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Description

The invention relates to a starchy polymer material, a method for the production thereof and formed parts, films and/or fibres produced from the material.

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Polymer blends which are based on starch, which contain starch in combination with one or a plurality of thermoplastic polymers, for example, polyesters, are generally known. The production and properties of plasticiser-free, starchy polymer blends are described, for example, in the publications EP 0 596 437 B1 and EP 0 917 540 B1.

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Plasticiser-free, starchy polymer blends generally contain starch up to a quantity of a maximum of approximately 33% by weight with respect to the entire composition of the polymer blend. Although another increase in the starch proportion would be desirable for economic and ecological reasons, this is not readily possible because an increase in the starch proportion is generally associated with a substantial worsening of the mechanical properties of the polymer.

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A plasticiser-free thermoplastic polymer blend which is based on starch, which is suitable in particular for blown film extrusion, flat film extrusion and injection-moulding of completely biologically degradable products is commercially available from the company Biotec GmbH & Co. KG in Emmerich (Germany) under the trade name "Bioplast® GF 106/02".

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WO 2005/017034 A1 describes biodegradable polyester compositions comprising 5 to 80% by weight of a polyester on the basis of aliphatic and aromatic dicarboxylic acids and aliphatic dihydroxy compounds and 20 to 95% by weight of a renewable raw material, for example natural starch, and furthermore 0.1 to 15% by weight of a component, which is suitable to form covalent bonds with the renewable raw material as well as the polyester, with respect to the total weight of polyester and renewable raw material.

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An object of the invention is to improve the mechanical properties of the starchy materials mentioned above and the products produced therefrom (for example, moulded components, films and/or fibres). In particular, an object of the invention is to provide plasticiser-

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free polymer blends which are based on starch, which have as high a starch content as possible with excellent mechanical properties at the same time.

This object is achieved according to the invention by a method for producing a starchy polymer material having a content of low-molecular substances of less than 3% by weight, with respect to the entire composition, wherein the low-molecular substances are selected from water, glycerine and sorbitol and/or admixtures thereof and wherein the end product has a water content of less than 1.5% by weight with respect to the entire composition of the admixture which is characterised by:

(a) producing an admixture containing at least

- from 1 to 75% by weight starch and/or starch derivative,
- from 10 to 85% by weight polyester and
- from 0.05 to 3 % by weight of a glycidyl(meth)acrylate-containing polymer;

(b) homogenising the admixture by supplying thermal and/or mechanical energy;

(c) adjusting the water content of the admixture so that the end product has a water content of less than 1.5% by weight with respect to the entire composition of the admixture.

Advantageous embodiments of the invention are described in the dependent claims.

A significant feature of the method according to the invention is the addition of a polymer containing epoxide groups. It was surprisingly found that the presence of polymers containing epoxide groups as an additive in the production of starchy polymer materials results in a substantial improvement in the mechanical properties of the material, in particular the tensile strength, elongation at break and dart drop values thereof.

The polymer material produced according to the method according to the invention is distinguished by excellent mechanical properties. For instance, a film produced from the polymer

material may have a tensile strength according to DIN 53455 of from 5 to 60 N/mm², in particular of from 10 to 40 N/mm² and/or an elongation at break according to DIN 53455 of from 100 to 1000%, in particular of from 200 to 800%.

- 5 With the method according to the invention, it is further possible for the first time to produce plasticiser-free polymer blends which are based on starch and which have a starch content which is greater than or equal to 34% by weight, with films produced from the polymer blends having an elongation at break according to DIN 53455 of at least 300% and/or a dart drop value according to ASTM D-1709 of at least 10 g/μm.

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The method according to the invention makes provision for homogenisation of an admixture containing starch or starch derivative, polyester and polymers containing epoxide groups.

- 15 The production of starchy thermoplastic polymers by homogenisation of a starchy initial admixture is generally known and is usually carried out in an extruder. Suitable production methods for starchy thermoplastic polymers are described, for example, in the publications EP 0 596 437 B1 and EP 0 917 540 B1.

- 20 The starch or the starch derivative used in the method according to the invention is preferably selected from native potato starch, tapioca starch, rice starch and maize starch.

- According to a preferred embodiment of the invention, the admixture contains 5 to 75% by weight, in particular 10 to 75% by weight, preferably 15 to 70% by weight, even more preferably 25 to 55% by weight, most preferably 34 to 51% by weight starch and/or starch derivative.
- 25

- The polyester contained in the admixture is preferably selected from the group consisting of aliphatic-aromatic copolyester, aliphatic polyester, aromatic polyester, PHA, PLA, PHB and PHBV.
- 30

For the method according to the invention, polyesters in particular (but not exclusively) may be considered which are biodegradable according to EN 13432 and/or which have a glass transition temperature (T_g) of less than 0°C , in particular less than -4°C , more preferably less than -10°C , even more preferably less than -20°C and most preferably less than -30°C . The polyesters used in the method according to the invention are further preferably thermoplastic.

