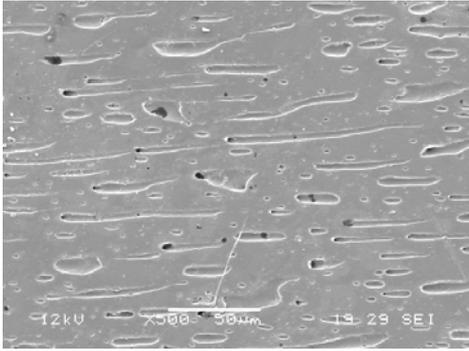
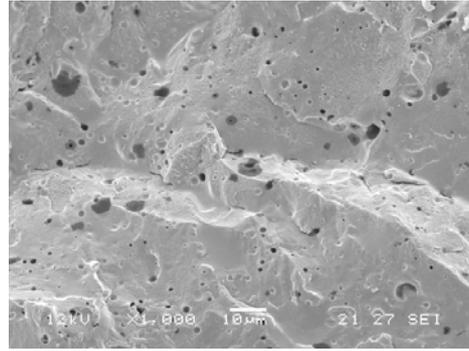


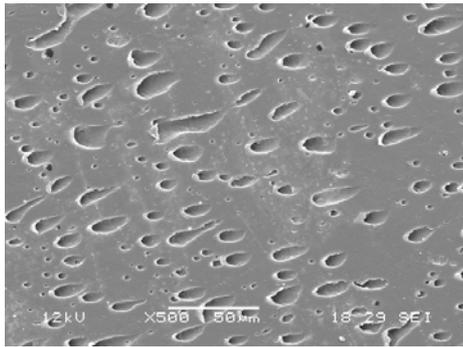
Fig. 4. Strain at break of the HC/LDPE blended films.



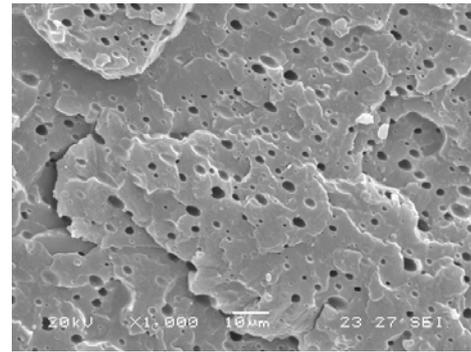
HC1/LDPE1 surface



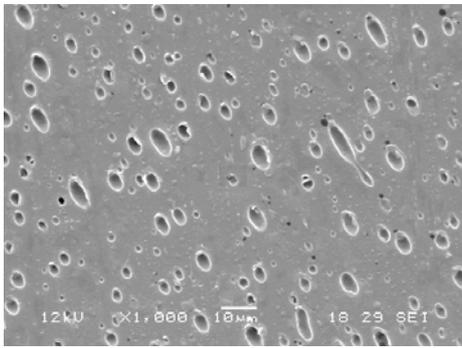
HC1/LDPE1 section



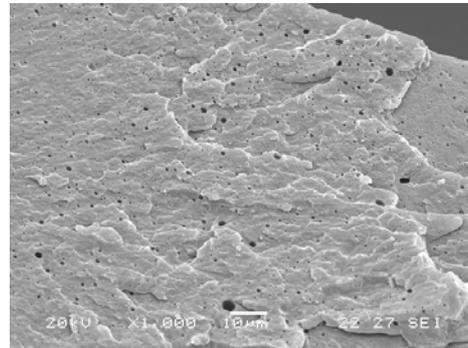
HC2/LDPE1 surface



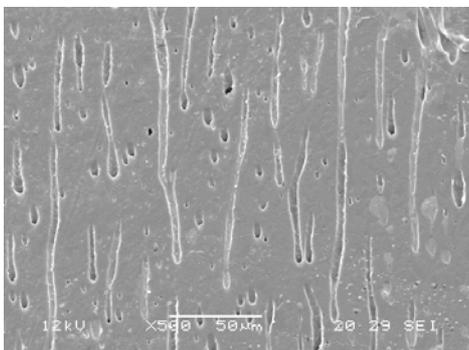
HC2/LDPE1 section



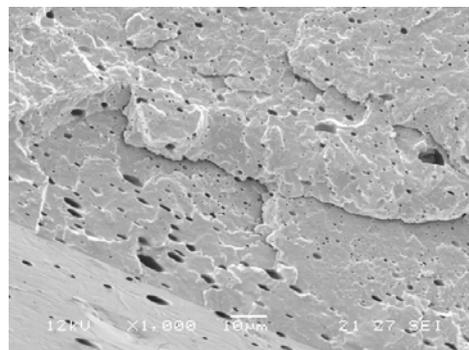
HC1/LDPE2 surface



HC1/LDPE2 section



HC2/LDPE2 surface



HC2/LDPE2 section

Fig. 5. SEM micrographs of surface and transversal section of the HCs/LDPEs blends at 20% HCs.

