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(54) Title: PROCESS FOR PRODUCTION OF STARCH-BASED THERMOPLASTIC MATERIALS

(57) Abstract: Process for production or processing of starch-based thermoplastic materials comprising: feeding of starch, water and any other components, as plasticizers, for example polyhydric alcohols, into a first section of a screw extruder; compression and homogenization of the material with formation of a melted mixture in said first section; compression of the mixture in a second section of a screw extruder and extrusion via an appropriately shaped die; process comprising the passage of said material through a pressure control valve located between said first and second section.



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Process for production of starch-based thermoplastic materials**FIELD OF THE INVENTION**

The present invention concerns a process for the processing or, more in particular, for the production, of polysaccharide-based thermoplastic materials, more in particular of starch-based thermoplastic materials.

Said materials are suitable, for example, for applications in the industrial, human and veterinary pharmaceutical, human and veterinary alimentary, agroindustrial and cosmetic fields.

PRIOR ART

Plastic materials are widely used in various fields: in particular in the field of packaging and other throwaway items such as disposable crockery, containers for food and other items, and articles for animals.

The large amount of waste generated by these products once they have been used has created a considerable problem. This fact has stimulated research in the chemical industry into biodegradable materials for replacing the synthetic polymers commonly used in this field such as polyethylene, polypropylene, polystyrene, polyethylene terephthalate and others which are biologically non-degradable. The biodegradable synthetic polymers produced have on average much higher production costs than those of the commonly used materials, thus preventing widespread use and limiting them to special applications in which the financial aspect is unimportant.

The process in question is geared to the use of largely natural raw materials, widely available, easy to find and with limited cost such as polysaccharides and more in particular starches, which are biodegradable, compostable and edible, qualities highly appreciated for applications in the field of food packaging.

Starches are natural carbohydrates present in nature in cereals, tubers, pulses and fruit. When extracted and refined, they have the form of a white or whitish powder. In the presence of natural plasticization agents, temperature and energetic mixing, starches are modified to form a biodegradable compostable thermoplastic material.

Starch, on its own, has modest physical-mechanical characteristics and is therefore processed together with other synergic components such as plasticizers

and natural additives; often synthetic polymers are also added to make the material more workable and/or improve its characteristics. Preferably the starch is first mixed cold with the other components, then the mixture is heated and pressurised, after which it is vigorously mixed and the melted material is extruded to form the finished, semi-finished or intermediate product required (for example granules). Due to the pressure and the heat, the presence of water and other components, it is modified until it forms a thermoplastic material, maintaining the biodegradability qualities of starch. Total biodegradability is obtained only if all the components in the mixture are biodegradable, hence it is desirable to avoid, in formulation of the product, the use of non-biodegradable components such as thermoplastic resins.

The working process must permit to accurately control the temperatures and pressures. For some applications, maintaining of the water content in the mixture during processing is particularly critical and uncontrolled evaporation must be avoided on the outcoming material due to the switch from the higher pressure inside the extruder to the ambient pressure in order not to cause the formation of bubbles in the melted material and consequent general decay of the extruded product. The need is felt for a process that is simple to apply, permitting adequate control of the parameters specified above.

SUMMARY

The above-mentioned problems have now been solved thanks to a process for producing polysaccharide-based thermoplastic materials comprising:

- feeding of components comprising at least one polysaccharide and water into a first section of a screw extruder;
- compression and homogenisation of the components with formation of a melted mixture in said first section;
- compression of the mixture in a second section of a screw extruder and extrusion through an appropriately-shaped die;
- process comprising the passage of said mixture through a pressure control valve positioned between said first and second section.

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The first and the second section are preferably part of one single extruder, but the screw extruder can also comprise a screw mixer, which constitutes the first section connected via said valve to a final extruder which constitutes said second section.

5 Preferably the pressure in the extruder immediately upstream of the valve is kept to at least 20 bars, preferably at least 40 bars.

