

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



WIPO | PCT



(10) International Publication Number  
**WO 2016/035021 A1**

(43) International Publication Date  
**10 March 2016 (10.03.2016)**

(51) International Patent Classification:

*C08J 5/18* (2006.01)      *C08L 89/06* (2006.01)  
*C08L 67/04* (2006.01)      *C08J 11/10* (2006.01)  
*C08L 89/00* (2006.01)      *B29C 67/00* (2006.01)  
*C08L 89/04* (2006.01)

(21) International Application Number:

PCT/IB2015/056660

(22) International Filing Date:

2 September 2015 (02.09.2015)

(25) Filing Language:

Italian

(26) Publication Language:

English

(30) Priority Data:

FI2014A000199 3 September 2014 (03.09.2014)      IT

(71) Applicants: **UNIVERSITA' DI PISA** [IT/IT]; Lungarno Pacinotti, 43, I-56126 Pisa (IT). **SOCIETÀ GENERALE PER LA GESTIONE DEL POLO TECNOLOGICO CONCIARIO SOCIETÀ CONSORTILE A RESPONSABILITÀ LIMITATA (PIÙ BREVEMENTE DENOMINATA PO.TE.CO. S.C.R.L.)** [IT/IT]; Via Buoni, 2/a, I-56029 Santa Croce sull'Arno (Pisa) (IT).

(72) Inventors: **VITOLO, Sandra**; Largo Lucio Lazzarino, 2, I-56126 Pisa (IT). **PUCINI, Monica**; Largo Lucio Lazzarino, 2, I-56126 Pisa (IT). **SEGGIANI, Maurizia**; Largo Lucio Lazzarino, 2, I-56126 Pisa (IT). **CASTIELLO, Domenico**; Via W. Tobagi, 30, I-56022 Castelfranco di Sotto (Pisa) (IT).

(74) Agents: **BRAZZINI, Silvia** et al.; Società Italiana Brevetti S.p.A., Corso dei Tintori, 25, I-50122 Firenze (IT).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))



WO 2016/035021 A1

(54) Title: THERMOPLASTIC POLYMER COMPOSITION

(57) Abstract: The present invention refers to thermoplastic polymer compositions, highly biodegradable, based on polycaprolactone and a proteic hydrolysate material, that are useful for the quick prototyping with 3D printers and for the manufacture of semi-finished products in the form of filaments, pellets and thin films by hot extrusion.

## THERMOPLASTIC POLYMER COMPOSITION

### DESCRIPTION

#### Field of the Invention

The present invention relates in general to the field of thermoplastic polymeric materials, and more precisely it relates to novel thermoplastic polymeric compositions defined better herein after that are useful for the manufacture, by hot melt extrusion, of biodegradable artefacts and packaging, compostable and having at the same time performances and costs comparable to those of the products obtained with the traditional non-biodegradable thermoplastic polymeric materials, such as the polyolefins.

#### State of the Art

In modern societies the problem of waste disposal has become increasingly important and, hand in hand, the awareness of the institutions and of the consumers for the properties of everyday materials has been growing with respect to their biodegradability, and therefore to the possibility of a more easy and safe disposal.

By "biodegradable" material it is meant a material which can be decomposed by microorganisms until its complete transformation into simple chemical compounds, which means for the processes of aerobic degradation into carbon dioxide and water, while for the anaerobic processes of degradation mainly into methane and carbon dioxide.

The biodegradability of a material therefore has a high added value in the context of the characteristics of that material, in particular for the end of life management of products made with that material, because their biodegradability makes them compatible with any route of disposal, including routes of disposal of the existing organic waste, for instance by treatment in composting plants for the production of compost, or by treatment in a plant for anaerobic digestion for production of biogas or in a plant for the biological treatment of wastewater. This is the case of food packaging, which is increasingly used, but which, when made with biodegradable materials, compared to traditional non-biodegradable plastics, has the advantage of being able to be disposed directly with the organic fraction of waste, without further separation operations from food residue, and without onerous cost of recovery and

disposal.

The replacement of the traditional plastics with biodegradable materials, although desirable, and also technically possible, has however encountered up to now limitations mainly due to the higher cost of production of biodegradable materials, sometimes due to the cost of raw materials but also to the low volumes of production. Another important limitation that has hampered to date the development of biodegradable plastic materials is represented by the fact that their mechanical performance was sometimes much scarcer compared to the performance of traditional plastic.

For these reasons up to date, as far as the Applicants are aware, it remains still unsolved the technical problem of having available plastic materials for the production of biodegradable artefacts and packaging, which are possibly compostable after use and are able to fully meet the requirements of the market both in terms of costs and in terms of mechanical performance and controlled biodegradability of the material.

#### Summary of the Invention

Now the Applicants have found that the synthetic polymer polycaprolactone, that is *per se* biodegradable, may be used in mixture with a proteic hydrolysate material coming from the operations of fleshing out/shaving of animal pelts in tanning industry, to obtain a novel thermoplastic polymer composition, hot processable by means of extrusion or filming known procedures, for the manufacture of a wide range of products that have been shown as completely biodegradable, compostable and as having performances and costs comparable to those of the traditional thermoplastic polymeric materials based on non-biodegradable polymers.

Advantageously, the aforesaid components of the novel composition, namely polycaprolactone and proteic hydrolysate, have shown a surprising mutual compatibility, in a wide range of ratios, giving rise to a polymer composition characterized by a high hot workability, for example much greater than the workability the polycaprolactone only, to produce artifacts and films completely homogeneous and of high mechanical resistance; all this being able to be achieved therefore without the addition of any compatibilising additive.

Particularly advantageous it is then the fact that the proteic hydrolysate of the

present compositions is a hydrolysed animal collagen originating from a waste of the tanning industry, or a proteic hydrolysate from wastes and/or by-products of other industrial processes, whose reuse for the preparation of the compositions of the invention, in addition to not burden the manufacturing costs of the compositions, represents a valorisation of a waste product or by-product, otherwise to be treated as industrial waste, or having up to now limited possibilities of use or recycling.

It is therefore a subject of the present invention a thermoplastic polymeric composition obtainable by mixing molten polycaprolactone and proteic hydrolysate in powder having average molecular weight lower than 10,000 g/mol, as defined in the first of the claims herein after.

A process for the preparation of the above said composition, its use for prototyping with 3D printers and for manufacturing semi-finished products in the form of filaments, pellets or thin films by hot extrusion, as well as the same so obtained products, as defined in the other subsequent independent claims herein after, are a further subject of the present invention.

Further important characteristics of the present composition, of the process for its preparation and of its use according to the invention, are provided in the following detailed description.

#### Brief Description of the Figures

- Figure 1 (COMPARISON): SEM (Scanning Electron Microscope) images of the surface (part A) and of the section (part B) of a sample of a PCL film;

- Figure 2: SEM images of the surface (part A) and of the section (part B) of a composition of the invention consisting of PCL+20%HYD obtained by fleshing out pelts;

- Figure 3 (COMPARISON): Thermogravimetric curves of PCL (continuous line) and of HYD (dashed line) obtained by shaving leather;

- Figure 4: Thermogravimetric curves of PCL alone (continuous line), and of the compositions of the invention respectively consisting of PCL with 10% of HYD (uniform dashed line) and with 20% of HYD (non-uniform dashed line);

- Figure 5: Scheme of a tensile test and geometry of the specimens prepared with the compositions of the invention;

- Figure 6: Stress-strain curve;
- Figure 7: Scheme of the system used for the evaluation of the biodegradability in soil of the semi-finished products obtained with the present compositions;
- Figure 8: Results of the biodegradability tests carried out in parallel for the compositions of the present invention in the form of film obtained in Example 2 herein after described and, by comparison, for PCL, for paper and for the commercial product Mater-Bi<sup>®</sup>, Novamont.

