US 20100098928A1

(19) **United States**

(12) **Patent Application Publication**

Britton et al.

(10) **Pub. No.: US 2010/0098928 A1**

(43) **Pub. Date: Apr. 22, 2010**

(54) POLYMER MIXTURE, A METHOD FOR PRODUCING AN EXTRUDED PRODUCT, METHODS FOR PRODUCING A STARTING MATERIAL FOR A FOAMED MOULDED PRODUCT AND METHODS FOR PRODUCING A FOAMED MOULDED PRODUCT, THE PRODUCTS OBTAINED WITH SAID METHODS AND APPLICATIONS THEREOF

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(21) Appl. No.: **12/595,926**

(22) PCT Filed: **Apr. 21, 2008**

(86) PCT No.: **PCT/NL2008/000108**

§ 371 (c)(1),
(2), (4) Date: **Dec. 9, 2009**

(30) **Foreign Application Priority Data**

Apr. 19, 2007 (NL) 1033719

Publication Classification

(51) **Int. Cl.**

B32B 3/26	(2006.01)
B29C 47/00	(2006.01)
C08L 67/00	(2006.01)

(52) **U.S. Cl.** **428/220**; 264/211; 264/299; 428/98; 525/415

(57) ABSTRACT

The present invention relates to a polymer mixture comprising polylactic acid. The invention furthermore relates to a method for producing an extruded product and the extruded product obtained therewith. The present invention furthermore relates to methods for producing a starting material for a foamed moulded product and the starting material obtained therewith. The present invention moreover relates to methods for producing a foamed moulded product and the moulded product obtained therewith. The present invention also relates to applications of these products.

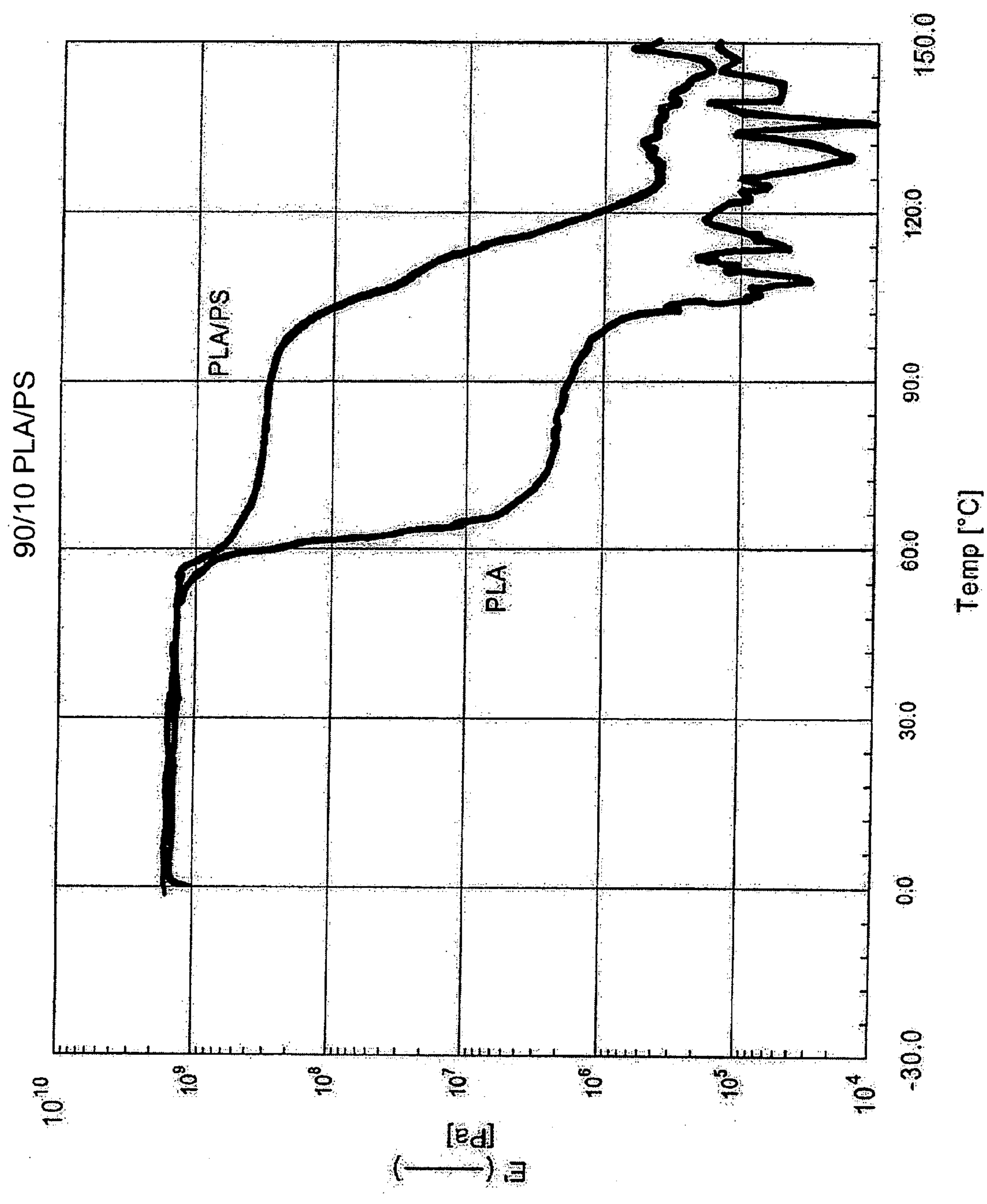
90/10 PLA/PS
PLA/PS
PLA
E' (——)
[Pa]
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
-30.0
0.0
30.0
60.0
90.0
120.0
150.0
Temp [°C]