According to a particularly preferred embodiment of the invention, an aliphatic-aromatic polyester or copolyester is used as the polyester, in particular a statistical copolyester, based on at least adipic acid. This is more preferably a copolyester or statistical copolyester based on 1,4-butanediol, adipic acid and terephthalic acid or terephthalic acid derivative (for example, dimethyl terephthalate DMT). This may in particular have a glass transition temperature (T_g) of -25 to -40°C , in particular -30 to -35°C , and/or a melting range of 100 to 120°C , in particular 105 to 115°C .

Suitable polyesters are further in particular aliphatic polyesters which are selected from the group consisting of polyhydroxyvalerate, polyhydroxybutyrate-hydroxyvalerate copolymer and polycaprolactone. Further preferred aliphatic polyesters are those based on succinate, wherein the polyester can in particular be selected from the group consisting of polybutylene succinate (PBS), polybutylene succinate adipate (PBSA) and polyethylene succinate (PES) or mixtures thereof.

The content of polyester in the admixture is preferably 20 to 85% by weight, in particular 30 to 80% by weight, more preferably 40 to 80% by weight with respect to the entire composition.

The polymer material according to the invention further contains a polymer containing epoxide groups, preferably being a copolymer containing epoxide groups. Polymers or copolymers containing epoxide groups which may be considered include in particular those which have a molecular weight (M_w) of from $1,000$ to $25,000$, in particular from $3,000$ to $10,000$.

The polymer containing epoxide groups is a glycidyl (meth)acrylate-containing polymer. A suitable glycidyl (meth)acrylate-containing polymer is, for example, a copolymer from (a) styrol and/or ethylene and/or methyl methacrylate and/or methylacrylate and (b) glycidyl (meth) acrylate. A polymer which is particularly suitable as a glycidyl (meth)acrylate-containing polymer is a copolymer which is selected from the group consisting of styrol-methyl-methacrylate-glycidylmethacrylate, ethylene-methylacrylate-glycidylmethacrylate and ethylene-glycidylmethacrylate. Glycidyl(meth)acrylate is preferably contained therein in a quantity of from 1 to 60% by weight, in particular 5 to 55% by weight, more preferably 45 to 52% by weight, with respect to the entire composition of the polymer containing glycidyl (meth)acrylate.

Polymers containing epoxide groups which may be considered further include epoxide-group-containing copolymers based on styrol, ethylene, acrylic acid esters and/or methacrylic acid esters.

The admixture contains 0.05 to 3% by weight, preferably 0.1 to 2% by weight polymer containing epoxide groups, with respect to the entire composition.

The admixture may also contain, in addition to the main constituents starch or starch derivative, polyester and polymer containing epoxide groups, conventional additives such as, for example, processing additives, plasticisers, stabilisers, flame retardants and/or filling materials.

The method according to the invention makes provision for the admixture to be homogenised. The homogenisation may be carried out by any means which are familiar to the person skilled in the art in the field of plastics technology. The homogenisation of the admixture is preferably carried out by dispersing, stirring, kneading and/or extruding. According to a preferred embodiment of the invention, shear forces act on the admixture during the homogenisation. Suitable production methods for starchy thermoplastic polymers which can also be applied analogously to the production of the polymer material according to the invention are described, for example, in the publications EP 0 596 437 B1 and EP 0 917 540 B1.

According to a preferred embodiment of the invention, the admixture is heated during the homogenisation (for example, in the extruder), preferably to a temperature of from 90 to 250°C, in particular 130 to 220°C.

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It is preferable according to the invention for the water content of the admixture to be kept as low as possible. The water content of the admixture is adjusted to less than 1.5% by weight, preferably, less than 1% by weight, with respect to the entire composition.

- 10 The water content is preferably adjusted by drying during the homogenisation. The drying operation may be carried out, for example, by degassing the admixture or the melt, expediently by removal of water vapour during extrusion.

- According to another preferred embodiment of the invention, the polymer material produced according to the method according to the invention has thermoplastic properties. The material can preferably be processed thermoplastically.