#### Detailed Description of the Invention

In the present invention, when not specified otherwise, the percentages of a product are to be considered as weight percentages of that product with respect to the total weight of the composition containing it.

By "polycaprolactone" or "PCL" is meant, in the present invention, the synthetic polyester poly- $\epsilon$ -caprolactone, obtainable from polymerisation of  $\epsilon$ -caprolactone. The PCL is endowed with good characteristics of biocompatibility, and with a high thermal stability; its modest mechanical properties and its relatively high manufacture cost up to date have meant that the use of the PCL did not go beyond the production of objects for biomedical applications. It is a biodegradable synthetic product that, for the scopes of the invention, is preferably used in the form of granules or pellets, of dimensions for instance of about 3 mm, whose properties are summarised in the following Table 1:

Table 1 – Main properties of the biodegradable polymeric matrix of PCL

Melting temperature, °C	58-60
Molecular weight, kDa	>80
MF1190°C/2, 16 Kg, g/10 min	2.01-4.03

In the present invention by the term "hydrolysed" or "proteic hydrolysed", indicated herein sometimes by the acronym "HYD", is meant a natural organic product in the form of a powder, obtained by hydrolysis of the animal fleshing, that is the waste product in the phase of mechanical removal of the subcutaneous tissue from the dermis, called fleshing out, or obtained by treatment of the processing residues of the operations of shaving of the pelts. The animal fleshing is a product mainly formed by fats and collagen fibres rather relaxed and degraded. The main characteristics of the proteic

hydrolysate obtained from wastes of fleshing out and shaving and used in the present compositions, are described in the following Table 2:

Table 2. Characteristics of the proteic hydrolysate from wastes of *fleshing out and shaving*

	from fleshing out	from shaving
Elementary analysis (% by weight on dry basis)		
C	33.4	42.21
H	5.3	6.37
N	10.3	15.71
O (by diff.)	51	35.71
Approximated analysis (% by weight on hydrolysate as such)		
Moisture	3.3	3.4
Volatile matter	---	69.9
Ash	23.4	5.7
Fixed carbon (by diff.)	---	21
NaCl (%)	17.6	6.3
pH in aqueous solution	5.49	6.79
Organic substance (%)	73.3	92.4

The fleshing out is that mechanical operation in the tanning process during which the flesh and subcutaneous tissue residues are removed from the skin. It is carried out immediately downstream of the phase so called of "liming" (during which hair and epidermis are removed) because in this phase the skin swells and therefore the fleshing out process is easier and stress less the collagen fibres. From this processing the "fleshed" skin is obtained, which is then conveyed to the subsequent processing, and a waste product called "fleshing" enriched in proteins (mainly collagen) and in fats.

Following the tanning operations, the skins are subjected to the process of shaving in order to equalize the thickness of the skin. The shaving is carried out with the

shaving machine whose principle of operation is similar to that of the fleshing machine. The hides treated in this phase of the tanning process provide residues mainly consisting of subcutaneous tissue (rich in collagen), of fats and of a smaller amount of salts with respect to the fleshing, since the skin has undergone numerous intermediate washings. Moreover, the residues of shaving obtained from tanned skins contain subcutaneous tissue and collagen, in particular, less degraded compared to that constituted by fleshing.

The fleshing, taken out from the collection tanks, or the residues coming from the phase of shaving, undergo a series of processings, described in detail hereinafter by way of example, that lead to the obtainment of the proteic hydrolysate for use in the present compositions.

In the present invention by the term "hydrolysate" or "proteic hydrolysate", is moreover meant a natural organic product in the form of powder, obtained by any treatments of hydrolysis of any proteic substrate of vegetal or animal origin, such as milk serum or soya. The production processes of hydrolysis industrially applicable on this type of proteic matrix may be processes of:

1. chemical hydrolysis, based on the formation of a strongly acid or alkaline environment;
2. thermal hydrolysis, based on an increase in temperature and pressure in the reaction environment;
3. enzymatic hydrolysis, based on the use of proteolytic enzymes that are able, under appropriate conditions of temperature and pH, to break the protein chains into fragments of peptides, polypeptides and amino acids of various length and molecular weight.

The application of these three different processes, both individually but also and often in synergy among each other, makes it possible to predetermine and maximize certain interesting aspects of the obtainable proteic hydrolysate, such as its solubility, the control of the degree of racemization or the degree of hydrolysis obtainable with the hydrolytic process. In all cases, it is anyway well defined the fingerprint of the amino acid profile determined by the starting matrix.

In general the process for obtaining the proteic hydrolysate may comprise, in addition to the actual hydrolysis step, a preliminary step of homogenization of the proteic

substrate used as a raw material, while after the hydrolysis it may comprise one or more operations to standardize, purify and/or stabilize the obtained product, and consisting for example of drying, screening, cooling, etc.

Any person skilled in the art can easily vary and diversify the characteristics of the obtainable proteic hydrolysate, such as the degree of hydrolysis, degree of racemization, distribution of molecular masses, and the content of free amino acids, modifying the phase of hydrolysis selected (chemical/thermal/enzymatic hydrolysis or their combination) and the related parameters of the process, according to the knowledge and procedures known to any person skilled in the field.

By way of example it is described in the following a process of alkaline hydrolysis process that is preferably chosen to obtain a proteic hydrolysate starting from a residue of shaving and of fleshing of the animal hide, which can also be used then in the following experiments. The fleshing coming from the fleshing of hide or the residue of shaving are subjected to alkaline hydrolysis, followed by a step of degreasing, a step of purification and concentration in multiple-effect evaporators, and by atomization. According to a preferred embodiment of the invention, the proteic hydrolysate from fleshing or from the shaving residue of animal pelts is obtained by subjecting a substrate, before the hydrolysis, to milling, then the milled substrate is hydrolysed under conditions of acid pH at temperature of about 70-80°C. At the end of hydrolysis, for example with the aid of mechanical means in a suitable separator, the fatty phase and the protein phase, which stratify during hydrolysis, may be then separated; more particularly, the saponified fatty phase, less dense, is touched on the surface to be separately recovered, while the peat protein is taken from the bottom of the separator and possibly let to pass through a special grid to eliminate the not dissolved coarser pieces, then subjected to sterilisation. The sterilisation is preferably carried out at a temperature of 133°C, 3 bars of pressure for a minimum time of 20 minutes. The obtainment of the proteic hydrolysate in powder, useful for preparing the polymer compositions of the present invention, includes a last drying phase, carried out for instance by concentration in a system of multiple-effect evaporators and atomization. Before drying, if necessary, the sterilised product is filtered to eliminate the insoluble organic component, and then subjected to oxidation in order to eliminate sulphides and then subjected to decalcification.



In general the proteic hydrolysate used to obtain the present compositions can therefore advantageously be obtained from the proteic substrate by chemical hydrolysis (alkaline or acid) and/or thermal and/or enzymatic hydrolysis under such conditions that result in a product having average molecular weight lower than 10,000 g/mol, and typically ranging between 1,000 and 5,000 g/mol, which is then subjected to degreasing and drying, preferably to atomisation, to obtain a solid product, substantially free of water, to be used in the form of powder. The so obtained hydrolysed product having average molecular weight in the range indicated above, ensures the best compatibility between PCL and the hydrolysate, and consequently allows obtaining a composition having optimal homogeneity for a better processability of the material. In the present invention, when reference is made to the molecular weight of the proteic hydrolysate, is meant the average molecular weight which was determined by size exclusion chromatography (SEC-HPLC).