Fig. 1

POLYMER MIXTURE, A METHOD FOR PRODUCING AN EXTRUDED PRODUCT, METHODS FOR PRODUCING A STARTING MATERIAL FOR A FOAMED MOULDED PRODUCT AND METHODS FOR PRODUCING A FOAMED MOULDED PRODUCT, THE PRODUCTS OBTAINED WITH SAID METHODS AND APPLICATIONS THEREOF

[0001] The present invention relates to a polymer mixture comprising polylactic acid. The invention also relates to a method for producing an extruded product and the extruded product thus obtained. The present invention furthermore relates to methods for producing a starting material for a foamed moulded product and the starting material thus obtained. The present invention moreover relates to methods for producing a foamed moulded product and the moulded product thus obtained. The present invention also relates to applications of these products.

[0002] Over the past years interest in polylactic acid, or PLA, as a renewable biologically degradable material for a broad range of applications has grown tremendously. In developing a foamed moulded product based on an expanded or foamed polylactic acid attention is now also being paid to recycling in connection with the constantly increasing volumes of waste and the growing concern for the environment and recycling issues. In the literature it is often claimed that polylactic acid is not recyclable, and causes problems in particular if it is involved in the process chains of other polymers in the form of contamination.

[0003] During their extensive research to find out whether contamination of polylactic acid in other polymers could cause recycling problems, the present inventors arrived at the present invention.

[0004] One of the objects of the present invention is to provide a polymer mixture comprising polylactic acid, which polymer mixture has improved processability and temperature resistance.

[0005] Another object of the present invention is to provide an extruded product formed from the polymer mixture with improved properties, such as ductility and impact strength.

[0006] Another object of the present invention is moreover to provide methods for producing extruded products and foamed moulded products using a polymer mixture comprising polylactic acid.

[0007] One or more of the above objects is accomplished by a polymer mixture comprising polylactic acid and a polymer having a glass transition temperature above 60° C.

[0008] The term "a polymer" as used herein is understood to mean a polymer other than polylactic acid. It is of course also possible for more than one other polymers to be contained in the present polymer composition besides polylactic acid. The present invention thus relates to a polymer mixture comprising at least two polymers, viz. polylactic acid and another polymer having a glass transition temperature above 60° C.

[0009] The present invention will be elucidated below via reference to FIG. **1**. FIG. **1** is a diagram showing the modulus of elasticity of polylactic acid alone and a present polymer mixture.

[0010] Polylactic acid is a collective term used for polymers based on polylactic acid monomers, in which the structure of the polylactic acid may vary according to the composition, from completely amorphous to semi-crystalline or crystalline. Polylactic acid can be produced from milk products or for example maize.

[0011] Lactic acid is the monomer of which polylactic acid is composed, and this monomer occurs in two stereoisomers, viz. L-lactic acid and D-lactic acid. So polylactic acid contains a certain proportion of L-lactic-acid monomers and a certain proportion of D-lactic-acid monomers. The ratio between the L- and D-lactic-acid monomers in polylactic acid determines its properties. This is also known as a D value or D-content, which represents the percentage of D-lactic-acid monomers in the polylactic acid. Polylactic acid that is at present commercially available has an L:D ratio of between 100:0 and 75:25; in other words, a D-content of between 0 and 25%, or between 0 and 0.25. When polylactic acid contains more than approximately 12% D-lactic acid it can no longer crystallise, and is hence completely amorphous. When the D-content is approximately 5%, it is referred to as semi-crystalline polylactic acid. The crystallinity of the polylactic acid can be determined by means of differential scanning calorimetry (DSC). The term "semi-crystalline" is understood to mean that the polymer is capable of crystallising and also melting. Thus it can be stated that the lower the D-content, the higher the crystallinity of the polylactic acid will be. The D-content is usually determined by using a known method, such as a so-called R-lactate determination using gas-liquid chromatography (GLC) after complete hydrolysis of the polymer. Another standard method is determination via optical rotation (measured in chloroform using a Jasco DIP-140 polarimeter at a wavelength of 589 nm).

[0012] In producing moulded products based on particulate expandable polylactic acid it is of the greatest importance that the fusion between the individual particles is sufficient to obtain a product that will not disintegrate into the individual particles under a slight load. The process conditions are also very important. In view of the limited thermal stability of polylactic acid in comparison with petrochemical polymers it is of the greatest importance that good fusion is realised even under mild process conditions.

