Polymer degradation and stability, 77, 35-41, 2002) and (Špitálsky Z., et al. Polymer degradation and stability, 91, 856 - 861, 2006).

In accordance with the present state of art in the given area, the main disadvantages of blends based on biodegradable polymeric materials, in particular from renewable resources, can be identified in the following way:

1. The required processing stability of these blends, as well as their suitable mechanical properties are achieved via addition of synthetic polymers, recently mainly using PBAT, however, this decreases the whole ecological value and ecological safety of these materials.
2. Solutions leading to technically acceptable materials are economically expensive, and not satisfactorily competitive with respect to synthetic non-biodegradable as well as synthetic biodegradable materials.
3. For reasons of drop in price of the expensive ecological polymers, starch (mainly in the plasticized form) is often used as one of components, but this causes a considerable worsening the processing and mechanical properties of the materials, especially the materials containing PHA.
4. Application of TPS containing polyol as a plasticizer in the materials with present PHA leads to an abrupt decrease of the processing stability and worsening mechanical properties, and this prevents their introduction in the standard industrial practise.

Summary

The mentioned disadvantages of the ecological polymer blends known till now are solved by a blend and method for its preparation of the present disclosure, wherein polymer components are represented by biodegradable polymers obtained or produced of raw materials from renewable sources, but with continuing use of PLA/PHA mixture, preferably a tough mixture according to (WO 2012/141660 A1), with an addition of TPS and modifier, wherein TPS is produced directly during blending with PLA, and its drying is not required prior to blending with PHA. TPS is effectively dispersed in the matrix of biodegradable polymers. A blend of PLA/PHA/TPS is produced with a good processing stability and good mechanical properties. Surprisingly, the produced homogenous blend of the present disclosure, containing simultaneously PHA and TPS, has better mechanical properties. The required effect can be achieved only in the case that the PLA/PHA/TPS blend contains also a suitable modifier, and is prepared according to the procedure where the modifier is added to a blend with starch and PLA, prior to addition of PHA to this blend. Despite the generally known fact that plasticisers for TPS, based on the substances containing the OH groups (in particular glycerol, and other organic substances containing the OH groups), cause a strong degradation of PHA, and in this way, they worsen mechanical properties of PHA, a solution of the present disclosure surprisingly allows to prepare a homogenous blend containing simultaneously PHA and TPS plasticized by a substances including the OH groups, wherein the final material, prepared according to the present disclosure, shows improved mechanical properties.

In one aspect of the present disclosure, there is provided a biodegradable polymer blend, characterized in that it contains at least one component (A), at least one component (B), and at least one component (D), wherein

- component (A) includes polymers based on lactic acid;

- component (B) includes thermoplastic starch, representing a mixture of starch, at least one plasticizer from the group of substances (C), and at least one modifier from the group of substances (E);

- group of substances (C) includes plasticizers for starch, comprising one-, two- and multiple hydroxyl groups containing alcohols and polyols, especially glycerine, ethylene glycol, propylene glycol, diols, triols and polyols, polyethylene glycol, polypropylene glycol, neopentyl glycol, sorbitol, mannitol;

- group of substances (E) which are modifiers that show a high reactivity with hydroxyl groups;

- component (D) includes homopolymers or copolymers of polyhydroxyalkanoates, and/or their mixtures;

and the biodegradable blend can optionally contain component (F), wherein

- component (F) includes plasticizers for PLA and/or for PHA, wherein the viscosity of the plasticizer for PLA a/and PHA, measured using the coaxial-cylinder rotational viscometer at 25 °C, is lower or equal to 20,000 mPas, and

wherein the blend containing components (A), (B) and (D) is prepared in a such way that components (A) and (B) are blended, wherein component (B) is present in the blend at least in one phase of the blending process where simultaneously at least one component (B) and at least one component (A) are blended, and this phase of the blending process precedes by at least one phase a second blending phase of the blending process where component (D) is added to the blending process, and optional component (F) can be added to the blend in any one or multiple phases of the blending process, either in one or in multiple doses.