The process can involve the formation of semi-finished products such as film, sheets or tubes, ready for direct use or for subsequent thermoforming process, or finished pieces by introducing the melted material coming out of the die directly into suitable moulds, or an intermediate material, such as granules which can then
10 be extruded in a subsequent process, which can be similar to the one described or injection moulded.

Preferably the polysaccharide is starch.

The process according to the present invention can be a production process, starting from pure starch but also from raw materials containing starch, such as
15 cereal flour and other types of flour, or processing of a material already produced in this way, alone or with the addition of other components.

The water, fed with the polysaccharide, performs a plasticizing and fluidising action in the melted material and can be the water naturally contained in it, or further water can be added as required. Other components can be present, such
20 as plasticizers or natural additives; preferably a natural plasticizer is present. Synthetic, preferably thermoplastic, resins can also be added.

According to a preferred aspect, in order to be able to accurately control the process, the extruder sections are thermoregulated, with areas provided with heating system, such as metal-clad electrical resistances to contribute the
25 necessary heat to the process, and areas provided with cooling system, for example by air, or preferably with diathermic liquid control unit (for example circulating in jackets or ducts provided in the extruder walls) to rapidly remove any excess heat or heat generated by the mechanical action of the screw or mixing devices. Preferably the first section comprises heating devices and the second
30 section comprises cooling devices. Cooling devices can also be provided for the first section, and heating devices can be provided for the second section, for

improved temperature control and for the management of transitory process phases such as start-up.

Preferably all the components are fed into the extruder together, optionally premixed in an appropriate manner, by means of a turbo-mixer for example.

- 5 According to a preferred aspect, the water content of the mixture is maintained the same throughout the process, from feeding into the extruder to final extrusion.

Preferably the water is present in over 2% in weight, preferably at least 8% in weight, more preferably at least 12% in weight out of the total components.

- The invention also concerns an extruder designed to perform a process according to any previous claim, comprising a first section for feeding, compression and homogenisation of the material supplied to said extruder, a second section comprising means for feeding and compression of said material and a pressure control valve positioned between the two sections, so that said valve constitutes an obligatory route for said material. Preferably said valve comprises means for control of the pressure upstream, such as mobile shutters or variable width sections, for example a shutter operated by a hydraulic cylinder.

According to a preferred aspect, upstream of said valve a homogenisation area is provided in which the profile and geometry of the screw changes, for example it is replaced by a series of appropriately-shaped cams.

20 LIST OF FIGURES

The present invention will now be illustrated via a detailed description of preferred but not exclusive forms of embodiment, provided purely as an example, with the help of the attached figures in which:

- figure 1 schematically represents a device comprising an extruder suitable for performing a process according to the present invention.

DETAILED DESCRIPTION OF A FORM OF EMBODIMENT

- Figure 1 shows a possible embodiment of the process. The components, preferably premixed, contained in the hopper 1, are fed to the extruder via the inlet 2, by means of the metering unit 7 (which can be a screw volumetric metering unit or a weight loss gravimetric metering unit or a metering unit, preferably adjustable, of any other type), into the first section 8 which runs from the inlet 2 to the valve 5. The shaft 3, provided with screw 9, conveys the components fed to a first