[0013] The D-content of the polylactic acid according to the present invention preferably ranges between 0 and 15%, in particular between 1 and 10%, more in particular between 2 and 5%, especially between 3 and 4.7%. The D-content is in particular less than 5 wt. %

[0014] The ratio between amorphous and (semi-)crystalline polylactic acid according to the present invention preferably ranges between 0 and 90% amorphous, more preferably between 10 and 75%, in particular between 30 and 60%. The quantity of (semi-)crystalline polylactic acid according to the present invention preferably ranges between 10 and 100%, more preferably between 25 and 90%,in particular between 40 and 70%.

[0015] The presence of a polymer having a glass transition temperature above 60° C. in the polymer mixture will ensure that the modulus of elasticity of the polymer mixture will decrease less at a temperature above the glass temperature of polylactic acid. This is evident in FIG. **1**, in which the bottom curve (PLA) represents polylactic acid alone (not according to the invention) and the top curve (PS/PLA) represents a polymer mixture according to the invention containing 10% polystyrene (PS) and 90% polylactic acid (PLA). As a result of this, the polymer mixture according to the present invention has a better processability and temperature resistance than polylactic acid alone. Such properties make it possible to use the polymer mixture in applications for which polylactic acid alone is unsuitable. A biologically degradable polyester such as Ecoflex, for example type ECOFLEX* F BX 7011 produced by BASF, has no clear Tg, but it does have a good high-temperature resistance, expressed as the heat deflection temperature HDT/A, of 80° C., measured according to ASTM-648. This is certainly also effective with respect to improving the intended improvement with respect to temperature resistance.

[0016] Amorphous polylactic acid has a glass transition temperature (Tg) of about 55° C. Such a low glass transition temperature leads to material having a highly restricted thermal stability. The thermal stability of semi-crystalline polylactic acid is better, as it has a higher glass transition temperature, viz. 90° C. (the height of the temperature is a function of the crystallinity). It is therefore preferable to use a mixture of amorphous and semi-crystalline polylactic acid as the polylactic acid part of the polymer mixture. The type of polylactic acid selected determines the hardness and thermal stability of the foamed moulded product ultimately obtained.

[0017] Preferably at least 70 wt. %, in particular at least 80 wt. %, more in particular at least 90 wt. %, and especially at least 95 wt. % of the polymer mixture consists of the combination of polylactic acid and the polymer having a glass transition temperature above 60° C. This weight ratio will lead to in particular the favourable properties mentioned in this description. The remaining part of the polymer mixture consists of other components, for example other polymers and processing aids.

[0018] In a preferred embodiment the polymer's glass transition temperature is higher than 95° C. Such a polymer mixture according to the present invention has an even better temperature resistance, as a result of which this polymer mixture can be used in applications at higher temperatures.

[0019] The present invention preferably relates to a polymer mixture for which the polymer—other than polylactic acid—is selected from the group comprising a polyvinylarene, cellulose diacetate and a combination thereof. Such polymers have a glass transition temperature that is higher than that of polylactic acid and hence increase the temperature resistance, which greatly improves the processability of polylactic acid. These polymers are also preferable because they can be reasonably easily obtained and are economically favourable.

[0020] In particular, the present invention relates to a polymer mixture as described above in which the polymer is polystyrene, expandable polystyrene or a combination hereof. Such polystyrene polymers have a high glass transition temperature, viz. one which, depending on the beater, may be 95-102° C. The Tg of EPS is 8° C. lower, depending on the percentage of pentane used as blowing agent per vol. % pentane, but the disappearance of this blowing agent makes it possible to realise an end situation with a Tg of 98° C. The Tg must therefore be measured after controlled removal of pentane.

[0021] The addition of such a polystyrene polymer to polylactic acid gives the polymer mixture better temperature resistance, which greatly improves the processability of polylactic acid. The term "expandable polystyrene" is understood to mean polystyrene particles that have been impregnated with a blowing agent.

[0022] In one embodiment of the present invention, the polylactic acid is preferably contained in the polymer mixture described above in an amount of between 0.1 and 35 wt. % relative to the combined weight of the polylactic acid and the polymer, preferably 2-25 wt. %, in particular 5-20 wt. %. Without wishing to be bound to any theory, the present inventors suspect that the polymer forms a continuous phase in which the polylactic acid is dispersed.

[0023] A first preferred embodiment of the present invention relates to extruded particles, also referred to as beads, with a high concentration of the polymer and a low concentration of polylactic acid. Such particles are produced by extruding the present polymer mixture or by extruding a mixture of polylactic acid particles and particles of the polymer to obtain particles of the present polymer mixture. Such particles can by means of optional prefoaming methods, optional coating methods and foaming methods be converted into foamed moulded products having a better ductility than foamed moulded products based on the polymer alone (see example 1 of the examples).