The present compositions essentially consist of proteic hydrolysate and polycaprolactone, with no need to add any kind of additive, thus guaranteeing the complete biodegradability of the obtained products, as also shown in the following experimental part. It is meant that the compositions in the molten state as well as the compositions in the solid state are comprised in the scope of the present invention.

The surprising aspect of the present compositions is the possibility to be easily hot processed, for instance by extrusion or filming, with no need of compatibilising additives or other additives of any kind, to obtain artefacts in different forms, from pellets to thin films, all having the stability and the mechanical characteristics required to the material of that form. This is surprising given the scarce thermoplastic properties of the pure PCL, which is not processable by hot extrusion or filming; on the contrary, the two products together, in a wide range of weight ratios, have shown a surprising ability to be hot processed, producing stable solid artefacts or resistant and flexible thin films.

The present compositions may have percentages of proteic hydrolysate ranging for instance between 5 and 60% by weight with respect to the total weight of the composition, and preferably ranging between 10 and 30%. The weight ratios

polycaprolactone: proteic hydrolysate according to the invention are for example of 90:10, 80:20, 70:30 and 60:40.

The proteic hydrolysate used in the present compositions may be a hydrolysate coming from fleshing out, from shaving or it may be a mixture of such two types of hydrolysate, or it may be a hydrolysate coming from the treatment of other proteic organic substrates different from fleshing or from the residues of processing of animal pelts, and identified above; according to a preferred embodiment of the invention it is a proteic hydrolysate coming from fleshing out animal hides.

The process for obtaining the present compositions includes the hot extrusion of molten PCL with a powder of proteic hydrolysate at temperatures ranging for example between about 90°C at the inlet of the extruder and about 130°C at the output. It is essential that the temperature at the inlet of the extruder is lower than the degradation temperature of the proteic hydrolysate, for example lower than 120°C, to avoid the degradation of the hydrolysate. The initial temperature or the temperature at the input of the extruder will therefore be advantageously comprised between about 90°C and about 120°C.

According to a preferred embodiment of the process of the invention, the PCL and the proteic hydrolysate powder are blended before entering the extruder, and are processed in a twin screw extruder that allows a uniform and effective mixing in the molten state of the material fed. The extruded material may be formed of the desired size and shape by moulding according to procedures known to any expert in the sector, including moulding with 3D printers, to obtain a solid plastic material of desired shape and size, or it may be sent to an apparatus for filming, for example for blown film extrusion, which allows to obtain thin films consisting of the present composition.

With the compositions of the invention various kinds of articles may be obtained, for instance thin films, films for packaging in general, pipes, wires, packets, bags or bottles.

The Applicants have carried out experiments, herein after described in the examples, in order to mainly verify morphology and thermal stability of the compositions of the invention, their processability by hot processings to obtain both

pellets and thin films; the properties of mechanical strength and of biodegradability of articles made from the present compositions have also been investigated.

It has thus been found that the addition of proteic hydrolysate to the PCL, in a wide range of weight ratios, makes it thermoplastic and able to be hot extruded with excellent results in terms of mechanical and thermal properties of the solid products obtained, which have also shown a complete biodegradability. This entails a plurality of advantages, both economic and environmental, since the PCL is a relatively expensive material, therefore the use of an organic filler to "cut" the PCL is advantageous, as well as it is advantageous that a new way was found to recycle the hydrolysate coming from wastes in leather processing, up to now used only in the form of an aqueous solution as a fertilizer.

The following experimental, non-limiting examples are given to illustrate the present invention.

#### EXAMPLE 1

##### *Production of pellets*

The polymer compositions of the invention have been obtained in the form of pellets by mixing in the molten state pellets of PCL with powder of proteic hydrolysate, coming from fleshing out or shaving, previously lyophilised, by using a twin screw extruder (model Thermo PRISM TSE 16/28mmTC).

The twin screw extruder allows a very efficient mixing thanks to the interaction between the polymer and the screws, in particular the mixing involves the entire mass fed, which melts quickly and uniformly in a space of very limited length and allows to obtain very high-performance results in short times, thus allowing shorter residence times and lower thermal stress for the materials under processing.

The twin screw extruder used for producing the mixtures, model Thermo PRISM TSE 16/28mmTC, was equipped with a single nozzle for the exit of polymer, from which flowed the extruded product, referred to as "spaghetti", air-cooled up to the cutter with which it was reduced to pellets.

The mixture of polymer and hydrolysate was fed to the extruder system described above through a loading hopper, after cold mixing. Compositions with various ratios between PCL and proteic hydrolysate were thus prepared, in particular

with 10, 20, 30 and 40% by weight of hydrolysate compared to the total weight of the composition, without adding any type of additive.

The speed of the screws was set to values between 30 and 60 revolutions per minute, while the temperature profile has been adapted to the pelletizing process by studying the suitable degree of homogeneity and viscosity of the strand produced by the machine. The extrusion temperatures for the mixtures produced with the thermoplastic polymer matrix in PCL and the charge of proteic hydrolysate are reported in the Table 3 below. In the first part it is important to maintain a sufficiently low temperature, since the proteic hydrolysate, already at 120°C, tends to deteriorate losing the volatile components and compacting, thereby preventing an optimum mixing even with the twin-screw extruder.

The processability for the production of pellets, of the present composition containing 10, 20, 30 and 40% by weight of the organic charge of proteic hydrolysate with respect to the total weight of the composition, was tested. In all cases, the strand produced resulted as continuous, uniform, stable and flexible, index of the good properties of the mixture and of the correct operating conditions adopted.

Table 3. Operative temperatures identified for the production of pellets

TS1(°C)	TS2 (°C)	TS3 (°C)	T <sub>0</sub> (°C)
90	100	120	130

TS1: Temperature of the first section or zone of transport of the solid

TS2: Temperature of second section or melting zone

TS3: Temperature of third section or zone of transport of molten material

T<sub>0</sub>: Temperature of the extrusion head

## EXAMPLE 2

### *Production of thin film*

The technology so called "film blowing", or blown film extrusion, is an industrial process used for the production of polymer thin films biaxially oriented. It is a continuous process for the production of a tubular film in a single operation and allows the adjustment of the circumference and of the thickness of the film by controlling the volume of air blown into the bubble, the parameters of the extrusion process and the speed of draw of the film in the course of the process.

The polymer fed to the equipment through a hopper, is conveyed and melted in an extruder; with a constant speed of flow of the mass, it is forced to enter inside a die of annular form to form a continuous "tube"; an internal pressure and an axial draw concur, instead, to the biaxial extension of the film. Leaving the annular mould, there is the formation of a polymeric tube, while the molten material flowing is cooled by air blowing along the film. During the period in which the polymer is in the fluid state, it will be stretched in two directions. Initially, the polymeric tube formed is inflated by an internal pressure, due to the blowing of air coming from an orifice in the annular mould, slightly higher than the atmospheric pressure. This creates a "bubble".

It should be noted that the air cannot escape from the bubble, since this is clamped by a calender ("nip rolls") upperly positioned. In this way the film is well stretched in the circumferential or in the transverse direction. At the end of the extrusion process, the winding of the film causes the elongation in the longitudinal direction and produces the stretching or "draw down". The solidified film is pulled upward and smoothed into a double layer film by the nip rolls that close the bubble and form a hermetic seal, in the final part.