compression area 10 (where the pressure increase can be obtained for example by narrowing of the passage section, for example due to the increase in diameter of the shaft 3, as in figure 1). The pressure is brought to an adequate value, and the mixture of components reaches the homogenisation area 4, where the shaft
5 can be provided with appropriate homogenisation devices; for example, this screw part can be replaced by a series of cams or other systems, which provide for homogenisation of the components without generating a forward thrust. In this way, an area with uniform pressure is created with adequate stay time. The pressure in this area, as already mentioned, is preferably above 20 bars. By
10 means of appropriate heating devices, such as thermal resistances positioned along the extruder casing, the temperature is brought to an adequate value to obtain the formation of a melted material with appropriate characteristics. In general, the temperature reached in this section, and in any case upstream of the valve 5, can be above 100°C; preferably it is at least 110°C. The stay time in the
15 homogenisation area, and in any case at the temperature and maximum pressure reached in the first section, is preferably above 5 s, more preferably at least 8 s. The mixture flows through the valve 5, which permits control of the pressure upstream. The valve 5 can be positioned on a duct 11 which can, for example, be obtained in the casing 13 of the extruder. According to a possible aspect of the
20 invention, the melted material is forced to flow through the valve due to the widened section 12 of the shaft 3 which, by creating a seal with the casing 13, prevents the mixture from flowing through the aperture 14 of the extruder. The mixture therefore flows to the second section 15, losing pressure (which can drop for example to values near ambient pressure). In the second section 15 heat is
25 removed from the mixture, bringing it rapidly to temperatures below those immediately upstream of the valve 5. According to an aspect of the invention, the temperature in this section is at least 10°C below that of area 4; the temperatures depend, however, on the components used and on other process requirements. For example, in particular if the components do not include synthetic thermoplastic
30 resins, it is preferable to maintain the temperature in the second section at values not exceeding 100°C. The removal of heat from the second section occurs without substantial evaporation of water from the mixture. Heat removal can occur through

the walls, for example by means of a cooling fluid fed into ducts present on the casing 13 or obtained in it. A compression area 16, similar to the area 10 of the first section, can be present in the second section. In this way the mixture can be pushed through the appropriately-shaped extrusion die 6 to produce semi-finished products such as sheets, tubes or other continuous profiles, or to produce finished pieces by direct moulding or to produce intermediate products such as granules or cubes by cutting.

The extruder can be provided with single or twin screw. In particular in the latter case it is possible to feed the components at several different points of the first section. According to a preferred aspect of the invention, the components are fed all together, as has been seen, at one single inlet point, after premixing them, in order to simplify the process.

The starch is the basic component of the mixture and can be introduced in the refined and pure form, but products can also be obtained with good physical-mechanical characteristics and at lower cost by using, for example, wholemeal cereals and flours that contain high percentages of starch. Non-restrictive examples of materials that can be used are: starches and flours in general, wheat flour (soft or hard), maize flour, rice flour and in general wheat gluten, micronised whole wheat, micronised whole maize, bread (for example bread-making scraps), micronised soft wheat bran (milling scraps) and others. The starch-based materials can preferably constitute 60-85% in weight (alone or as a mixture) of the component mixture, plus other materials of natural origin.

Plasticizers can be present, preferably of pharmaceutical or alimentary class; preferred plasticizers are polyhydric alcohols in general, glycerol, sorbitol, propylene glycol, polyethylene glycol, esters of fatty acids and others. The plasticizers can preferably constitute 1-35% in weight (alone or as a mixture) of the component mixture.

If necessary structure or process additives can be introduced or technological auxiliaries such as zinc or calcium stearate, waxes, stearic acid and derivatives, paraffin, colourings, fragrances, aromas, preservatives (such as citric acid, potassium sorbate, isobutyl vanillate.) Common percentages for these components (in weight, alone or as a mixture) are usually 0.1-5%.

According to a preferred aspect synthetic resins are not present, however special applications can be envisaged where the same are required. Examples of synthetic resins that can be used are: polyvinyl alcohol, polyvinyl acetate, carboxymethyl cellulose, polyethylene, ethylene/acrylic acid polymers, polylactate and others.

By appropriately selecting the components, edible and/or partially biodegradable and/or totally biodegradable products can be obtained.

It has been found that the presence of the pressure regulation valve between the two sections permits control of the process and optimisation of the physical-mechanical characteristics of the products in a wide range of compositions.