[0024] In a different embodiment the polymer is preferably contained in the polymer mixture described above in an amount of 0.1-35 wt. % relative to the total polymer mixture, in particular 2-25 wt. %, and above all 5-20 wt. %. Without wishing to be bound to any theory, the present inventors suspect that the polylactic acid forms a continuous phase in which the polymer is dispersed.

[0025] A second preferred embodiment of the present invention hence refers to extruded particles or beads with a high concentration of polylactic acid and a low concentration of polymer. Such particles are produced by extruding the present polymer mixture or by extruding a mixture of particles of polylactic acid and particles of the polymer to obtain particles of the present polymer mixture. Such particles can by means of optional prefoaming methods, optional coating methods and foaming methods be converted into foamed moulded products with better impact strength and temperature resistance than foamed moulded products based on the polymer alone. The polymer is preferably polystyrene (see example 2 of the examples). Because such foamed moulded products are no longer affected by the disadvantages of the low glass transition temperature of polylactic acid they have a broader field of application. Such foamed moulded products also have a broader field of application because they have a higher temperature resistance, which makes them suitable for use in the production of objects in which heat is used.

[0026] A third preferred embodiment of the present invention relates to an extruded film having a high concentration of polylactic acid and a low concentration of the polymer. Such films are produced by extruding the present polymer mixture or by extruding a mixture of particles of polylactic acid and particles of the polymer to obtain a film of the present polymer mixture. Such films can by means of reduction methods (for example slicing or cutting) be converted into strips that can be used to reinforce foamed moulded products preferably based on polystyrene, which strips exhibit improved impact strength, temperature resistance and adhesion to foamed moulded products (see example 3 of the examples).

[0027] A method for the production of such moulded products with reinforcing strips is known from NL 1022503. Reinforcing strips made of polylactic acid alone are not suitable for such applications because of their low temperature resistance. Because of this low temperature resistance polylactic acid reinforcing strips are deformed by the high temperature during the expansion process. Reinforcing strips made of the polymer mixture according to the present invention have a higher temperature resistance. These reinforcing strips can be used at higher temperatures that are used for example in expansion to obtain plastic foamed material.

[0028] Another favourable property, besides the high temperature resistance, of reinforcing strips made of a polymer mixture according to the present invention is that, contrary to reinforcing strips made of polyvinyl arene alone, they exhibit very good adhesion to expanded polyvinyl arenes. It is hence preferable for reinforcing strips according to the present invention to be used in foamed moulded products made of polyvinyl arenes. The present inventor found particularly good adhesion between a reinforcing element according to the present invention and foamed moulded products made of polystyrene. It is therefore more preferable for reinforcing strips according to the present invention to be used in foamed moulded products made of polystyrene.

[0029] The present films can by means of forming methods known per se (for example moulding and thermoforming) be converted into moulded products to be used for a large number of applications, for example packaging material for foodstuffs, other packaging materials or plant pots.

[0030] The addition of a small amount of the polymer to polylactic acid thus greatly improves the processability of the polymer mixture both for extrusion of for example films and particles and for the production of moulded products from the extruded particles.

[0031] In a preferred embodiment of the present invention, the polymer mixture contains a chain extender to increase the melt strength of the polylactic acid, which chain extender can for example be selected from the group consisting of polyepoxides and diepoxides (Joncryl 4368C supplied by BASF), diisocyanates, oxazines and oxazolines, cyclic dianhydrides (for example PMDA) and the like. Zinc stearate can optionally be added as a catalyst.

[0032] In another embodiment of the present invention, the polymer mixture also contains a nucleating agent or foam-nucleating agent to improve the foam quality, preferably selected from the group consisting of polyolefine wax, such as polyethylene wax or polypropylene wax (for example Polywax P3000 supplied by Baker Hughes Corp.), or talcum or nano clay.

[0033] In yet another preferred embodiment of the present invention, the polylactic acid also contains an (external) lubricant, for example selected from the group consisting of zinc stearate or other metal salts of stearates. If zinc stearate is selected, it can also act as a catalyst of the chain extender.

[0034] The particle size of the particulate extruded product preferably ranges between 0.5 mm and 5 mm. A particle size of less than 0.5 mm is very difficult to obtain without loss of the desired properties, and a particle size of more than 5 mm leads to less advantageous foam properties on account of the reduced ratio between the area and volume of the particle. The particle size in particular ranges between 0.5 mm and 1.5 mm, with a view to obtaining optimum foam properties.

[0035] The bulk density (tapped) of non-prefoamed particles according to the present invention preferably ranges between 700 g/l and 1000 g/l.

[0036] The density of prefoamed particles preferably ranges between 10 g/l and 100 g/l, in particular between 15 g/l and 60 g/l. The present inventors have found that this leads to good results in particular in the forming of the foamed moulded product that is ultimately obtained. They have also found that this leads to an optimum result in the use of the coating and the fusion improved for that purpose.

[0037] It is also possible for the particles to be coated, as described in NL1033719. It is preferable for the coating to be present in an amount of between 0.5 wt. % and 15 wt. %, in particular between 2 and 10 wt. % based on the weight of the particulate polylactic acid.