The properties of the film thus formed are controlled by the molecular orientation and by the stress induced by the crystallisation. An important requirement for this type of processing is the stability of the bubble in order to allow continuous process operations and the production of a film with satisfactory properties.

The equipment chosen for the experimentation is a single-screw extruder Rheomex 19/25 Thermo Scientific QC, equipped with a system of winding of the film produced. Such equipment allows evaluating the processability of the materials for blow extrusion, by faithfully replicating the industrial extrusion process.

It was tested the processability with the "film blowing" technology of the mixtures containing PCL with 10% and 20% by weight of the organic charge of proteic hydrolysate with respect to the total weight of the composition, either by fleshing or from shaving, without addition of any additive. These mixtures were processed without difficulty and a homogeneous and flawless film was obtained, transparent and flexible, having a thickness comprised between 0.02 and 0.06 mm. The operating temperatures employed for the processing of the materials are reported in Table 4.

Table 4. Operative temperature for the blown film extrusion of materials

TS1(°C)	TS2 (°C)	TS3 (°C)
120	120	125

TS1: Temperature of the first section or zone of transport of the solid

TS2: Temperature of the second section or melting zone

TS3: Temperature of the third section or zone of transport of molten material

### EXAMPLE 3

*Characterisation of the products obtained from Examples 1 and 2*

#### *Morphological analysis*

In Figure 1 it is shown the SEM image, i.e. the image obtained by scanning electron microscopy, of the surface (part A) and of the section (part B) of a film sample of pure PCL, obtained by bubble extrusion; the surface and the section of the thermoplastic matrix are homogeneous and free from impurities. Such images are shown herein by way of comparison with the compositions of the invention, demonstrating the fact that the addition of the organic charge of proteic hydrolysate to the PCL does not alter the homogeneity, even when the compositions are used to form thin films.

To demonstrate this, in Figure 2 the SEM images are shown of the surfaces (Part A) and of the section (part B) for a sample of the composition of the invention consisting of PCL with 20% by weight of proteic hydrolysate from fleshing with respect to total weight of the composition, produced in the form of thin films as described above in Example 2. From these images it can be seen how both the surface and the section of the film are homogeneous and show a good incorporation of the proteic hydrolysate in the polymer matrix of PCL.

#### *Thermogravimetric analysis*

The thermal stability at high temperatures of the compositions of the present invention was evaluated by thermogravimetric analysis (TGA). A sample of PCL (approx. 50 mg) was placed in a platinum sample holder, subjected to a nitrogen flow (100 mL/min) and heated from room temperature to a temperature of 600°C with a heating rate of 10°C/min. The weight variations of the sample tested (thermogravimetric curves TG) and the related speed (DTG) were continuously

recorded as a function of time and temperature. The same was done with a sample of proteic hydrolysate, and the results of the thermogravimetric analysis of the two samples are illustrated in Figure 3.

As you can see in Figure 3, the proteic hydrolysate, after the initial loss of weight around 100°C due to moisture, shows a first peak around 170°C linked to the loss of the lightest volatile components and a high loss of weight with peak around 300°C. The amplitude of this range of temperature depends on the composition of the proteic hydrolysate, consisting of more or less long peptide chains and of free amino acids. The residual weight at end of the test (27%) is constituted by the residual carbonaceous matrix and by the inorganic salts contained in the hydrolysate. The curve related to the PCL biodegradable polymer matrix shows instead a thermal stability up to 320°C and a single peak for weight loss around 410°C, corresponding to the degradation of the polymer.

The thermogravimetric analyses on the compositions of the invention consisting of polymer matrix of polycaprolactone and hydrolysate are shown in Figure 4. In particular, the compositions in the form of pellets with the PCL with 10% or 20% by weight of hydrolysate were tested, obtained as described above in Example 1.

As can be seen from this figure, the thermal stability of PCL remains practically unchanged even after the addition of the hydrolysate. The weight losses observed in the temperature range below 350°C are in fact attributable to the hydrolysate while the more consistent loss around 400°C is attributable to the thermal degradation of the polymer matrix.

The residue increases with increasing content of hydrolysate, as it is entirely attributable to the hydrolysate.

#### *Evaluation of the tensile mechanical properties*

The standard tensile test allows establishing the strength and stiffness of a material. The instrument used to perform the test with the compositions of the invention was composed of a base on which was placed a fixed clamp and two columns on which flows the bar which supports a second clamp. These clamps are self-locking, i.e. their grip increases with the progress of the deformation by the action of a pneumatic control.

The sample must be aligned with the direction in which the strain is applied so as to avoid rotatory movements that may induce the specimen to scroll. During the test the distance between the clamps is varied and, through a load cell placed between the upper jaw and the guide, it is recorded the effort that the specimen offers in terms of resistance. The software that manages the tool allows adjusting the rate of deformation and the different criteria for the calculation of the mechanical characteristics of the tested material. To perform the test it is necessary to characterize the specimen from the geometrical point of view, because this information is used by the software to normalise the results obtained. A representation of the tensile test and the geometry of the specimen used in the tests is illustrated in Figure 5.

From the tensile test of polymeric materials stress-strain curves are obtained of the type shown in Figure 6, wherein the stress values ( $\sigma$ ) and the strain values ( $\epsilon$ ) are reported as nominal values. The nominal values are defined as follows:

$$\sigma = \frac{P}{A_0}$$

wherein  $P$  is the load and  $A_0$  is the initial section of the unloaded specimen (i.e. of the portion with constant section) and

$$\epsilon = \frac{\Delta L}{L_0}$$

wherein  $\Delta L$  is the variation of length caused by the load and  $L_0$  is the initial length of the useful part of the specimen. The point A in Figure 6 represents the elastic limit. This value indicates the maximum stress that the material can withstand if it is desired that it returns exactly to its original size after unloading. If it is urged over the edge A, the material undergoes a deformation at least partially plastic. For the majority of materials the point A corresponds to the limit of proportionality, defined by the value of the stress for which the graph deviates from a straight line. The proportionality constant between stress and strain (given by the slope of the curve in the part between the origin and the point A) is called the modulus of normal elasticity or Young's modulus ( $E$ ).

The tensile test on specimens in the form of thin films obtained with the compositions of the present invention as described in the Example 2 above, was carried out in compliance with ASTM D882 and ASTM D638M regulations concerning



the methods for testing the tensile properties of thin films. The mechanical analyses have been carried out by using the Instron Model 5564, testing twelve samples for each type of material; the values shown in the Table 5 below were obtained as the arithmetic mean of the valid tests.

The mechanical properties of the specimens were evaluated both in the longitudinal direction and in the transverse direction of the film formation.

Table 5. Results of the mechanical analysis of tensile strength.

Mixture	Longitudinal direction			Transverse direction		
	E (GPa)	$\sigma$ (MPa)	$\varepsilon$ (%)	E (MPa)	$\sigma$ (MPa)	$\varepsilon$ (%)
PCL	0.211	26.1	494.8	0.067	16.1	163.8
PCL+10% HYD from fleshing	0.527	22.2	511.9	1.445	12.3	279.8
PCL+20% HYD from fleshing	0.394	23.5	494.1	0.395	7.1	373.8
PCL+10% HYD from shaving	0.638	12.8	400.3	0.747	16.1	314.1
PCL+20% HYD from shaving	0.303	12.7	489.6	0.768	10.8	196.9
Commercial material	0.062	17.9	132.1	0.153	11.0	152.3

From the results obtained and reported in the table above it can be noted that the values of load and of strain at rupture for the films of the invention are definitely better than those with PCL only, even if they decrease with the increasing content of proteic hydrolysate in the compositions; in this sense, it is noticed that they diminish to a lesser extent with the use of organic charge coming from the residues of fleshing of the skins in the case of the mechanical properties measured in the longitudinal direction, with respect to the specimens with organic charge of proteic hydrolysate coming from shaving.