- It is possible with the method according to the invention to produce plasticiser-free thermoplastic polymer blends which are based on starch, which have a starch content of at least 34% by weight and, at the same time, have outstanding mechanical properties. The term plasticiser-free means in this context in particular that the polymer blends do not contain any glycerol and/or sorbitol. It is possible to produce, from the polymer material produced according to the method according to the invention, in particular films which have an elongation at break according to DIN 53455 of at least 200% and/or a dart drop value according to ASTM D-1709 of at least 5 g/μm.

Therefore, the invention further relates to a starchy thermoplastically workable polymer material, wherein

- (a) the polymer material contains less than 3% by weight, with respect to the entire composition, of low-molecular substances and no glycerine and/or sorbitol, wherein low-molecular substances are substances with a molecular weight of less than 500 g/mol,
- (b) the starch proportion of the polymer material is at least 34% by weight,

(c) a film produced from the polymer material has an elongation at break in accordance with DIN 53455 of at least 200% and/or has a dart drop value in accordance with ASTM D-1709 of at least 5 g/ μ m

(d) the polymer material contains polyester and an epoxide-group-containing copolymer
5 with a molecular weight (M_w) of from 1,000 to 25,000.

The starchy material according to the invention contains less than 3% by weight of low-molecular substances and is thereby substantially free from plasticisers. The term low-molecular substances is intended to be understood according to the invention to be substances
10 having a molecular weight less than 500 g/mol, in particular less than 250 g/mol. Low-molecular substances according to the invention are in particular water, glycerol, sorbitol and/or mixtures thereof.

The polymer material according to the invention does not contain glycerol and/or sorbitol.
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According to a preferred embodiment of the invention, the starch proportion of the polymer material is at least 35% by weight, in particular at least 36% by weight, preferably at least 37% by weight, more preferably at least 38% by weight and, most preferably, at least 39% by weight.
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The polymer material according to the invention further contains, as further constituent, a polyester, preferably in a quantity of less than 70% by weight, in particular less than 65% by weight, even more preferably less than 60% by weight, most preferably less than 55% by weight.
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The polymer materials according to the invention are suitable for extremely varied purposes. The materials are suitable in particular for producing moulded components, films or fibres. Consequently, the invention also relates to moulded components, films or fibres produced from the materials according to the invention.
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The invention is described in greater detail below with reference to embodiments.

Example 1*Preparation of glycidyl-modified, starchy polymer material*

- 5 An admixture of native potato starch, aliphatic-aromatic copolyester and polymer containing epoxide groups in the quantity ratios set out below was poured into a two-shaft extruder.

A statistical copolyester based on 1,4-butanediol, adipic acid and terephthalic acid having a glass transition temperature (T_g) of -30 to -35°C and a melting range from 105 to 115°C
10 was used as the aliphatic-aromatic copolyester.

A statistical copolymer based on styrol-methyl methacrylate-glycidyl methacrylate having a molecular weight M_w of approximately 6800 and an epoxide group equivalent weight of 285 g/mol was used (additive A) as the polymer containing epoxide groups (glycidyl additive).
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The admixture was intensively mixed in the extruder in a temperature range from 150 to 190°C, the melt simultaneously being degassed in order to remove water from the admixture. There was produced a homogeneous melt which was able to be drawn off and granulated. The water content of the mass which is homogenised in the manner described and
20 which can be processed thermoplastically was less than 1% by weight.

By means of the starch being mixed and homogenised with aliphatic-aromatic copolyester, there was obtained a two-phase blend in which the starch forms the dispersed phase and the aliphatic-aromatic copolyester forms the continuous phase. The addition of polymer
25 containing epoxide groups (that is to say, polymer containing glycidyl) brought about an intramolecular and intermolecular chemical linkage of starch and aliphatic-aromatic copolyester, which significantly affected the mechanical properties of the thermoplastic blend produced.

30 Films having a thickness of approximately 40 µm were produced from the materials produced by blown film extrusion. To that end, the granulate was introduced into a single-shaft extruder (L/D = 30, cooled intake, sieve 250 µm), melted at from 165 to 190°C, blown over

an annular nozzle (mono, nozzle aperture 0.8 mm) to form the film hose (inflation ratio 3.5) and removed after being laid flat.

Example 2

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In this example, the influence of glycidyl additive on the mechanical properties of blown films having different starch contents was investigated.

10 Various starchy polymer materials were produced from an aliphatic-aromatic copolyester (from 59.5 to 66.1% by weight), native potato starch (from 33.4 to 40% by weight) and copolymer containing epoxide groups (0.5% by weight) according to Example 1. The quantity of the native potato starch was gradually varied at the expense of the aliphatic-aromatic copolyester between 33.4 and 40% by weight (see Figures 1 and 2).