In another aspect of the present disclosure, there is provided a method for preparation of the biodegradable polymer blend disclosed herein, characterized in that the composition containing components (A), (B) and (D) is prepared in a such way that components (A) and (B) are blended, wherein component (B) is present in the blend at least in one phase of the mixing process where simultaneously at least one component (B) and at least one component (A) are blended, and this phase of the blending process precedes by at least one phase that blending phase of the blending process where component (D) is added to the blending process, and optional components (F) and (G) can be added to the blend in any one or multiple phases of the blending process, either in one or in multiple doses.

Blends according to the present disclosure are characterized by having a better tensile strength at break and/or a better relative elongation at break. The present disclosure is aimed at preparing a homogenous biodegradable polymer blend with improved mechanical properties.

For purpose of the present disclosure, individual terms in the present text shall have the following meaning:

Starch

"Starch" is to be understood as a substance deposited in plants through the process of photosynthetic assimilation, representing a mixture of amylose and amylopectin, and that can, in addition to these polymers, optionally contains also a small quantity of lipids, proteins and a limited quantity of water. For purposes of the invention, the term starch corresponds to a starch in the form obtained from plants by a mechanical way: via grinding and washing, without any other chemical or physical processing. For purposes of the invention, the term starch is to be understood as a starch produced from any plant, such as corn, potatoes, cereals, rice, amaranth, and further plants.

Component (A)

The term "component (A)" includes polymers based on lactic acid, mainly homopolymers of PLLA, PDLA, as well as copolymers thereof, or mixtures of homopolymers, mixtures of their homopolymers and copolymers, or mixtures of their copolymers, preferably PLA polymers exhibiting the relative elongation at break 10% or less, preferably 5% or less, and more preferably 3% or less, wherein determination of relative elongation at break is performed according to the methodology mentioned in description of the invention.

Component (B)

The term "component (B)" includes a thermoplastic starch (TPS), representing a mixture of starch, at least one

PATENT CLAIMS

1. A biodegradable polymer blend, **characterized in that** it contains at least one component (A), at least one component (B), and at least one component (D), wherein

- component (A) includes polymers based on lactic acid;

- component (B) includes thermoplastic starch, representing a mixture of starch, at least one plasticizer from the group of substances (C), and at least one modifier from the group of substances (E);

- group of substances (C) includes plasticizers for starch, comprising one-, two- and multiple hydroxyl groups containing alcohols and polyols, especially glycerine, ethylene glycol, propylene glycol, diols, triols and polyols, polyethylene glycol, polypropylene glycol, neopentyl glycol, sorbitol, mannitol;

- group of substances (E) which are modifiers that show a high reactivity with hydroxyl groups;

- component (D) includes homopolymers or copolymers of polyhydroxyalkanoates and/or their mixtures;

and the biodegradable blend can optionally contain component (F), wherein

- component (F) includes plasticizers for PLA and/or for PHA, wherein the viscosity of the plasticizer for PLA a/and PHA, measured using the coaxial-cylinder rotational viscometer at 25 °C, is lower or equal to 20,000 mPas, and

wherein the blend containing components (A), (B) and (D) is prepared in a such way that components (A) and (B) are blended, wherein component (B) is present in the blend at least in one phase of the blending process where simultaneously at least one component (B) and at least one component (A) are blended, and this phase of the blending process precedes by at least one phase a second blending phase of the blending process where component (D) is added to the blending process, and optional component (F) can be added to the blend in any one or multiple phases of the blending process, either in one or in multiple doses.

2. The biodegradable polymer blend of claim 1, **characterized in that** the polymers based on lactic acid are homopolymers of PLLA, PDLA, as well as their copolymers, or mixtures of their homopolymers, mixtures of their homopolymers and copolymers, or mixtures of their copolymers.

3. The biodegradable polymer blend of claim 1, **characterized in that** the plasticizers for starch are monohydric alcohols and polyols.

4. The biodegradable polymer blend of claim 1, **characterized in that** the plasticizers for starch are diols and triols.

5. The biodegradable polymer blend of claim 1, **characterized in that** the plasticizers for starch are glycerine, ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, neopentyl glycol, sorbitol, mannitol.

6. The biodegradable polymer blend of claim 1, **characterized in that** the modifiers are saturated or unsaturated carboxylic acids, saturated or unsaturated anhydrides, and mixed anhydrides of carboxylic acids, substances containing isocyanate groups, substances containing expoxide groups, acyl halides, acyl imidazoles, acylphosphates, thioesters of acids, or a combination thereof.