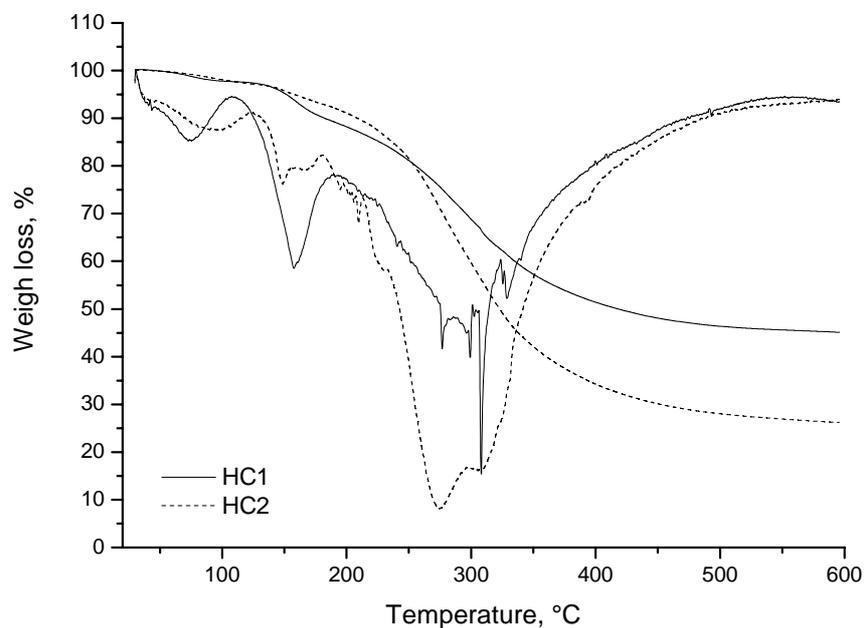


Fig. 6. Weight loss and derivative weight loss of the collagen hydrolyzates in the thermogravimetric tests.

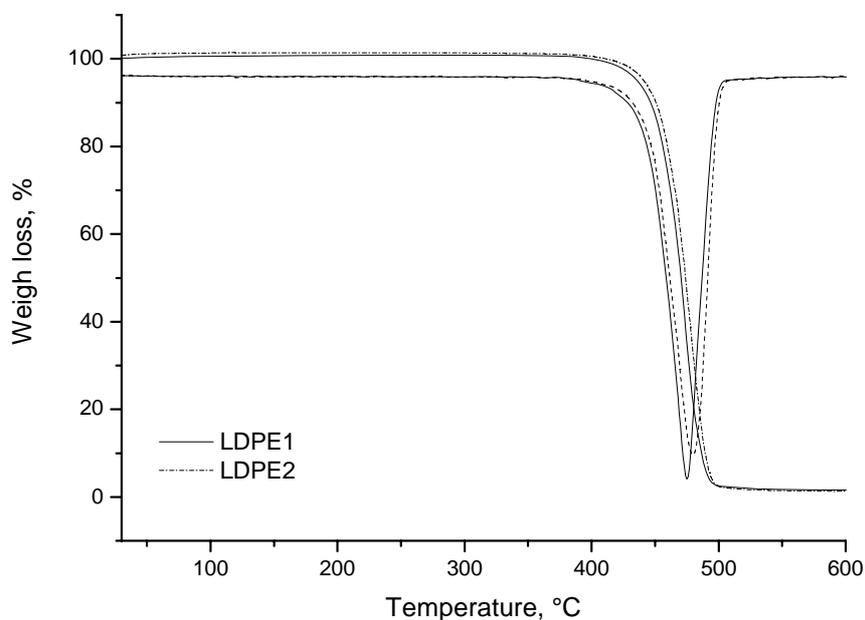


Fig. 7. Weight loss and derivative weight loss of the polyethylenes in the thermogravimetric tests.