15 By way of a comparative formulation, polymer material was produced according to the procedure described in Example 1 without any glycidyl additive from aliphatic-aromatic copolyester (66.6% by weight) and native potato starch (33.4% by weight).

20 After compounding the different formulation variants, blown films were produced from the polymer materials produced and the mechanical properties thereof determined. In particular, the tensile strength (ZF), elongation at break (RD), MFR (Melt Flow Rate) and dart drop values (puncture resistance) of the films were determined.

25 Figure 1 shows the tensile strengths and elongations at break of the films produced with different contents of starch.

In comparison with a standard film produced from the comparative formulation without glycidyl additive, the corresponding glycidyl-modified film having the same starch content (33.4% by weight) has a substantially higher tensile strength. This difference results, owing
30 to the tensile values which generally decrease with an increasing proportion of starch, in comparable tensile strengths of standard films having 33.4% of starch and glycidyl-modified films having 40% of starch.

Provided that the starch content is the same, the value for the elongation at break of the glycidyl-modified film does not differ from that of the standard film. Owing to the use of glycidyl additive, however, the level of elongation at break (= elasticity) can be kept above 400% even for a film having a starch proportion of 40%.

It should be taken into consideration that films composed of a polymer material having the same composition without glycidyl additive having a starch proportion of more than 34% are extremely granular, brittle and fragile so that it is practically impossible to establish mechanical parameters.

Figure 2 illustrates the MFR (Melt Flow Rate) and the dart drop values (puncture resistance) of glycidyl-modified films with increasing starch content.

Figure 2 sets out that both lines only descend slightly with increasing starch content. Whereas the dart drop values for the standard formulation without glycidyl additive and the modified formulation are at the same level, the glycidyl additive brings about an MFR reduction to less than half of the standard value.

The MFR level of the glycidyl-treated formulations, which is significantly reduced in comparison with the standard film without glycidyl additive, may be attributed – without being bound by any particular theory - to the epoxide-induced cross-linking of the polymer chains. Therefore, the MFR appears to be a suitable parameter for assessing the chemical conversion of corresponding chain-extending/cross-linking agents.

Noteworthy in Figure 2 are also the dart drop values which are stable over the entire range of the enrichment with starch. This provides confirmation of the observation which has already been made through plotting tensile strength and elongation at break (Figure 1), to the effect that material embrittling which generally increases with an increase in the starch proportion can be effectively combatted by the addition of reactive glycidyl additives.

Example 3

In this example, the influence of different glycidyl additives on the mechanical properties of blown films containing starch was investigated.

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Example 2 was repeated with three different polymers containing epoxide groups (glycidyl additives).

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Different starchy polymer materials were produced from an aliphatic-aromatic copolyester (59.5 to 66.1% by weight), native potato starch (33.4 to 40% by weight) and a copolymer containing epoxide groups (additive A, B or C, see below) (0.5% by weight) according to the procedure described in Example 1. The quantity of the native potato starch was varied stepwise between 33.4 and 40% by weight at the expense of the aliphatic-aromatic copolyester (see Figures 3 and 4).

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By way of a comparative formulation, polymer material without glycidyl additive was produced from aliphatic-aromatic copolyester (66.6% by weight) and native potato starch (33.4% by weight) according to the procedure described in Example 1.

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A statistical copolymer based on styrol-methyl methacrylate-glycidyl methacrylate having a molecular weight M_w of approximately 6800 and an epoxide group equivalent weight of 285 g/mol was used as additive A.

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A statistical copolymer based on ethylene methacrylate-glycidyl methacrylate having approximately 24% by weight of methacrylate, 68% by weight of ethylene and 8% by weight of glycidyl methacrylate and an epoxide group equivalent weight of 1775 g/mol was used as additive B.

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A statistical copolymer based on ethylene glycidyl methacrylate having approximately 92% by weight of ethylene and 8% by weight of glycidyl methacrylate and an epoxide group equivalent weight of 1775 g/mol was used as additive C.

The glycidyl additives used differ in particular in terms of their content of reactive epoxide units. The mass-related concentration of epoxide units is higher in additive A by a factor of 6.23 than in additives 2 and 3. Accordingly, additive B and additive C contain less than a sixth of the reactive epoxide groups in comparison with additive A, respectively, for the same original quantity by weight.

This significant difference affects in a correspondingly clear manner the properties of formulations produced in a comparable manner.

Figures 3 and 4 show by way of example the starch content-dependent development of the tensile strength and MFR of starchy polymer materials according to example 2, mixed with 0.5% respectively of the additives A, B or C.