[0038] The coating is preferably selected from the group consisting of polyvinyl acetate, polyvinyl-acetate-based polymer, polyvinyl alcohol, polycaprolactone, polyester, polyester amide, protein-based material, polysaccharide, natural wax or grease and acrylate or one or more combinations thereof. The coating may also be amorphous polylactic acid or a combination hereof with the other coatings.

[0039] Examples of a coating based on polyvinyl acetate and polyvinyl-acetate-based polymers are Vinnex and Vinnapas polymers supplied by Wacker Chemie. The coating based on protein-based material is preferably selected from the group consisting of gelatine, collagen, casein and soy protein and one or more combinations thereof. The coating based on polysaccharide is preferably selected from the group consisting of cellulose, cellulose derivative, starch, starch derivative, chitosan, alginate, pectin, carrageenan, Arabic gum and gellan gum. The coating based on natural wax or grease is preferably selected from the group consisting of beeswax, carnauba wax, candelilla wax, paraffin wax, polyethylene wax, fatty acid, monoglyceride and shellac. The coating may optionally also contain a plasticiser preferably selected from the group comprising glycerol and urea. The plasticiser may also be sorbitol.

[0040] The present invention also relates to a method for producing an extruded product according to the present invention comprising the supplying of the polymer mixture according to the present invention and the subsequent extrusion of the polymer mixture obtained in order to obtain an extruded product.

[0041] The extruded product according to the present invention has a good modulus of elasticity, impact strength and temperature resistance.

[0042] Further advantages have already been mentioned above. All the embodiments mentioned above with respect to the polymer mixture and the products also apply to the methods and vice versa.

[0043] The present invention also relates to the use of the extruded product in the form of a film according to the present invention, as reinforcing strips for foamed moulded products, which preferably consist of polystyrene. In particular, this extruded product consists of polylactic acid to which a small amount of the polymer—other than polylactic acid—has been added. Thanks to the improved temperature resistance of the extruded product according to the present invention relative to polylactic acid alone, such reinforcing strips may be present during the expansion of the expandable polystyrene without the risk of deformation. Reinforcing strips according to the present invention are preferably used in polystyrene foamed moulded products because they adhere better to polystyrene granules. Such an application results in a foamed moulded product that is more capable of absorbing tensile forces without breaking.

[0044] The present invention also relates to methods for producing a starting material for a foamed moulded product and methods for producing a foamed moulded product.

[0045] A preferred embodiment of the present invention concerns methods for producing the starting material for a foamed moulded product. In a first embodiment, this method is characterised in that it comprises the following steps:

[0046] i) supplying a polymer mixture according to the present invention to an extruder,

[0047] ii) extruding the mixture supplied in i), and

[0048] iii) reducing the material obtained in step ii) to particles.

[0049] In a second embodiment this method is characterised in that it comprises the following steps:

[0050] a) supplying polylactic acid particles, particles of the polymer and a blowing agent to an extruder,

[0051] b) extruding the mixture supplied in a), and

[0052] c) reducing the material obtained in step b) to particles of a polymer mixture according to the present invention.

[0053] It is particularly desirable to carry out these methods using a twin-screw extruder, as the present inventors assume that this will ensure optimum mixing of the starting materials supplied to the extruder. Although it is stated that in step a) only three components and in step i) only one component are (is) supplied to the extruder, it will be clear that the presence of the usual processing aids, for example flame retardants, agents enhancing the insulating value, flow agents, release agents, anticoagulants and the like, is not excluded, which processing aids may or may not already be mixed with the other starting materials. It is also possible for a blowing agent to be added in step i) or step ii).

[0054] In the second embodiment it is preferable for the further processing of the particles thus reduced to comprise a prefoaming step (step 1), in which an amount of steam is in an expansion vessel passed through a layer of the particles thus obtained, causing the blowing agent contained in the particles, preferably pentane, to evaporate, after which the foaming of the particles takes place. After a storage time of about 4-48 hours, which is also referred to as curing (step 2), the granule thus prefoamed is introduced into a mould, in which the granules are further expanded under the influence of steam. During step 2) and step 3) a blowing agent may be added if insufficient blowing agent, or none at all, was added during the process for obtaining a starting material, or if prefoaming has taken place and there is insufficient remaining blowing agent. The mould used in the first and second embodiments has small openings via which the blowing agent still present can escape during the expansion (step 2 or step 3), while the granules fuse into the desired shape. The foamed parts thus obtained have good ductility and good temperature resistance. The size of the moulded product thus foamed is in principle not restricted, it being possible to produce blocks for the building industry and meat trays, fish containers or packaging units.

[0055] Examples of blowing agents that may be used are CO_2, MTBE, nitrogen, air, (iso)pentane, propane, butane and the like or one or more combinations hereof. If prefoaming is carried out, the blowing agent can for that purpose be injected into the polylactic acid melt before or during step b) or the particles can be impregnated with blowing agent afterwards.

[0056] Further embodiments are given in the claims.

[0057] The present invention also relates to methods for producing foamed moulded products.