#### *Biodegradability test in the soil*

In general the biodegradability test determines the amount of carbon dioxide released from the biological decomposition of the organic carbon contained in the

tested specimen, due to the action of a microbial population present in a soil sample, used as solid substrate and inoculum.

Among the available methods, it was chosen the procedure proposed by Chiellini et al. "Biodegradation of thermally-oxidized, fragmented low-density polyethylenes" in *Polymer Degradation and Stability*, Vol. 81, 2003, pp. 341-351. The biodegradability of the samples was evaluated by measuring the CO<sub>2</sub> developed by portions of the films tested, placed on a soil duly selected, positioned in containers kept at room temperature and in the absence of light. To get results with statistical value, the test was performed in triplicate for each sample and the average values were considered. The test was conducted, for a comparison, also on portions of paper, used as a positive control, and only on the soil: as a matter of fact, the paper is a biodegradable material, and it allows verifying that, inside the receptacles, the microorganisms are able to implement the degradative processes and, as the soil contributes to the production of CO<sub>2</sub>, being an excellent substrate for the microorganisms, it is necessary to quantify this carbon dioxide in order to calculate then by difference the amount of CO<sub>2</sub> actually produced by the tested samples.

Figure 7 shows a scheme of the system for the evaluation of the biodegradability of the materials produced. The sample is placed in contact with the soil placed in a sealed flask. Inside of a test tube, perforated in the upper part, it is contained a solution of KOH; in this way the CO<sub>2</sub> developed by biodegradation processes reacts with the potassium hydroxide and the subsequent titration to determine the residual KOH allows to quantify the carbon dioxide produced. Titrations are repeated at precise time frames taking into account the estimated daily production of CO<sub>2</sub> and of the amount of O<sub>2</sub> inside the container.

The biodegradability in the soil was then evaluated for the films containing 10% and 20% by weight of proteic hydrolysate in mixture with PCL prepared as described above in Example 2.

Figure 8 shows the results obtained in about five months of experiments, in terms of cumulative production of CO<sub>2</sub> (expressed in mg) over time. The trend of the values for the paper biodegradation is indicative of the presence, in the system used, of appropriate conditions able to ensure the development of microorganisms. Moreover it

is possible to note that the mixtures containing HYD from fleshing and 20% of HYD from shaving exhibit a greater tendency to be degraded, even higher than that of the paper and of the commercial material known as Mater-Bi<sup>®</sup>, Novamont.

From the amount of CO<sub>2</sub> produced by the samples it was then possible to derive a biodegradability index based on the amount of carbon dioxide that the samples could produce in theory, calculated on the basis of the weight of the samples and of the content of organic carbon in them. The values of the biodegradability index of the tested samples, reached in approximately five months of the trial, are shown in the Table 6 below. The paper has reached an index close to 30%. The films obtained with the compositions of the invention have a biodegradability index fairly high, comparable to the value obtained for the paper and higher than that of the commercial material.

Table 6. Biodegradability index of the present compositions

Sample	Biodegradability index (%)
PCL	32.2
10% HYD from fleshing	69.5
20% HYD from fleshing	34.5
10% HYD from shaving	28.2
20% HYD from shaving	28.0
MaterBi <sup>®</sup>	12.5
Paper	29.0

From the experimental data illustrated above it clearly emerges that the use of proteic hydrolysate in mixture with polycaprolactone makes possible the processability by hot extrusion, also obtaining a fully biodegradable material, having good mechanical and thermal properties, properties that are considerably improved compared to those of the polymer matrix of PCL alone. This also allows the advantageous disposal of a waste material of the leather tanning industry, such as the proteic hydrolysate obtained from fleshing out or from shaving of cowhides to be submitted to tanning.

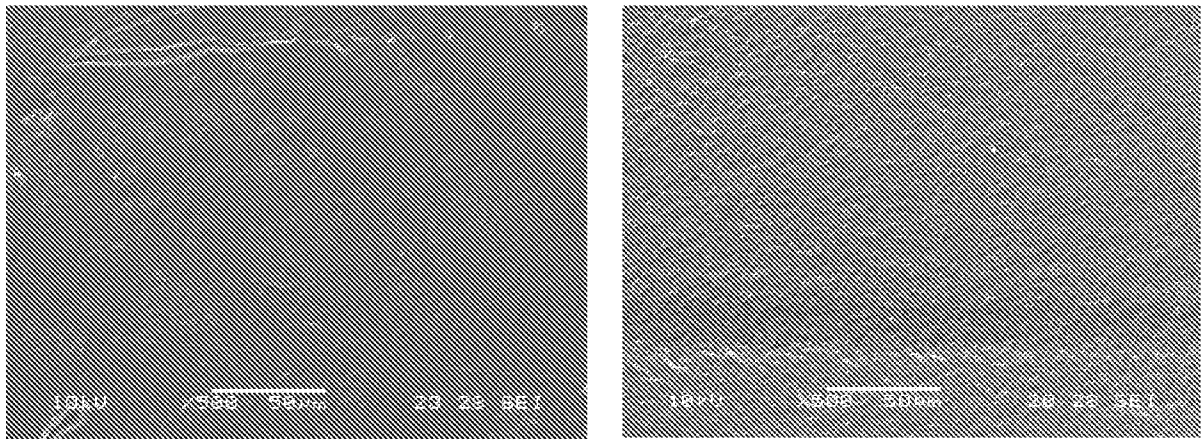
\*\*\*\*\*

The present invention was herein described with reference to a preferred embodiment. It is to be understood that there may be other embodiments afferent to the same inventive core, as defined by the scope of protection of the claims set out below.

CLAIMS

1. A thermoplastic, biodegradable, polymer composition obtainable from a mixture of molten polycaprolactone and of at least a proteic hydrolysate in powder form having average molecular weight lower than 10,000 g/mol.
2. The composition according to claim 1, wherein said proteic hydrolysate has average molecular weight comprised between 1,000 and 5,000 g/mol.
3. The composition according to any of the preceding claims, wherein said proteic hydrolysate is substantially water-free.
4. The composition according to any of the preceding claims, wherein said proteic hydrolysate is a natural, organic product obtained by hydrolysis, followed by degreasing and drying, of a proteic substrate of vegetal or animal origin.
5. The composition according to claim 4, wherein said proteic substrate of vegetal or animal origin is selected from animal fleshing coming from fleshing out of animal pelts, residue of shaving leather, whey, and soy.
6. The composition according to claim 5, wherein said proteic substrate of vegetal or animal origin is animal fleshing coming from fleshing out of animal pelts.
7. The composition according to any of the preceding claims, wherein the percentage of said proteic hydrolysate is comprised between 5 and 60% by weight with respect to the total weight of the composition.
8. The composition according to claim 7, wherein the percentage of said proteic hydrolysate is comprised between 10 and 30% by weight with respect to the total weight of the composition.
9. A process for the preparation of the thermoplastic, biodegradable, polymer composition as defined in claims from 1 to 8, comprising the hot extrusion of polycaprolactone and of at least a proteic hydrolysate in powder form having average molecular weight lower than 10,000 g/mol at a starting temperature, at the entrance of the extruder, which ranges between the melting temperature of said polycaprolactone and the degradation temperature of said proteic hydrolysate.
10. The process according to claim 9, wherein said polycaprolactone and said proteic hydrolysate are mixed before entering the extruder and they are subjected to extrusion by means of a twin-screw extruder.

