A biodegradable material containing starch, a polyvinyl alcohol-co-vinyl acetate copolymer and plasticizer is provided. The material is injection moldable to produce articles such as those for entertaining animals.
BIODEGRADABLE MATERIAL FOR INJECTION MOLDING AND ARTICLES OBTAINED THEREWITH

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from Italian Application MI2006A002374, filed Dec. 12, 2006 disclosure of which is incorporated herein by reference.

[0002] The present invention relates to a starch based biodegradable material and to articles obtained therefrom, in particular articles to entertain animals.

[0003] More particularly, the invention refers to articles in the form of a bone or other object for chewing, thus being more attractive to the animals such as pets.

[0004] Said articles can be molded according to the injection molding technique, with short molding cycles, even in the event of considerable thickness.

[0005] Moreover, said articles are digestible in conditions simulating those of the gastric and intestinal environment.

[0006] Starch based materials utilized to produce articles to entertain animals are known in the literature. For example, the U.S. Pat. No. 5,419,283 describes a chewable article for animals obtained from a degradable composition comprising a first material chosen in the group consisting of starch, hydrolyzed starch, dextrins derived from starch and mixtures thereof, and a degradable ethylene copolymer chosen in the group consisting of polyethylene-acrylic acid, polyethylene-vinyl-alcohol, and mixtures thereof, wherein the weight ratio between said ethylene copolymer and said first material is in the range between 1:6 and 2:1. The copolymer present in the chewable article described in said patent nonetheless has poor properties of digestibility in the gastric and intestinal environment. In the event of accidental ingestion of fragments of said article by the animal, this could therefore cause problems linked to the poor digestibility.

[0007] Moreover, the polymer mixture described in the U.S. Pat. No. 5,419,283 has low fluidity in the usual processing conditions with injection molding press, which causes a high consumption of energy during processing with industrial processing plants.

[0008] A further disadvantage of the polymer mixture described in the aforesaid patent lies in the fact that it has low crystallization temperatures. Short molding cycles, on industrial injection molding plants, are therefore difficult to achieve, with evident negative effects on production.

[0009] The object of the present invention is to overcome said drawbacks, and in particular to provide a starch based biodegradable material suitable to be processed industrially. Said material is particularly suitable to produce articles to entertain animals endowed with properties of digestibility at gastric and intestinal level. These properties would, in fact, be extremely desirable as the entertainment articles according to the invention are susceptible to ingestion by the animal.

[0010] A further object of the present invention is to provide a starch based biodegradable material with increased fluidity in injection molding conditions and a higher crystallization temperature, thereby allowing the industrial output to be improved.

[0011] The aforesaid objects are achieved by means of a biodegradable material comprising starch, a polyvinyl alcohol-co-vinyl acetate copolymer and at least one plasticizer.

[0012] The characteristics and advantages, with respect to prior art, of the biodegradable material according to the invention, and of the articles obtained therewith, will be evident from the description below.

[0013] FIG. 1 shows an embodiment of the biodegradable material according to the invention, in the form of a bone for dogs.

[0014] The biodegradable material according to the present invention comprises starch, a polyvinyl alcohol-co-vinyl acetate copolymer and at least one plasticizer. The term starch is intended herein as all types of starch, namely: flour, native starch, chemically and/or physically modified starch, hydrolyzed starch, dehydrostarch, gelatinized starch, thermoplastic starch. Particularly suitable according to the invention are potato starch, corn starch, wheat starch, pulse, tapioca, yucca and sorghum starch. In the mixture according to the invention, the dry starch is present in an amount between 20 and 90%, preferably between 25 and 80%, and even more preferably between 30 and 70% by weight with respect to the total weight of the composition.

[0015] With regard to the polyvinyl alcohol-co-vinyl acetate copolymer, it is present in a quantity ranging between 5 and 50%, preferably between 10 and 40% and even more preferably between 15 and 35% by weight, with respect to the total weight of the composition.

[0016] It has a degree of hydrolysis >95%, preferably >97% and even more preferably >99%.