7. The biodegradable polymer blend of claim 1, **characterized in that** the modifiers are polycarboxylic acids.

8. The biodegradable polymer blend of claim 1, **characterized in that** the modifiers are dicarboxylic acids or tricarboxylic acids.

9. The biodegradable polymer blend of claim 6, **characterized in that** the substances containing isocyanate groups are diisocyanates.

10. The biodegradable polymer blend of claim 1, **characterized in that** the component (D) includes homopolymers or copolymers based on PHB and/or their mixtures.

11. The biodegradable polymer blend of claim 1, **characterized in that** the plasticizers for PLA and/or for PHA are esters and low-viscosity polyesters.

12. The biodegradable polymer blend of claim 11, **characterized in that** the esters and low-viscosity polyesters are esters or low viscosity polyesters of citric acid, esters or low viscosity polyesters of polyols, esters or low viscosity polyesters of phosphoric acid, esters or low viscosity polyesters of sebacic acid, esters or low viscosity polyesters of adipic acid, or esters or low viscosity polyesters of phthalic acid.

13. The biodegradable polymer blend of claim 11, **characterized in that** the esters and low-viscosity polyesters are esters or low viscosity polyesters of glycerine or esters or low viscosity polyesters of diols.

14. The biodegradable polymer blend of claim 12, **characterized in that** the esters and low-viscosity polyesters are other liquid esters and/or low viscosity polyesters and copolyesters, or their mixtures.

15. A biodegradable polymer blend of claim 1, **characterized in that** the mixture shows tensile strength σ_M equal or higher than 15 MPa, wherein relative elongation at break ε_b is higher or equal than 2.0%, and the parameters relative elongation at break ε_b and tensile strength σ_M are evaluated by analysis of tensile curves.

16. A biodegradable polymer blend of claim 1, **characterized in that** it further contains component (F), and shows relative elongation at break ε_b is higher or equal than 100%, wherein tensile strength σ_M is higher or equal than 3.0 MPa, %, and the parameters relative elongation at break ε_b and tensile strength σ_M are evaluated by analysis of tensile curves.

17. The biodegradable polymer blend of any one of claims 1 to 16, **characterized in that** the ratio (A):(D) is from 95:5 to 5:95.

18. The biodegradable polymer blend of any one of claims 1 to 16, **characterized in that** the quantity of starch used in component (B) shall be such that the ratio [(A)+(D)]:(starch) is from the interval 97:3 - 40:60.

19. The biodegradable polymer blend of any one of claims 1 to 16, **characterized in that** the quantity of substance from the group (C) in component (B) shall be such that the ratio of a substance from the group (C): (starch) is at least 5:95.

20. The biodegradable polymer blend of any one of claims 1 to 16, **characterized in that** in the component (B), the ratio of a substance from the group (E) : [(starch+substance from the group (C)] is at least 0.05:100.

21. The biodegradable polymer blend of any one of claims 1 to 17, **characterized in that** the ratio (F) : [(A)+(D)]is at least 5:95.

22. The biodegradable polymer blend of any one of claims 1 to 17, **characterized in that** the blend further contains component (G) to modify processing and/or utility properties of the blend, wherein the component (G) includes mainly inorganic or organic fillers, compatibilizers and interphase agents, pigments and dyes, nucleating agents, processing aids, anti-block and slip additives, cross-linking additives, foaming agents, antistatic additives, flame retardants, antidegradants, and other additives and modifiers, including polymers and oligomers.

23. The biodegradable polymer blend of claim 22, **characterized in that** the component (G) includes processing aids.

24. The biodegradable polymer blend of claim 22, **characterized in that** the component (G) includes other additives and modifiers, including polymers and oligomers.

25. A method for preparation of the biodegradable polymer blend of any one of claims 1 to 24, **characterized in that** the composition containing components (A), (B) and (D) is prepared in a such way that components (A) and (B) are blended, wherein component (B) is present in the blend at least in one phase of the mixing process where simultaneously at least one component (B) and at least one component (A) are blended, and this phase of the blending process precedes by at least one phase that blending phase of the blending process where component (D) is added to the blending process, and optional components (F) and (G) can be added to the blend in any one or multiple phases of the blending process, either in one or in multiple doses.