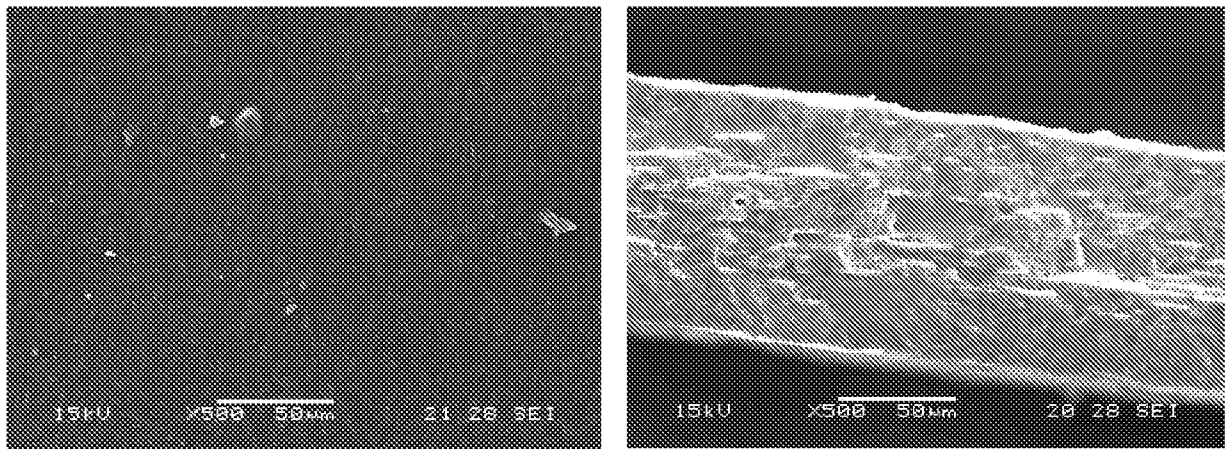
11. A solid article obtainable by printing or by film technology of the polymer composition as defined in claims from 1 to 8.
12. Use of the polymer composition as defined in claims from 1 to 8, for the manufacture of solid articles by printing or by film technology.
13. The use according to claim 12, for the manufacture of thin films, packaging films, tubes, wires, packets, bags and bottles.