EXAMPLES

In a single-screw extruder, diameter 80 mm, configured as in the drawing and description, different compositions were processed to produce granules by means of dry crosscutting on the die 6 and air cooling. With these granules test pieces were produced on which density, hardness, tensile strength and elongation tests were performed (after conditioning for 24h at 25°C and 55% relative humidity).

The working temperatures are indicated by the letters from A to F corresponding to the various areas of the extruder, roughly marked in Fig. 1: A corresponds to an intermediate area between the inlet 2 and the first compression area 10; B corresponds to the first compression area 10; C corresponds to the homogenisation area 4; D corresponds to an intermediate area between the outlet of the duct 11 in the second section and the compression area 16; E corresponds to an intermediate area between the compression area 16 and the die 6; F corresponds to the die 6.

Example 1)

Mixture: maize starch 73% + glycerol 20% + water 5% + additives 2%

Screw speed 50 r.p.m.

Temperature A) 100° -B) 110° -C) 115° -D) E) F) 98°C

Back pressure (pressure immediately upstream of the valve): 20 bars

Results:

- Specific weight = 1.27 g/cm³
- Shore hardness A = 72

- Tensile strength = 5.9 N/mm^2
- Elongation 65%

Example 2)

Mixture: micronised whole wheat 77% + propylene glycol 15% + water

5 5% + additives 3%

Screw speed 55 r.p.m.

Temperature A) 105° -B) 115° -C) 140° -D) E) F) 100°C

Back pressure: 30 bars

Results:

- 10
- Specific weight = 1.28 g/cm^3
 - Shore hardness A = 88
 - Tensile strength = 6.8 N/mm^2
 - Elongation 35%

Example 3)

15 Mixture: Maize flour 50% + Maize starch 27% + propylene glycol 12% + sorbitol 6% + water 3% + additives 2%

Temperature: A) 100° - B) 115° - C) 130° - D) E) F) 98°C

Screw speed 70 r.p.m.

Back pressure: 40 bars

20 Results:

- Specific weight = 1.28 g/cm^3
- Shore hardness A = 91
- Tensile strength = 7.6 N/mm^2
- Elongation = 38%

25 Example 4)

Mixture: Maize starch 55% + Glycerol 12% + Polyvinyl alcohol 20% + Wheat gluten 4% + water 6% + additives 3%

Temperature: A) 120° - B) 140° - C) 155° - D) 120° – E) 110° - F) 102°C

Screw speed: 30 r.p.m.

30 Back pressure: 70 bars

Results:

- Specific weight = 1.26 g/cm^3

- Shore hardness A = 93
- Tensile strength = 11.2 N/mm²
- Elongation > 100 %

Example 5)

- 5 Mixture: Maize starch 60% + Glycerol 10% + Sorbitol 6% + Polylactate 22% + Additives 2%

Temperature: A) 130° - B) 145° - C) 160° - D) 130° - E) 120° - F) 110°C

Screw speed: 40 r.p.m.

Back pressure: 50 bars

10 Results

- Specific weight = 1.29 g/cm³
- Shore hardness A = 94
- Tensile strength = 10.2 N/mm²
- Elongation = 28%

CLAIMS

1. Process for producing polysaccharide-based thermoplastic materials comprising:
feeding of components, comprising at least one polysaccharide and water, into a
5 first section of a screw extruder;
compression and homogenisation of the components with formation of a melted mixture in said first section;
compression of the mixture in a second section of a screw extruder and extrusion via an appropriately shaped die;
10 process comprising the passage of said mixture through a pressure control valve located between said first and second section.
2. Process according to claim 1 where said first and second section are part of one single extruder.
3. Process according to any previous claim in which said polysaccharide is starch.
- 15 4. Process according to any previous claim in which heat is supplied to said first section through the walls of the extruder.
5. Process according to any previous claim in which heat is removed from said second section through the walls of the extruder.
6. Process according to any previous claim in which the water
20 represents at least 2% in weight of the total components fed.
7. Process according to claim 6 in which the water represents at least 8% in weight of the total components fed.
8. Process according to claim 7 in which the water represents at least 12% in weight of the total components fed.
- 25 9. Process according to any previous claim in which a temperature of at least 100°C is reached upstream of said valve.
10. Process according to any previous claim in which a pressure of at least 20 bars is reached upstream of said valve.
11. Process according to claim 10 in which a pressure of at least 40 bars is
30 reached upstream of said valve.
12. Process according to any previous claim in which, downstream of said valve, the temperature is below 100°C.