26. The method for preparation of the biodegradable polymer blend of claim 25, **characterized in that** all phases of the blending process are carried out in one blending step, preferably in one extrusion step.

27. The method for preparation of the biodegradable polymer blend of claim 25, **characterized in that** all phases of the blending process are carried out in one extrusion step.

28. The method for preparation of the biodegradable polymer blend of any one of claims 25-27, **characterized in that** at the beginning of blending process, a dryblend is prepared by mixing at laboratory temperature, wherein the dryblend

contains of starch and at least one modifier (E), and the dryblend optionally can contain one or more components (C), and together with the dryblend, also a polymer from the group (A) can be added to the blend, wherein at least one substance from the group (C) is added to the blend at latest in that phase of the blending process which precedes by at least one phase the phase of the blending process in which component (D) is added to the blend, and at least one substance from the group (A) is added to the blend in that phase of the blending process which precedes at least one phase that phase of the blending process in which component (D) is added to the blend, wherein the order of dosing substances from the group (A) and (C) is discretionary, and one or multiple components (D) are added to the blend in a such phase of the blending process, which follows by at least one phase of the blending process the phase in which are simultaneously blended: starch, at least one component (A), at least one substance from the group (C), and at least one substance from group (E); wherein components (F) and (G) can be added to the blend in any phase of the blending process; and before the output of a hot-melt from the last blending step, an excessive humidity of the blend is removed by atmospheric or vacuum degassing, and the produced blend in hot-melt form is:

(i) cooled by liquid or gas, and granulated

(ii) or led to a die for producing final products or intermediates.

29. The method for preparation of the biodegradable polymer blend of claim 28, **characterized in that** before the output of a hot-melt from the last extrusion step, an excessive humidity of the blend is removed by atmospheric or vacuum degassing.

30. The method for preparation of the biodegradable polymer blend of claim 28, **characterized in that** the produced blend in hot-melt form is cooled by water or air.

31. The method for preparation of the biodegradable polymer blend of claim 28, **characterized in that** the produced blend in hot-melt form is led to a die for producing final products or intermediates by technologies based on extrusion.

32. The method for preparation of the biodegradable polymer blend of claim 28, **characterized in that** the produced blend in hot-melt form is led to a die for producing final products or intermediates for production of cast, blown or biaxially oriented films, extruded profiles and other products or intermediates based on extrusion.

33. The method for preparation of the biodegradable polymer blend of claim 28, **characterized by** a multiple step method of production, and hot-melt of the blend containing at least one component (A) and at least one component (B) without presence of component (D) is, without removal of excessive water on output from the given blend step, cooled by liquid or gas, and granulated, and the produced pellets are fed to the next blending step, wherein also a polymer from the group (D) is added to the blend together with the pellets, or the polymer from the group (D) is added to the blend at latest in the last but one blending phase of the given blending step, and the excessive humidity is removed by atmospheric of vacuum degassing before the completion of the last blending step, prior to output from the blending device, and the produced blend in a form of hot-melt is then:

(i) cooled by liquid or gas, and granulated

(ii) or led to a die for producing final products or intermediates.

34. The method for preparation of the biodegradable polymer blend of claim 33, **characterized in that** the produced blend in a form of hot-melt is then cooled by water or air.

35. The method for preparation of the biodegradable polymer blend of claim 33, **characterized in that** the produced blend in a form of hot-melt is then led to a die for producing final products or intermediates by technologies based on extrusion.

36. The method for preparation of the biodegradable polymer blend of claim 33, **characterized in that** the produced blend in a form of hot-melt is then led to a die for producing final products or intermediates for production of cast or blown or biaxially oriented films, extruded profiles and other products or intermediates based on extrusion.

37. The method for preparation of the biodegradable polymer blend of claim 33, **characterized by** production performed in a blending device.

38. The method for preparation of the biodegradable polymer blend of claim 37, **characterized by** production performed in an extruder.

39. The method for preparation of the biodegradable polymer blend of claim 37, **characterized by** production performed in a blending device in two blending steps.

40. The method for preparation of the biodegradable polymer blend of claim 39, **characterized in that** the two blending steps are two extrusion steps and hot-melt of the blend is cooled.

41. The method for preparation of the biodegradable polymer blend of claim 40, **characterized in that** the hot-melt of the blend is cooled by water or air.