Figure 3 shows that the tensile strength of the films increases linearly for additive A with an increasing starch content whereas it decreases for the additives 2 and 3.

Figure 4 shows that the MFR values, which all decrease slightly in a linear manner with an increasing starch proportion, are at a very low level for the material treated with additive A. However, a comparison of the materials treated with the additives 2 and 3 with a standard film without glycidyl additive does not allow identification of any significant influence of the glycidyl additive on the melt flow rate.

The line progressions illustrated in Figures 3 and 4 show that a perceptible influence of the additives 2 and 3 on the mechanical properties of the films can scarcely be established for the concentration used of 0.5% by weight. Nevertheless, an improvement of the compatibility of the constituents starch and polyester in comparison with the comparative formulation without glycidyl additive was also established for the additives B and C in the concentration used.

Example 4

In this example, the influence of different concentrations of polymer containing epoxide groups (glycidyl additive) on the mechanical properties of blown films having a starch content of up to 42% by weight was determined.

On a production installation (ZSK 70/7), the efficacy of different additive concentrations was first examined. To that end, materials having three different concentrations of additives were compounded (0.1% by weight of glycidyl additive, 0.5% by weight of glycidyl additive and a comparative formulation (standard) without any additive). Additive A from example 3 was used as the polymer containing epoxide groups.

Different starchy polymer materials were produced from aliphatic-aromatic copolyester (57.5 to 66.5% by weight), native potato starch (from 33.4 to 42% by weight) and a polymer containing epoxide groups (0.1 or 0.5% by weight) according to example 1. The quantity of the native potato starch was varied stepwise at the expense of the aliphatic-aromatic copolyester between 33.4 and 42% by weight (see Figures 5 and 6). Similarly, the quantity of the polymer containing epoxide groups (additive A) was varied at the expense of the aliphatic-aromatic copolyester.

Polymer material without glycidyl additive was produced as comparative formulation from aliphatic-aromatic copolyester (66.6% by weight) and native potato starch (33.4% by weight) in accordance with the procedure described in example 1.

Figure 5 shows the progression of the melt flow rate (MFR) of blown films produced from the materials in dependence on the starch content and the additive concentration. The values show that the melt flow rate (MFR) (i.e. the flowability) is reduced with increasing starch content and increasing glycidyl concentration in the materials. In comparison with the standard formulation (circle), the MFR value of the formulation having 42% by weight of starch and 0.5% by weight of glycidyl additive decreases to less than a fifth (triangle), an indication of extensive cross-linking of the polymers contained.

Without being bound by a specific theory, this progression may be explained by a cross-linking reaction of the glycidyl additive with the polyester or the starch. The abrupt halving of the MFR at 40% by weight of starch in the transition from the solid line to the broken line shows that the decreasing MFR value may not be attributed solely to an increase in the starch proportion (as is the case in the case of the solid line between 33 and 40% by weight) but instead decisively also to an increased conversion of the glycidyl additive which is used in a greater concentration.

Figure 6 illustrates the progression of the tensile strength (TS), elongation at break (EB) and dart drop (DD) for films having different contents of starch and glycidyl additive. Whereas TS and EB decrease with increasing starch content, the DD value remains at a constant level.

Figure 6 shows that the elongation at break, which decreases linearly with increasing starch proportion, is not perceptibly influenced by the addition of glycidyl additive. Even with 0.5 % by weight of additive proportion (solid line), the value decreases further after 40% by weight of starch is exceeded. The dart drop value (DD) remains at a constant level over the entire range investigated.

Without being bound to a specific theory, it is supposed that the effect of a DD value which generally decreases with an increase in the starch proportion (that is to say, the film becomes more brittle) is compensated for by the polymer cross-linking with the glycidyl additive. The strand linkage which is more extensive at a higher glycidyl additive content can be shown by a significantly higher tensile strength with the same starch proportion (abrupt transition of the broken line at 40% by weight of starch).

Example 5

In this example, the glycidyl additives 1 and 2 from example 3 were compared for equivalent glycidyl proportions.

Firstly, a starchy polymer material was produced from aliphatic-aromatic copolyester (59.9% by weight), native potato starch (40% by weight) and *additive A* from example 3 (0.1% by weight) according to the procedure described in example 1.

- 5 Subsequently, a starchy polymer material was produced from aliphatic-aromatic copolyester (59.4% by weight), native potato starch (40% by weight) and *additive B* from example 3 (0.6% by weight) according to the procedure described in example 1.

10 The two materials produced in that manner or blown films produced therefrom were compared with each other. Figure 7 shows the results.