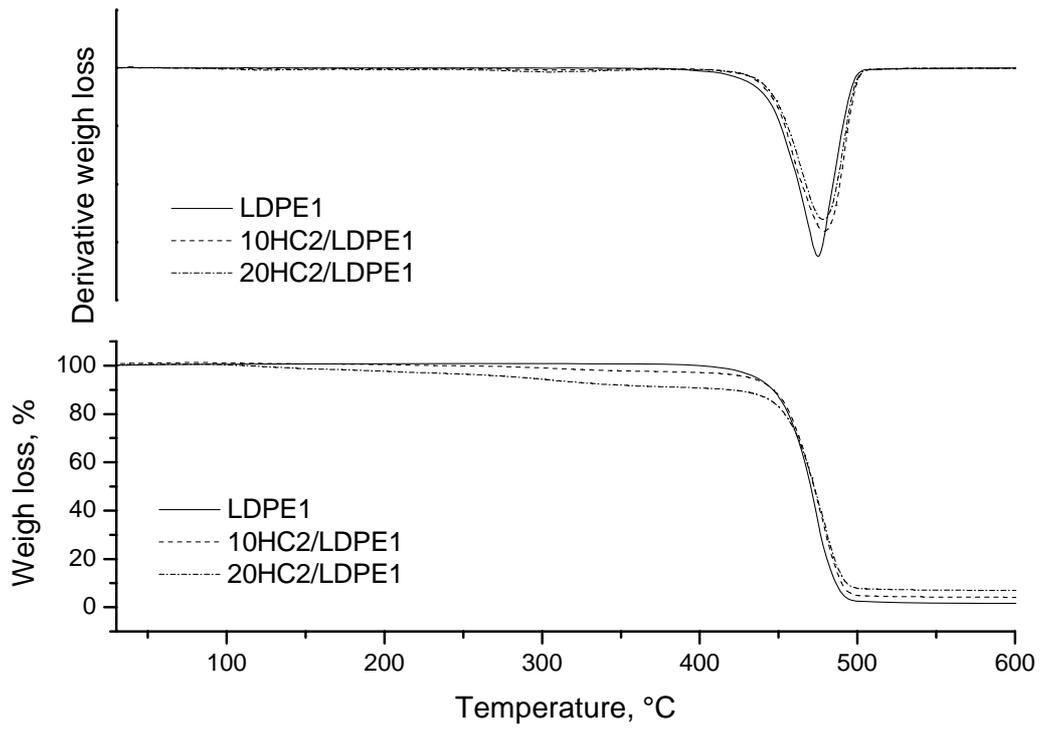


Fig. 8. Weight loss and derivative weight loss of the HC2/LDPE1 blends in the thermogravimetric tests.

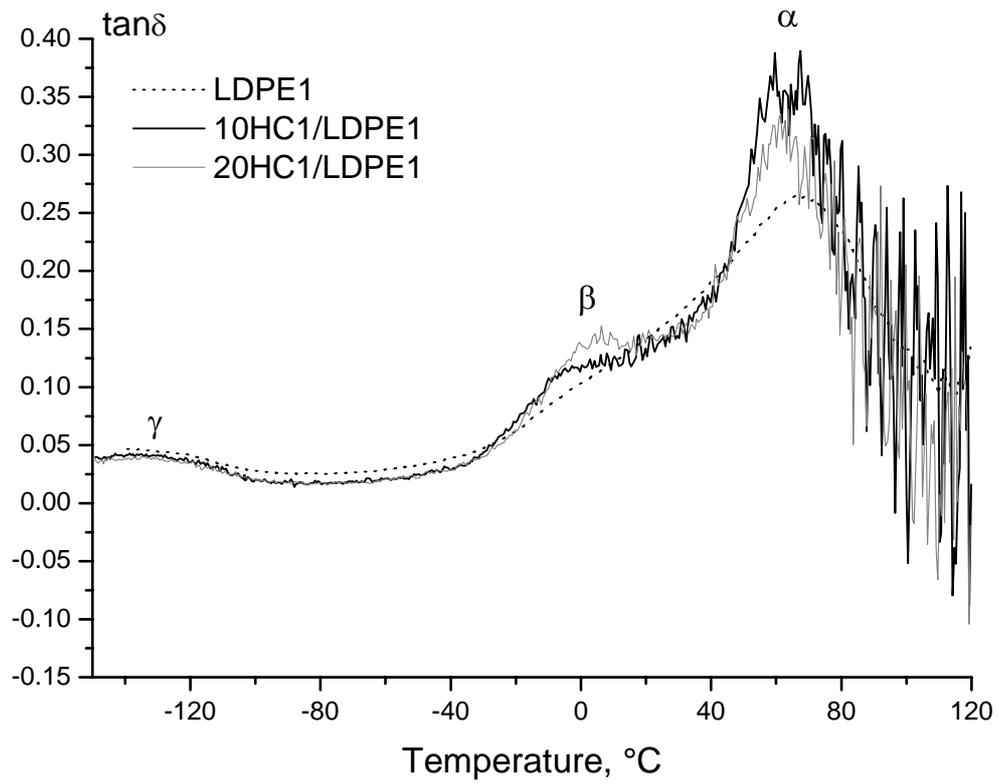


Fig. 9. $\tan\delta$ versus temperature for HC1/LDPE1 blends.