A

B

FIG. 1



A

B

FIG. 2

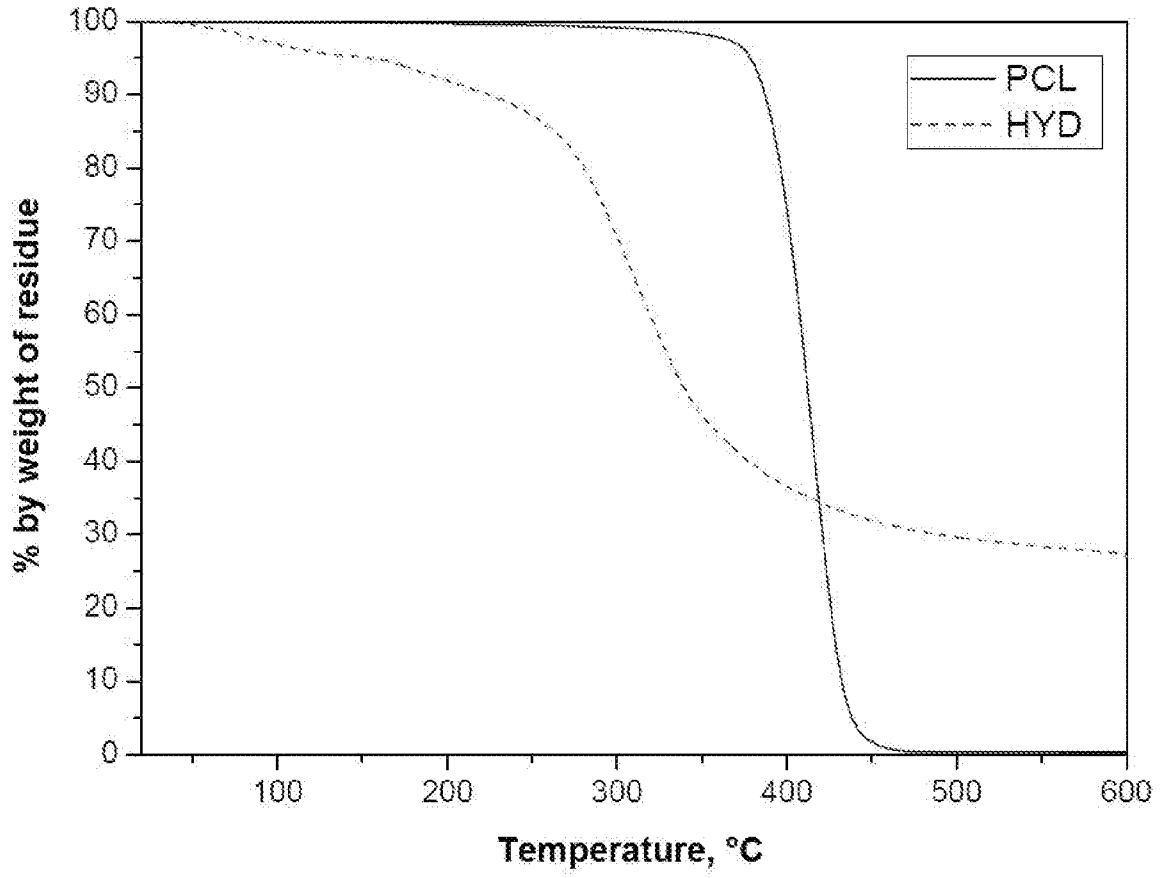


FIG. 3

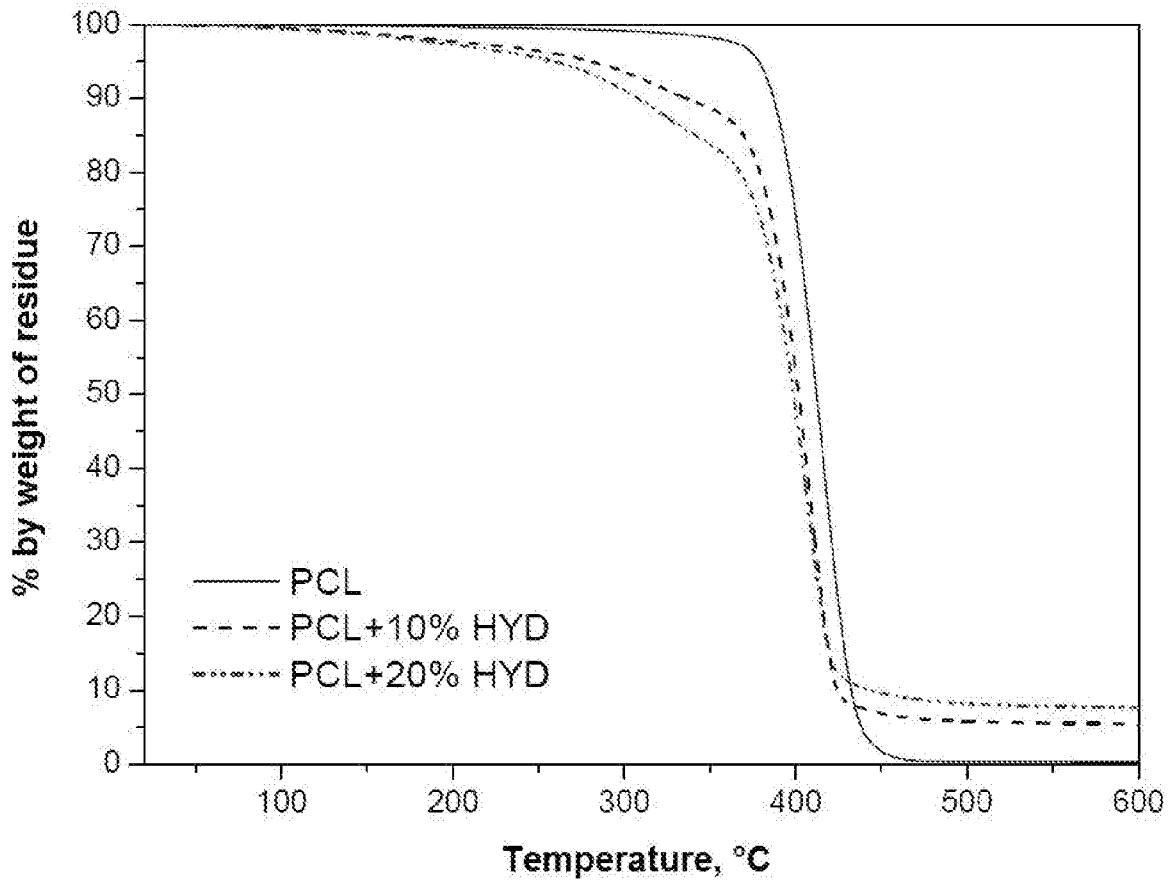


FIG. 4



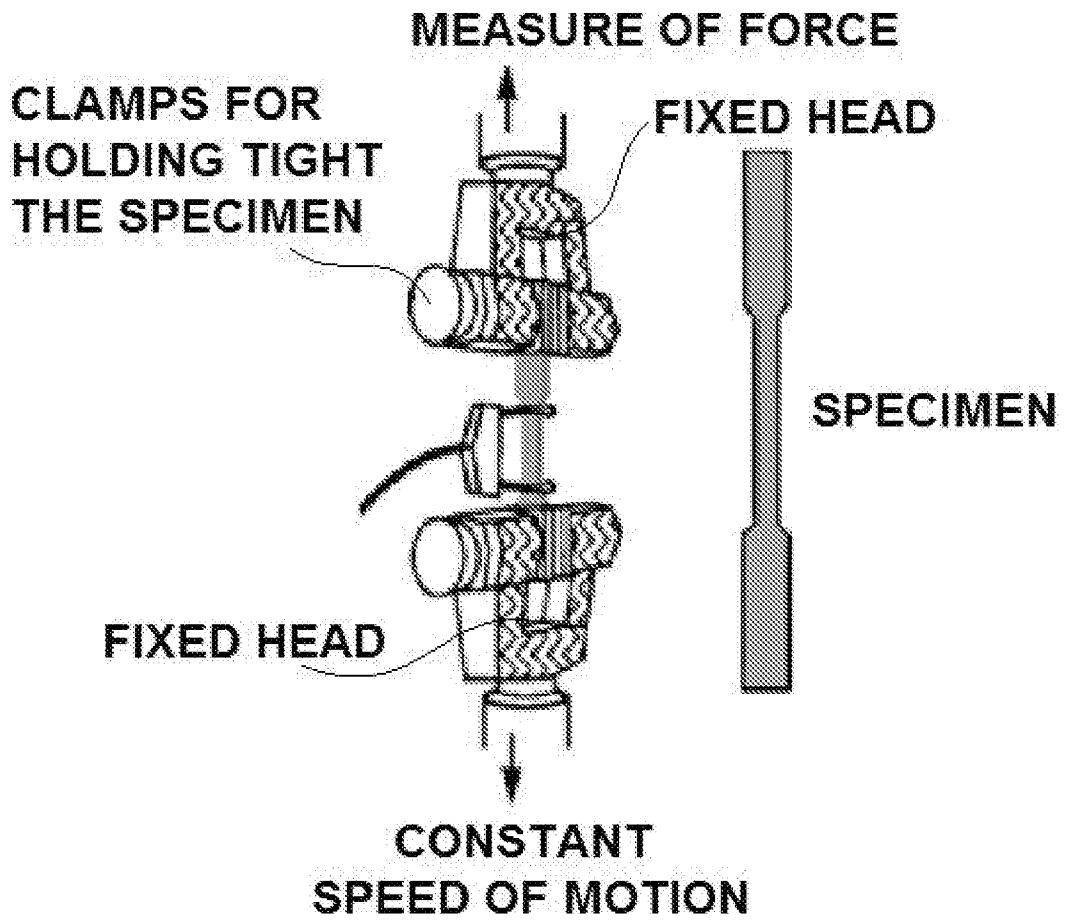


FIG. 5

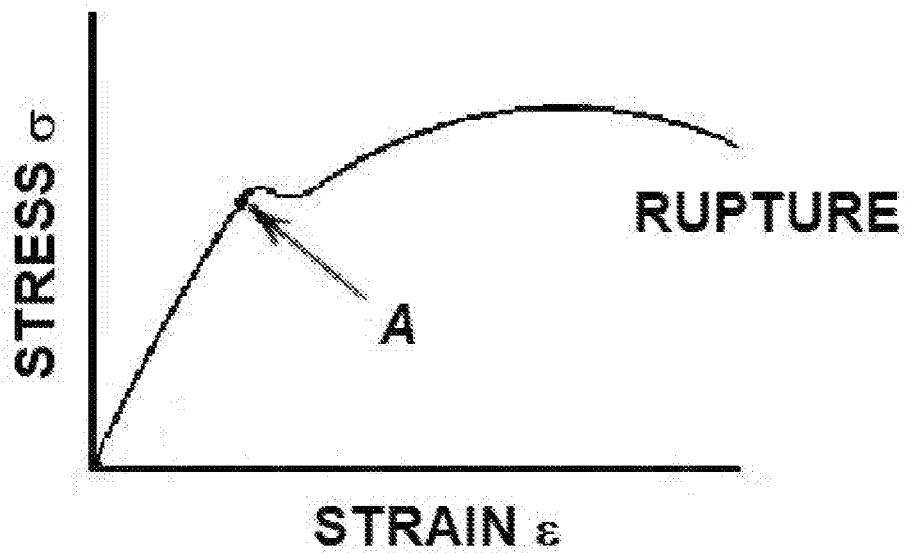


FIG. 6

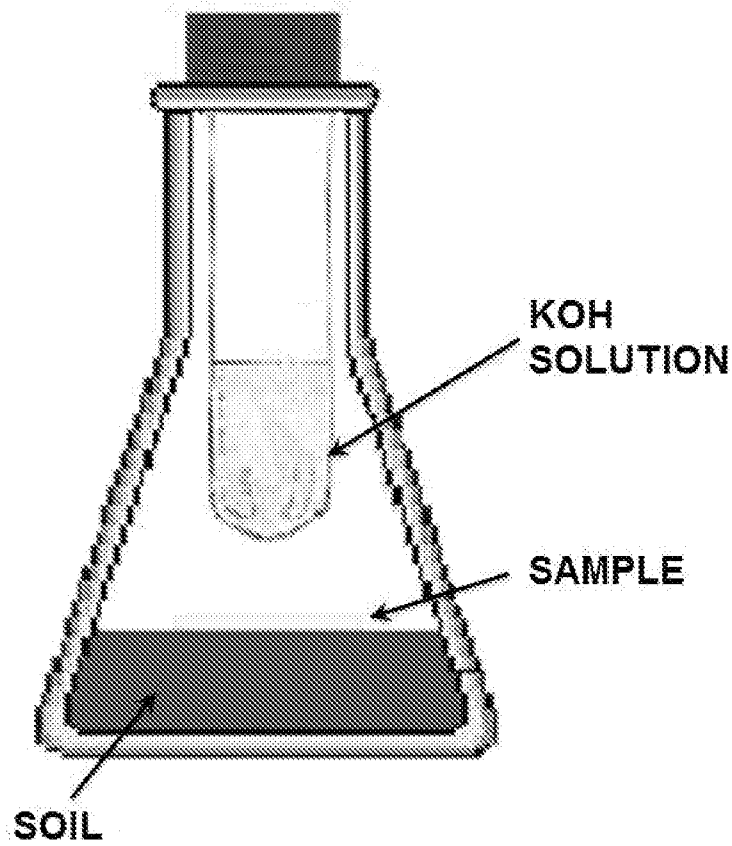


FIG. 7

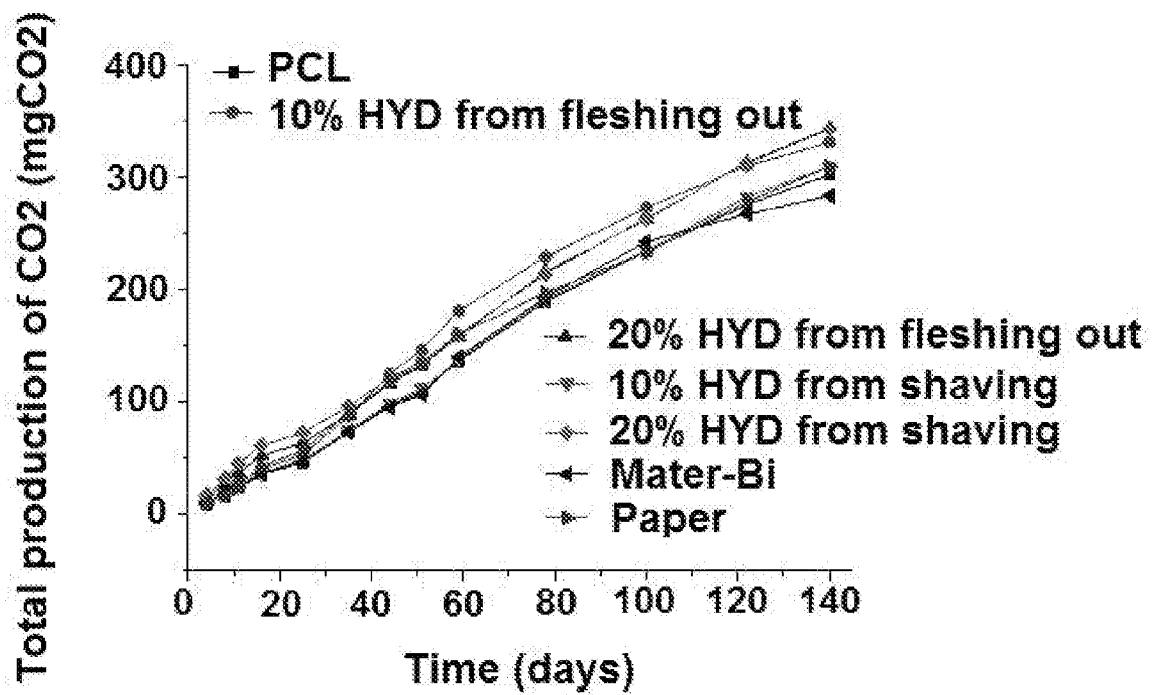


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2015/056660

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. C08J5/18 C08L67/04 C08L89/00 C08L89/04 C08L89/06  
 C08J11/10 B29C67/00  
 ADD.  
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
 Minimum documentation searched (classification system followed by classification symbols)  
 C08J C08L B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/06785 A1 (SILBIGER JAKOB [CH]) 19 February 1998 (1998-02-19)	1-11
Y	examples 5, 6, 7g	12,13
X	WO 2007/104322 A1 (BECKER & CO NATURINWERK [DE]; ETAYO GARRALDA VICENTE [ES]; KOTLARSKI O) 20 September 2007 (2007-09-20)	1-11
Y	claim 17 page 11, lines 17-22 page 12, lines 3-9 page 12, line 28 - page 13, line 4	12,13
X	US 6 632 925 B1 (ZHANG JINWEN [US] ET AL) 14 October 2003 (2003-10-14)	1-5,7-11
Y	column 12, line 30 - column 13, line 28 column 8, line 64 - column 9, line 9	12,13
	----- -/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>
---	---

Date of the actual completion of the international search  20 November 2015	Date of mailing of the international search report  30/11/2015
---	--

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Gerber, Myriam
--	--

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2015/056660