Figure 7 shows that the additives 1 and 2 result in comparable material properties of the polymer material for glycidyl proportions (0.1% by weight of *additive A* versus 0.6% by weight of *additive B*) which are equivalent in terms of quantity. Only the value for the elongation at break (EB) is perceptibly higher for the film containing additive B.

15

As a result, the following can be established on the basis of the tests carried out:

20 The material properties of starchy polymer materials of the generic type can be significantly changed by the addition of additives containing glycidyl. Whereas conventional starchy polymer materials without glycidyl additive have unsatisfactory mechanical properties above approximately 34% by weight, even a content of 0.1% of glycidyl additive allows the production of a polymer material having a starch content of 40% by weight with outstanding mechanical properties at the same time.

25 Whereas the increase in the starch proportion is necessarily at the expense of the elasticity of the glycidyl-modified material, the puncture resistance of the glycidyl-modified material is not influenced by an increase in the starch proportion.

Without being bound to a specific theory, it is supposed that the glycidyl additive acts as a compatibiliser between the otherwise incompatible polymers starch and polyester. The efficiency of the polymer cross-linking manifests itself in increased tensile strength values with a simultaneously low melt flow rate (MFR).

5 The invention has been described above with reference to exemplary embodiments by way of example. It will be understood that the invention is not limited to the exemplary embodiments described. Instead, various development and modification possibilities arise for the person skilled in the art within the scope of the invention and the protective scope of the invention is fixed in particular by the appended patent claims.

The invention further relates to the following embodiments 1 to 41:

1. Method for producing a starchy polymer material, characterised by:

15 (a) producing an admixture containing at least

- from 1 to 75% by weight of starch and/or starch derivative
- from 10 to 85% by weight of polyester and
- 20 – from 0.01 to 7% by weight of a polymer containing epoxide groups;

(b) homogenising the admixture by supplying thermal and/or mechanical energy;

(c) adjusting the water content of the admixture, so that the end product has a water content of less than approximately 12% by weight with respect to the entire composition of the admixture.

2. Method according to embodiment 1, characterised in that the admixture contains 5 to 75% by weight, in particular 10 to 75% by weight, preferably 15 to 70% by weight, more preferably 25 to 55% by weight, most preferably 34 to 51% by weight of starch and/or starch derivative.

3. Method according to embodiment 1 or 2, characterised in that the admixture contains 20 to 85%, in particular 30 to 80% by weight, more preferably 40 to 80% by weight of polyester.

5 4. Method according to any one of the preceding embodiments, characterised in that the admixture contains 0.01 to 5% by weight, in particular 0.05 to 3% by weight, more preferably 0.1 to 2% by weight of a polymer containing epoxide groups.

10 5. Method according to any one of the preceding embodiments, characterised in that the polymer material is biodegradable in accordance with EN 13432.

6. Method according to any one of the preceding embodiments, characterised in that the polyester is selected from the group consisting of aliphatic-aromatic copolyester, aliphatic polyester, aromatic polyesters, PHA, PLA, PHB and PHBV.

15 7. Method according to any one of the preceding embodiments, characterised in that the polyester has a glass transition temperature (T_g) of less than 0°C , in particular less than -4°C , more preferably less than -10°C , even more preferably less than -20°C and most preferably less than -30°C .

20 8. Method according to any one of the preceding embodiments, characterised in that a copolyester, in particular a statistical copolyester, is used as the aliphatic-aromatic polyester, based at least on adipic acid.

25 9. Method according to any one of the preceding embodiments, characterised in that a copolyester, in particular a statistical copolyester, is used as the aliphatic-aromatic polyester, based at least on 1,4-butanediol, adipic acid and terephthalic acid or terephthalic acid derivative (e.g. dimethyl terephthalate DMT).

30

10. Method according to embodiment 10, characterised in that the polyester has a glass transition temperature (T_g) of -25 to -40°C , in particular -30 to -35°C , and/or a melting range of 100 to 120°C , in particular 105 to 115°C .

5 11. Method according to any one of the preceding embodiments, characterised in that the polyester is an aliphatic polyester selected from the group consisting of polyhydroxyvalerate, polyhydroxybutyrate-hydroxyvalerate copolymer and polycaprolactone.

10 12. Method according to any one of the preceding embodiments, characterised in that the polyester is an aliphatic polyester based on succinate, wherein the polyester is in particular selected from the group consisting of polybutylene succinate (PBS), polybutylene succinate adipate (PBSA) and polyethylene succinate (PES).

15 13. Method according to any one of the preceding embodiments, characterised in that the polyester is biodegradable in accordance with EN 13432.