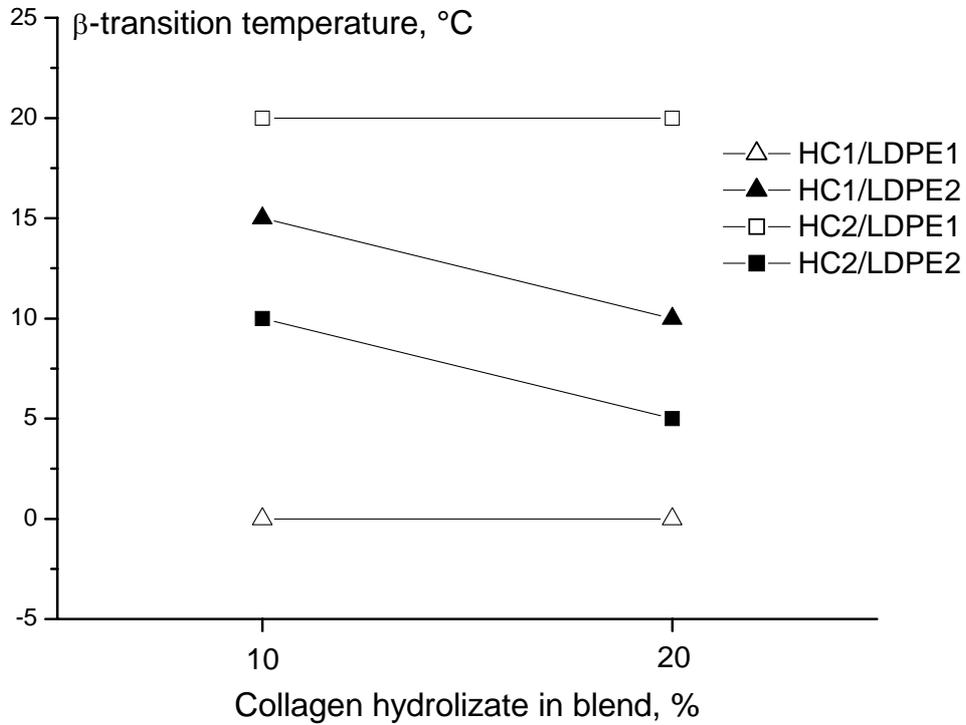


Fig. 10. β -transition temperatures of HC/LDPE blends.

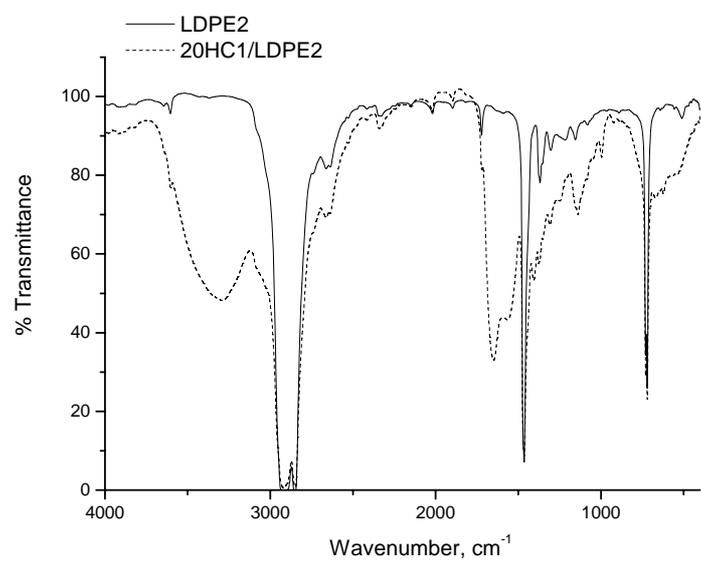
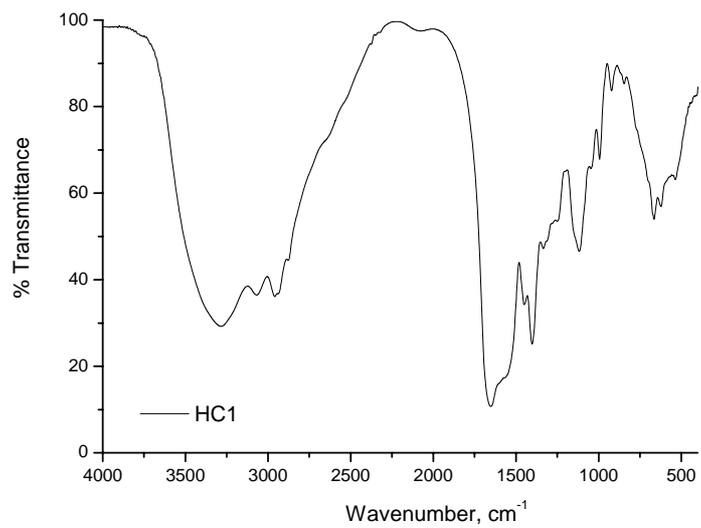


Fig. 11. IR spectra of the pure HC1 and LDPE2 and of their blend.