13. Process according to any previous claim in which the components are fed premixed into the extruder, at one single inlet point.
14. Process according to any previous claim in which the extruder is a twin-screw extruder.
- 5 15. Process according to claim 13 in which the extruder is of the single-screw type.
16. Process according to any previous claim in which said components comprise a polyhydric alcohol.
17. Process according to any previous claim in which said components comprise a
10 polylactate.
18. Extruder designed to perform a process according to any previous claim, comprising a first section (8) comprising means for conveying, compression and homogenisation of material fed to said extruder, a second section (15) comprising means for conveying and compression of said material and a pressure control
15 valve (5), positioned between the two sections.
19. Extruder according to claim 18 comprising means for heating and means for cooling said material.
20. Single-screw extruder according to claim 18 or 19.
21. Twin-screw extruder according to claim 18 or 19.

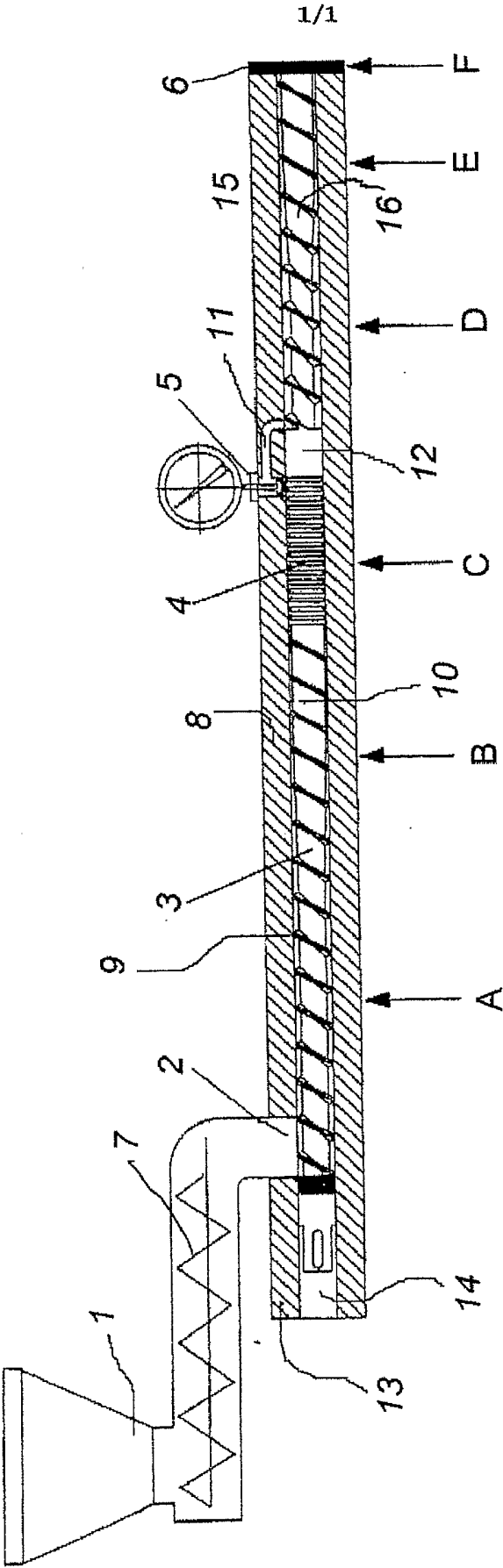


Fig. 1