14. Method according to any one of the preceding embodiments, characterised in that the polymer containing epoxide groups is a copolymer.

20 15. Method according to any one of the preceding embodiments, characterised in that the polymer containing epoxide groups is a glycidyl(meth)acrylate-containing polymer.

25 16. Method according to Embodiment 15, characterised in that the glycidyl(meth)acrylate-containing polymer is a copolymer from (a) styrol and/or ethylene and/or methyl methacrylate and/or methyl acrylate and (b) glycidyl(meth)acrylate.

17. Method according to embodiment 15 or 16, characterised in that the glycidyl(meth)acrylate-containing polymer is an epoxide group-containing copolymer based on styrol, ethylene, acrylic ester and/or methacrylic ester.

18. Method according to any one of embodiments 15 to 17, characterised in that the glycidyl(meth)acrylate-containing polymer is a copolymer which is selected from the group consisting of styrol-methylmethacrylate-glycidylmethacrylate, ethylene-methylacrylate-glycidylmethacrylate and ethylene-glycidylmethacrylate.

5

19. Method according to any one of embodiments 15 to 18, characterised in that the glycidyl(meth)acrylate-containing polymer contains glycidyl(meth)acrylate in a quantity of 1 to 60% by weight, in particular 5 to 55% by weight, more preferably 45 to 52% by weight with respect to the entire composition of the glycidyl(meth)acrylate-containing polymer.

10

20. Method according to any one of the preceding embodiments, characterised in that the polymer containing epoxide groups has a molecular weight (M_w) of 1,000 to 25,000, in particular 3,000 to 10,000.

15 21. Method according to any one of the preceding embodiments, characterised in that the admixture is homogenised by dispersing, stirring, kneading and/or extruding.

22. Method according to embodiment 21, characterised in that the admixture is homogenised by extrusion.

20

23. Method according to any one of the preceding embodiments, characterised in that the admixture is homogenised by shear forces acting on the admixture.

24. Method according to any one of the preceding embodiments, characterised in that during homogenisation or extrusion the admixture is heated to a temperature of 90 to 250°C, in particular 130 to 220°C.

25. Method according to any one of the preceding embodiments, characterised in that the water content of the admixture is set to less than 10% by weight, in particular to less than 7% by weight, more preferably to less than 5% by weight, in particular to less than 3% by weight, more preferably to less than 1.5% by weight and most preferably to less than 1% by weight with respect to the entire composition.

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26. Method according to any one of the preceding embodiments, characterised in that the water content of the admixture is set during homogenisation.

- 5 27. Method according to any one of the preceding embodiments, characterised in that the water content of the admixture is set by degassing the admixture, in particular by degassing the melt.

- 10 28. Method according to any one of the preceding embodiments, characterised in that the water content of the admixture is set by drying the admixture during homogenisation or extrusion.

- 15 29. Method according to any one of the preceding embodiments, characterised in that a film produced from the polymer material has a tensile strength in accordance with DIN 53455 of 5 to 60 N/mm², in particular of 10 to 40 N/mm².

30. Method according to any one of the preceding embodiments, characterised in that a film produced from the polymer material has an elongation at break in accordance with DIN 53455 of 100 to 1,000 %, in particular of 200 to 800 %.

20

31. Polymer material produced according to a method according to any one of embodiments 1 to 30.

P a t e n t k r a v

5 1. Fremgangsmåde til fremstilling af et stivelsesholdigt polymert materiale med et indhold af lavmolekylære substanser på mindre end 3 vægt-%, i forhold til den samlede sammensætning, hvor de lavmolekylære substanser er udvalgt blandt vand, glycerin, sorbitol og/eller blandinger deraf, og hvor slutproduktet har et vandindhold på mindre end 1,5 vægt-% i forhold til blandingens samlede sammensætning, **kendetegnet ved:**

- 10 (a) Fremstilling af en blanding indeholdende mindst
- 1 til 75 vægt-% stivelse og/eller stivelsesderivat,
- 10 til 85 vægt-% polyester og
- 0,05 til 3 vægt-% af en glycidyl(meth)acrylatholdig polymer;
(b) homogenisering af blandingen under tilførsel af termisk og/eller mekanisk energi;
15 (c) indstilling af blandingens vandindhold, således at slutproduktet har et vandindhold på mindre end 1,5 vægt-% i forhold til blandingens samlede sammensætning.