[0058] A first embodiment of these methods is characterised in that the method comprises the following steps:

[0059] I) providing a starting material for a foamed moulded product obtained in one of the methods for the production of a starting material;

[0060] II) bringing the material obtained in step I) under specific temperature and pressure conditions so that a foamed moulded product is obtained.

[0061] A second embodiment of this method is characterised in that it comprises the following steps:

[0062] 1) prefoaming the particles obtained in one of the methods for the production of a starting material;

[0063] 2) curing the prefoamed particles obtained in step 1), and

[0064] 3) bringing the material obtained in step 2) under specific temperature and pressure conditions so that a foamed moulded product is obtained.

[0065] The present invention will now be further elucidated with reference to a number of non-limiting examples.

EXAMPLES

Example 1

[0066] Expandable polystyrene particles (EPS particles) containing 5.5% blowing agent and having a size of between 1.6 and 2.4 mm were mixed with extruded polylactic acid particles (PLA particles) of type 2002D and extruded. Additional blowing agent was added during the extrusion because only the EPS particles already contained blowing agent and the PLA particles are supplied without blowing agent. This mixture was subsequently extruded to particles having a particle size of approx. 1.0 mm, with blowing agent being supplied during the extrusion. The usual nucleating agents and chain extenders were also co-extruded to ensure that the foam would have a good cell structure. The employed blowing agent was a mixture of n-pentane and isopentane, in a typical weight ratio of 75/25 or 80/20. The particles were then given a 0.4 wt. % coating of zinc stearate and glycerol monostearate and glycerol tristearate [add type of coating]. The particles obtained were subsequently subjected to so-called prefoaming in a prefoaming device of type Erlenbach K1. Next, the prefoamed particles were moulded into a foamed moulded product at a steam pressure of 1 bar. In the case of 5 wt. % the moulding was successful and in the case of 20 wt. % it was partly successful [explain]. The density at 0.4 bar was determined. The results are shown in Table 1 below. The foamed moulded products exhibited ductile fracture.

TABLE 1

PLA particles (wt. %)	EPS particles (wt. %)	extra blowing agent based on total weight of the particles	net blowing agent based on total weight of the particles	density obtained at 0.4 bar	ductility relative to ductility of polystyrene
5	95	0.50 wt. %	5.7 wt. %	15	improved
20	80	1 wt. %	5.4 wt. %	90	improved

[0067] This example shows that extruded polylactic acid can be successfully processed, contrary to what was known in the state of the art, and that the ductility of polystyrene is improved by mixing in small quantities of polylactic acid.

Example 2

[0068] An extruded product was produced using a mixture of polylactic acid (Zhejiang Hisun Biomaterials type expansion grade PLA: PLA type 1 or NatureWorks 2002 D: PLA type 2) and polystyrene (Synbra Technology) using a twin-screw extruder (Berstorff ZE 40A), which extruded product had a particle size of 1.0-1.2 mm. The particles were then impregnated with 8% CO_2 and subsequently prefoamed in a prefoamer to a certain density (kg/m^3).

[0069] Next, three types of prefoamed particles were coated with 4.9% Vinnex 2501 from Wacker Chemie (coating 1) or 5.0% casein in water (coating 2) and then re-impregnated with CO_2 in a pressure vessel at 10 bar for 10 minutes until a CO_2 concentration of 3.5% was reached. The re-impregnated particles were fed to an industrial production unit for foamed moulded products in which the particles fused with the aid of steam. This led to the production of a plate-shaped material measuring 5×5×5 cm. The results are shown in Table 2.

TABLE 2

PLA wt. %	PLA type	PS wt. %	Density (kg/m^3)	Type of coating	Moulding result
95	2	5	60	1	+
100	2	0	60	1	○
100	1	0	35	1	+
95	1	5	45	1	+
90	1	10	65	2	+

evaluation criteria:
+ reasonable to good
○ reasonable

Example 3

[0070] The present polymer mixture was processed in a film extruder in which HIPS (High-Impact Polystyrene) is usually processed into film. The device is a twin-screw extruder (Berstorff ZE 40A), which was operated at a processing temperature of 180-200° C. The extruded film was 50 mm wide and 0.7 mm thick. The results of experiments using 0, 5, 10, 20, 50, 70, 90 and 100 wt. % polylactic acid are given in Table 3. The present inventors noted that at a certain polylactic acid concentration the film acquired a very white appearance and was characterised by a desirable mother-of-pearl structure, predominantly at a concentration of between 40 and 70 wt. % polylactic acid. The Charpy impact strength was determined according to standard ISO 179-1:2000. In addition, the temperature resistance was determined at 60, 70, 80, 90 and 100° C. The extent of fusion with foamed polystyrene moulded products was also determined.