[0017] The plasticizer can be any substance known to one averagely skilled in the art for this use such as, for example, glycerol, water, sorbitol and pentaerythritol. The water can be that contained in the starch.

[0018] Particularly suitable are solid plasticizers at ambient temperature, such as sorbitol and pentaerythritol. The plasticizer is present in an amount preferably between 5 and 45%, more preferably between 10 and 43% and even more preferably between 15 and 40% by weight with respect to the total weight of the composition.

[0019] In a particularly preferred embodiment, glycerol, water and sorbitol are advantageously utilized as plasticizers of the starch and of the polyvinyl alcohol-co-vinyl acetate copolymer. The biodegradable material described in the present invention has a viscosity in molten state, measured at T=180° C. and γ<sub>ω</sub>=105 s<sup>-1</sup>, <1200 Pa·s, preferably <800 Pa·s, more preferably <600 Pa·s and a crystallization temperature >105° C., preferably >110° C.

[0020] The biodegradable material according to the invention therefore has high fluidity which allows improved industrial processability and a high crystallization temperature which brings about an increase in productivity.

[0021] Generally, the biodegradable material according to the invention contains water in a range between 2.5 and 8%, preferably between 3 and 6% in weight with respect to the composition.

[0022] Naturally, other substances can be added to said material, such as colorings, flavorings, food supplements, fibers and process additives such as fluidifying and slip agents.

[0023] The process additives are preferably chosen in the group consisting of calcium stearate and zinc stearate and are present in a quantity between 0.1 and 5%, preferably between 0.5 and 3% by weight with respect to the total weight of the composition.

[0024] The articles for entertaining animals obtained from the biodegradable material according to the invention have a
Digestibility of >80%, preferably >85%, expressed in terms of loss of weight of the sample, in a gastric and intestinal environment.

Moreover, if immersed in water at T_{ambient} for 3 minutes said articles are not slippery and do not release sticky residues.

Finally, a further advantage of the aforesaid articles is given by the fact that, when exposed for 12 hours to a T of 23° C., in low humidity conditions (50% RH or under a nitrogen flow), they maintain sufficient breaking energy to avoid self-fracturing. This makes the use of costly protective packaging unnecessary.

The biodegradable material according to the invention can also advantageously be used to produce, for example, thermoformed and framed films and for lacquer coating and layers of multilayers with other plastic materials, of cellulose or aluminum.

The invention will now be described by means of some embodiments, provided purely by way of example.

**EXAMPLE 1**

A twin screw extruder with D=30 mm, L/D=35, was supplied with:

- 48.8% corn starch (containing 12% water)
- 23.7% PVOH-co-vinyl acetate with degree of hydrolysis of 99%
- 10.8% glycerol
- 15.6% sorbitol
- 1.1% calcium stearate

Operating conditions of the extruder:

- Thermal profile: 30-90-170x7-160x4
- Flow rate: 10.1 kg/h
- RPM = 170
- Active degassing

The material delivered from the production line was cut at the head thereof to obtain granules which are air cooled.

The granules thus obtained were characterized by a water content of 4% in weight.

The granules thus obtained were subjected to rheological and thermal characterization tests.

**Rheological Characterization**

The mixture with the composition as per Example 1 was melted in a capillary rheometer mod. Goettfert (L/D=30) and the viscosity was then measured (η_ave) at T=180° C. and γ_{ave}=103 s⁻¹. A value of η_ave=329 Pa s was recorded.

**Thermal Characterization**

DSC analysis of a mixture with a composition as per Example 1 highlights a crystallization temperature of 120.1° C.

Subsequently, the granules obtained according to the process described above were fed to an injection molding press.

The operating conditions of the injection press mod. Sandretto 8/7, in which a bone-shaped mold according to the drawing 1 is present, were as follows:

- Thermal profile: 140-150-160-170° C.
- Injection speed: 40 cm³/s

The bone is molded in a 22 second cycle.

The bone thus obtained was subjected to a gastric and intestinal digestibility test and to a soiling test.