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	D. AITHANI ET AL.: "Value-Added New Materials from Byproduct of Corn Based Ethanol Industries: Blends of Plasticized Corn Gluten Meal and Poly(epsilon-caprolactone)", INDUSTRIAL AND ENGINEERING CHEMISTRY RESEARCH, vol. 45, 27 July 2006 (2006-07-27), pages 6147-6152, XP002739084, *"2.2. Preparation of Blends" on page 6148*; abstract	1
X	----- WO 2012/058278 A2 (GILLER EUGENE [US]) 3 May 2012 (2012-05-03) paragraphs [0008], [0042]; claim 11 -----	12,13

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2015/056660

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 9806785	A1	19-02-1998	AT 209669 T	15-12-2001
			CA 2263290 A1	19-02-1998
			DE 59705574 D1	10-01-2002
			DK 0918825 T3	25-03-2002
			EP 0918825 A1	02-06-1999
			ES 2168652 T3	16-06-2002
			US 6284838 B1	04-09-2001
			WO 9806785 A1	19-02-1998
-----				
WO 2007104322	A1	20-09-2007	AR 059832 A1	30-04-2008
			AT 455153 T	15-01-2010
			AU 2006339903 A1	20-09-2007
			BR PI0621510 A2	13-12-2011
			CL 2007000665 A1	18-01-2008
			CN 101400738 A	01-04-2009
			CY 1109990 T1	10-09-2014
			DK 2004753 T3	25-05-2010
			EP 2004753 A1	24-12-2008
			ES 2340606 T3	07-06-2010
			JP 5225868 B2	03-07-2013
			JP 2009529591 A	20-08-2009
			NZ 571108 A	29-07-2011
			PE 01202008 A1	19-03-2008
			PT 2004753 E	10-05-2010
			RU 2008140320 A	20-04-2010
			SI 2004753 T1	30-06-2010
			US 2009226557 A1	10-09-2009
WO 2007104322 A1	20-09-2007			
-----				
US 6632925	B1	14-10-2003	NONE	
-----				
WO 2012058278	A2	03-05-2012	CN 103180125 A	26-06-2013
			EP 2632696 A2	04-09-2013
			JP 2013540629 A	07-11-2013
			KR 20130079539 A	10-07-2013
			US 2014162033 A1	12-06-2014
			WO 2012058278 A2	03-05-2012
-----				