TABLE 3

wt. % PLA	wt. % PS	notch impact strength (KJ/m^2)	temp. resist. at 60° C.	temp. resist. at 70° C.	temp. resist. at 80° C.	temp. resist. at 90° C.	temp. resist. at 100° C.	colour	fusion with PS
0	100	7	+	+	+	+	d	w	○
5	95	4	+	+	+	+	d	w	++
10	90	3.8	+	+	+	+/c	d	p	++
20	80	2.7	+	+	+	+/c	d	p	++
50	50	2.5-9.1	+	+	+/c	+/c	d	p	++
70	30	5.2	+	+	+/c	+/c	d	l/p	++
90	10	4.6	+	+	+/c	+/c	d	l/p	++
100	0	1.5	v	−	−	−	−	t	++

evaluation criteria:
++ excellent
+ good
○ reasonable
− poor
d deformed
c curled
w white
p mother-of-pearl
l light
t translucent

[0071] From Table 3 it can be concluded that polystyrene can be used as an impact modifier for polylactic acid and that this may also have a pleasing aesthetic effect.

[0072] Strips made of the aforementioned polymer mixtures having a thickness of 0.7 mm, a width of 5 cm and a length of 20 cm were tested. What improved above all was the temperature resistance of these strips as soon as a small added quantity of polystryrene was contained in the polylactic acid. The employed 100% polylactic acid had lost its form and structure completely at 60° C. (its Tg was 60° C.). The self-supporting capacity was determined by placing an arbitrary weight of 3 grams on the strips, and all the strips were capable of supporting this weight, except for 100% polylactic acid. Only at 90° C. did the supporting properties rapidly decrease. At 100° C. all the strips were completely deformed, just like HIPS.

[0073] DMTA (Dynamic-Mechanical Thermal Analysis) measurements were carried out. This is a dynamic measurement because a sinusoidal elongation is applied and two moduli are determined: E' (the modulus of elasticity as a measure of a material's stiffness) and E" (the modulus of loss as a measure of a material's energy dissipation; not shown). During a DMTA measurement the mechanical properties are measured (via E') as a function of temperature, and this makes DMTA suitable for measuring Tgs (glass transition temperatures) and Tms (melt temperatures). E' exhibits an abrupt decrease at a transition. In FIG. **1** the addition of 10% polystyrene causes the modulus of elasticity E' of polylactic acid to remain much higher after the Tg (at approx. 50° C.) (top curve: PS/PLA) until the Tg of polylactic acid is reached (approx. 100° C.).

[0074] Thus it can be concluded that, in spite of the low percentage of polylactic acid, there is a substantial effect on the modulus of elasticity E' of the polymer mixture as a function of temperature. The same curve obtained for 100% polylactic acid (bottom curve: PLA) indicates that the modulus exhibits a far more pronounced decrease above 60° C.

Example 4

[0075] A film was produced using mixtures of HIPS (supplied by Synbra technology), polylactic acid (supplied by Nature Works, type 2002D) and a number of other substances, viz. starch and cellulose diacetate. The material could be thermoformed in the usual manner using a thermoforming machine. It was used to produce packaging for foodstuff (noodle containers). The loss of shape was determined through immersion in hot water of 60, 70, 80 and 90° C. The results are shown in Table 4.

TABLE 4

wt. % PLA	wt. % HIPS	Starch	Cellulose diacetate	60° C.	70° C.	80° C.	90° C.
100	0	0	0	1	n.r.	n.r.	n.r.
95	5	0	0	5	5	5	4
90	10	0	0	5	5	5	4
80	20	0	0	5	5	5	3
95	0	0	5	5	5	3	2
70	10	20	0	5	5	2	1

Evaluation criteria:
5: no loss of shape
4: very slight loss of shape
3: slight loss of shape
2: pronounced loss of shape
1: complete deformation

[0076] From the above table it is evident that the 100% polylactic acid deforms completely on immersion in water of 60° C. Material containing polystyrene does not exhibit such deformation; this was not observed up to a higher temperature of 90° C. This shows that the addition of a slight amount of 5-10% PS/HIPS greatly improves the temperature properties, along with the modulus of elasticity. In spite of its low percentage, polystryrene has a substantial effect on the E' modulus of elasticity of the polymer mixture as a function of temperature.

[0077] This means that the applicability of film and the products produced from it, for example disposable products and horticultural trays, are greatly improved. This is because the glass temperature of polylactic acid of 60° C. is a problem for many applications.

[0078] A film containing 10% polystyrene, 20% starch and 70% PLA was then also produced. The starting material was dried in a vacuum drier prior to the extrusion. Film produced herefrom was subsequently thermoformed. The produced packaging was found to exhibit no deformation following brief immersion in water of 60° C. This was repeated at 70° C. and 80° C. and the effect closely resembled that observed in the previous experiment.

[0079] From this it may be concluded that the addition of a polymer having a higher Tg (polystyrene and in a more general sense polyvinyl arenes and also cellulose diacetate) greatly improves the temperature resistance, and hence also the processability, of polylactic acid. The only possibility so far described is the addition of poly-D-lactic acid to polylactic acid by the formation of a stereocomplex. This is a costly process requiring the use of poly-D-lactic acid (Improving heat resistance of PLA using poly-D-Lactide, Sicco de Vos, Bioplastics magazine February 2008).