**Digestibility Test**

- The test was conducted according to the method of Van Der Meer and Perez. A description of the method of Van Der Meer and Perez is given in the Journal of the Science of Food and Agriculture, 1992, vol. 59, n°3, pp. 359-363.
- Samples of fragments of bone according to the invention of the weight of 10-20 grams were made to react in pH conditions simulating first the gastric and then the intestinal environment, consecutively.
- A weight loss of the sample of >85% is recorded; the residue was soft and easily digestible.

**Soiling Test**

- Bones produced according to the invention were subjected to an experimental test to assess their potential to soil garments or fabrics during their use. After immersion in water for 3 min at T_{ambient}, it was observed that they were not slippery and did not release sticky residues. Moreover, following rubbing on a black fabric cloth, it was observed that they left no visible solid residue but a film composed mainly of 95% water. After drying of the cloth only small traces of solid powder were observed.

**COMPARISON EXAMPLE 1**

The extruder of Example 1 was supplied with:

- 49.4% corn starch (containing 12% water)
- 18.3% of EVOH
- 8.5% of glycerol
- 23.4% of sorbitol
- 0.4% erucamide

Operating conditions of the extruder:

- Thermal profile: 30-100-170x14
- Flow rate: 10.1 kg/h
- RPM = 170
- Active degassing

The material delivered from the production line was cut at the head thereof to obtain granules which were air cooled.

The granules thus obtained were characterized by a water content of 5% in weight.

The granules thus obtained were subjected to rheological and thermal characterization tests.

**Rheological Characterization**

The mixture with a composition as per Comparison Example 1 was melted in a capillary rheometer mod. Goettfert (L/D=30) and the viscosity was then measured (η_ave) at T=180° C. and γ_{ave}=103 s⁻¹. A value of η_ave=791 Pa s was recorded.

**Thermal Characterization**

DSC analysis of a mixture with a composition as per Comparison Example 1 highlights a crystallization temperature of 96° C.

Subsequently, the granules obtained according to the composition and the process as per Comparison Example 1 above were fed to the injection molding press of Example 1 and subjected to a molding cycle in the same operation conditions as Example 1.

The bone is molded in a 35 second cycle.

The bone thus obtained was subjected to a gastric and intestinal digestibility test.
Digestibility Test

The test was conducted according to the method of Van Der Meer and Perez previously mentioned (see Example 1).

A weight loss of the sample of <26% was recorded; the residue was rubbery in consistency, without sharp edges.

COMPARISON EXAMPLE 2

The extruder of Example 1 was supplied with:

- 35.5% corn starch (containing 12% water)
- 29.7% PVOH-co-vinyl acetate with degree of hydrolysis of 88%
- 9.0% of glycerol
- 12.9% of sorbitol
- 12.9% of water

Operating conditions of the extruder:

- thermal profile: 30-90-170x8-150x4
- flow rate: 10.1 kg/h
- rpm=170
- active degassing

The material delivered from the production line was cut at the head thereof to obtain granules which were air cooled.

The granules thus obtained were characterized by a water content of 5% in weight.

The granules thus obtained were subjected to rheological and thermal characterization tests.

Rheological Characterization

The mixture with a composition as per Comparison Example 2 was melted in a capillary rheometer mod. Goettfert (L/D=30) and the viscosity was then measured ($\eta_{np}$) at T=180°C and $\gamma_{np}$=103 s⁻¹. A value of $\eta_{np}$=1229 Pa s was recorded.

Subsequently, the granules obtained according to the composition and the procedure as per Comparison Example 2 were fed to the injection molding press of Example 1 and subjected to a molding cycle in the same operating conditions as Example 1.

The bone was molded in a 40 second cycle.

The bone thus obtained was subjected to a soiling test.

Soiling Test

Bones produced according to the composition and the process as per Comparison Example 2 were subjected to an experimental test to assess their potential to soil garments or fabrics during their use. After immersion in water for 3 min at $T_{soil}$, it was observed that they become flaky on the surface and release sticky residues.

1. Biodegradable material characterized in that it comprises:
   - starch, present in an amount between 20 and 90% by weight with respect to the total weight;
   - a polyvinyl alcohol-co-vinyl acetate copolymer present in an amount between 5 and 50% by weight with respect to the total;
   - at least one plasticizer, present in an amount between 5 and 45% with respect to the total; wherein said polyvinyl alcohol-co-vinyl acetate copolymer has a degree of hydrolysis of >95%.

2. Biodegradable material as claimed in claim 1, characterized in that said degree of hydrolysis is >97%.

3. Biodegradable material as claimed in claim 1, characterized in that said degree of hydrolysis is >99%.

4. Biodegradable material as claimed in claim 1, characterized in that said starch is present in an amount between 25 and 80% by weight.

5. Biodegradable material as claimed in claim 1, characterized in that said starch is present in an amount between 30 and 70% by weight.

6. Biodegradable material as claimed in claim 1, characterized in that said polyvinyl alcohol-co-vinyl acetate copolymer is present in an amount between 10 and 40% by weight with respect to the total weight.

7. Biodegradable material as claimed in claim 1, characterized in that said polyvinyl alcohol-co-vinyl acetate copolymer is present in an amount between 15 and 35% by weight with respect to the total weight.

8. Biodegradable material as claimed in claim 1, characterized in that said plasticizer is present in an amount between 10 and 43% by weight with respect to the total weight.

9. Biodegradable material as claimed in claim 1, characterized in that said plasticizer is present in an amount between 15 and 40% by weight with respect to the total weight.

10. Biodegradable material as claimed in claim 1, characterized in that said starch is corn starch.

11. Biodegradable material as claimed in claim 1, characterized in that said plasticizer is selected from the group consisting of glycerol and water.

12. Biodegradable material as claimed in claim 11, characterized in that said plasticizer is the water present in the starch.

13. Biodegradable material as claimed in claim 1, characterized in that said plasticizer is solid at ambient temperature.

14. Biodegradable material as claimed in claim 13, characterized in that said plasticizer is selected from the group consisting of sorbitol and pentaerythritol.

15. Biodegradable material as claimed claim 1, characterized in that it has a viscosity in molten state, measured at T=180°C and $\gamma_{np}$=103 s⁻¹, ≤1200 Pa s.

16. Biodegradable material as claimed claim 1, characterized in that it has a viscosity in molten state, measured at T=180°C and $\gamma_{np}$=103 s⁻¹, ≤800 Pa s.

17. Biodegradable material as claimed claim 1, characterized in that it has a viscosity in molten state, measured at T=180°C and $\gamma_{np}$=103 s⁻¹, ≤600 Pa s.

18. Biodegradable material as claimed in claim 1, characterized in that it has a crystallization temperature >105°C.

19. Biodegradable material as claimed in claim 1, characterized in that it has a crystallization temperature >110°C.

20. Biodegradable material as claimed in claim 1, characterized by further comprising a substance selected from the group consisting of colorings, flavorings, food supplements and fibers.

21. Biodegradable material as claimed in claim 21, characterized by further comprising a substance selected from the group consisting of process additives.

22. Biodegradable material as claimed in claim 21, characterized in that said process additives comprise fluidifying and slip agents, preferably chosen in the group constituted by calcium stearate and zinc stearate.
23. Biodegradable material as claimed in claim 21, characterized in that said process additives are present in an amount from 0.1 to 5% by weight with respect to the total weight of the composition.

24. Biodegradable material as claimed in claim 21, characterized in that said process additives are present in an amount between 0.5 and 3% by weight with respect to the total weight of the composition.

25. Article to entertain animals obtained from biodegradable material as claimed in claim 1.

26. Article to entertain animals as claimed in claim 25, characterized in that it has a digestibility >80% in terms of loss of weight, in a gastric and intestinal environment.

27. Article to entertain animals as claimed in claim 25, characterized in that it has a digestibility >85% in terms of loss of weight, in a gastric and intestinal environment.

28. Article to entertain animals as claimed in claim 25, characterized in that said article is preferably in the form of a bone.

29. Films, thermoformed and foamed, obtained from the biodegradable material as claimed in claim 1.

30. Biodegradable material as claimed in claim 1, utilizable for lacquer coating and layers of multilayers with other plastic materials, of cellulose or aluminum.

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