Example 5

[0080] A number of strips produced according to example 4 were also incorporated in foamed moulded products having a wall thickness of 1 cm made of polystryrene. The strips were incorporated in the foam halfway through the thickness. Moulding was effected by steaming expanded polystryrene particles having a density of 25 kg/m3 and thus processing them into a foamed moulded product. The results are shown in Table 5.

TABLE 5

wt. % PLA	wt. % PS	impact value (KJ/m^2)	colour	fusion with PS
0	100	7	w	○/–
5	95	4	w	○
10	90	38	p	○
20	80	27	p	○
50	50	2.5-9.1?	p	○
70	30	52	l/p	++
90	10	46	l/p	++
100	0	15	t	++

evaluation criteria:
++ excellent
+ good
○ reasonable
○/– acceptable

[0081] The present inventors' experience is that strips of HIPS can be incorporated, but can actually be fairly easily pulled loose. The above experiments showed that strips with a certain minimum concentration of PLA, i.e. between 50% and 100%, exhibited amazingly good adhesion to polystyrene, while strips with concentrations above 70% could even no longer be pulled loose, that is, the strips could only be pulled loose destructively. So the fusion between strips and polystyrene is better when polylactic acid has been added to polystyrene strips. Polylactic acid works as an incorporated adhesion improver.

[0082] The strips were subsequently incorporated in a commercial founding system of IsoBouw Systems, the Powerkist, in which the strips act as a medium for absorbing tensile forces, as described in NL1022503C.

[0083] Without reinforcing strips there is no good possibility of absorbing tensile forces. The use of material having a high percentage of polylactic acid results in substantially improved adhesion to the polystyrene granules, but at the outer surface, where the material comes into direct contact with steam, 100% polylactic acid deforms. When the polylactic acid contains a concentration of polystyrene, the temperature resistance improves and the strip adheres to the polystyrene-based foamed moulded product. When the moulded products were tested, a significantly higher crushing strength was observed, probably because the polylactic acid adheres to the polystyrene-based foamed moulded product and thus ensures a higher shear force.

1. A polymer mixture comprising polylactic acid and a polymer having a glass transition temperature above 60° C.

2. The A polymer mixture according to claim **1**, wherein the polymer glass transition temperature is above 95° C.

3. The A polymer mixture according to claim **1** wherein the polymer is selected from the group consisting of a polyvinyl arene, cellulose diacetate and a combination thereof.

4. The A polymer mixture according to claim **3**, wherein the polymer is comprises polystyrene, expandable polystyrene or a combination hereof.

5. The A polymer mixture according to claim **1** wherein polylactic acid is present in an amount of 0.1-35 wt. % of the combined weight of the polylactic acid and the polymer, preferably 2-25 wt. %, in particular 5-20 wt. %.

6. The A polymer mixture according to claim **1** wherein the polymer is present in an amount of 0.1-35 wt. % of the combined weight of the polylactic acid and the polymer.

7. A method for producing an extruded product comprising supplying a polymer mixture comprising polylactic acid and a polymer having a glass transition temperature above 60° C.; subsequently extruding the polymer mixture to obtain an extruded product.

8. An extruded product obtained by the method according to claim **7**.

9. The extruded product according to claim **8**, wherein the extruded product is a film having a thickness of 0.2-2.0 mm.

10. The extruded product according to claim **9**, wherein the extruded product comprises a film processed into strips, which strips are 1-10 cm wide.

11. The extruded product according to claim **8**, wherein the extruded product is in the form of particles.

12. A reinforcement strip for a foamed molded product comprising the extruded product of claim **10**.

13. A method for the production of a starting material comprising the steps of: i) supplying a polymer mixture comprising polylactic acid and a polymer having a glass transition temperature above 60° C. to an extruder, ii) extruding the polymer mixture supplied in step i), and iii) reducing the extruded polymer mixture material obtained in step ii) to particles to thereby obtain the starting material.

14. A method for the production of a starting material comprising the steps of: a) supplying polylactic acid particles, particles of a polymer having a glass transition temperature above 60° C. and a blowing agent to an extruder, b) extruding the result of step a), and c) reducing the result obtained in step b) to particles to thereby obtain the starting material.

15. A method for producing a foamed molded product, comprising the steps of:

I) supplying a starting material obtained according to claim **13**.
II) bringing the starting material obtained in step I) under temperature and pressure conditions so that a foamed molded product is obtained.

16. A method for producing a foamed molded product comprising the steps of:

1) prefoaming the starting material obtained in claim **13**;
2) curing the prefoamed starting material obtained in step 1), and
3) bringing the result obtained in step 2) under temperature and pressure conditions so that a foamed molded product is obtained.

17. The method according to claim **15** wherein step II) air or steam having a temperature of between 60 and 160° C. is used.

18. The method according to claim **15** wherein step II) a pressure of between 0.1 and 2.0 bar is used.

19. A foamed molded product obtained according to the method of claim **15**.

20. A foamed moulded product according to claim **19**, wherein said foamed molded product has a density of between 10 g/l and 100 g/l.

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