20 2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** blandingen indeholder 5 til 75 vægt-%, især 10 til 75 vægt-%, fortrinsvis 15 til 70 vægt-%, mere foretrukket 25 til 55 vægt-%, mest foretrukket 34 til 51 vægt-% stivelse og/eller stivelsesderivat; og/eller
at blandingen indeholder 20 til 85 vægt-%, især 30 til 80 vægt-%, mere foretrukket 40 til 80 vægt-% polyester; og/eller
25 at blandingen indeholder 0,05 til 3 vægt-%, mere foretrukket 0,1 til 2 vægt-%, glycidyl(meth)acrylatholdig polymer.

30 3. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** det polymere materiale kan nedbrydes biologisk i henhold til EN 13432.

35 4. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** polyesteren er udvalgt fra gruppen bestående af alifatisk-aromatisk copolyester, alifatisk polyester, aromatisk polyester, PHA, PLA, PHB og PHBV; og/eller at polyesteren har en glasovergangstemperatur (Tg) på mindre end 0°C, især mindre end -4°C, mere foretrukket mindre end -10°C, endnu mere foretrukket

mindre end -20°C og mest foretrukket mindre end -30°C.

5. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** der som alifatisk-aromatisk polyester anvendes en copolyester, især en statistisk copolyester, på basis af mindst adipinsyre; og/eller at der som alifatisk-aromatisk polyester anvendes en copolyester, især en statistisk copolyester, på basis af 1,4-butandiol, adipinsyre og hhv. terephthalsyre og terephthalsyrederivat (f.eks. dimethylterephthalat DMT), hvor polyesterens eventuelt har en glasovergangstemperatur (T_g) på -25 til -40°C, især -30 til -35°C, og/eller et smelteområde på 100 til 120°C, især 105 til 115°C.
6. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** polyesterens er en alifatisk polyester udvalgt fra gruppen bestående af polyhydroxyvalerat, polyhydroxybutyrat-hydroxyvalerat-copolymer og polycaprolacton; og/eller at polyesterens er en alifatisk polyester på succinat-basis, hvor polyesterens især er udvalgt fra gruppen bestående af polybutylensuccinat (PBS), polybutylensuccinatadipat (PBSA) og polyethylensuccinat (PES); og/eller at polyesterens kan nedbrydes biologisk i henhold til EN 13432.
7. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** den glycidyl(meth)acrylatholdige polymer er en copolymer.
8. Fremgangsmåde ifølge krav 7, **kendetegnet ved, at** den glycidyl(meth)acrylatholdige polymer er en copolymer af (a) styren og/eller ethylen og/eller methylmethacrylat og/eller methylacrylat og (b) glycidyl(meth)acrylat; og/eller at den glycidyl(meth)acrylatholdige polymer er en epoxidgruppeholdig copolymer på basis af styren, ethylen, acrylsyreester og/eller methacrylsyreester; og/eller at den glycidyl(meth)acrylat-holdige polymer er en copolymer, som er udvalgt fra gruppen bestående af styren-methylmethacrylat-glycidylmethacrylat, ethylen-methylacrylat-glycidylmethacrylat og ethylen-glycidylmethacrylat; og/eller at den glycidyl(meth)acrylatholdige polymer indeholder glycidyl(meth)acrylat i en mængde på 1 til 60 vægt-%, især 5 til 55 vægt-%, mere foretrukket 45 til 52 vægt-%, i forhold til den samlede sammensætning af den glycidyl(meth)acrylatholdige polymer.

9. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** den glycidyl(meth)acrylatholdige polymer har en molekylvægt (M_w) på 1.000 til 25.000, især 3.000 til 10.000.

5 **10.** Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** homogeniseringen af blandingen foregår ved dispergering, omrøring, æltning og/eller ekstrudering; og/eller at homogeniseringen af blandingen foregår ved indvirkning fra forskydningskræfter på blandingen.

10 **11.** Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** blandingen opvarmes ved hhv. homogenisering og ekstrudering til en temperatur på 90 til 250 °C, især 130 til 220 °C; og/eller at blandingens vandindhold indstilles til mindre end 1,5 vægt-%, fortrinsvis mindre end 1 vægt-%, i forhold til den samlede sammensætning; og/eller at blandingens vandindhold indstilles under homogeniseringen; og/eller at blandingens vandindhold indstilles ved afgangning af smeltemassen, især ved afgangning af smeltemassen; og/eller at blandingens vandindhold indstilles ved tørring af blandingen under hhv. homogeniseringen og ekstruderingen.

20 **12.** Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** en folie, der er fremstillet af det polymere materiale, har en trækstyrke i henhold til DIN 53455 på 5 til 60 N/mm², især på 10 til 40 N/mm²; og/eller at en folie, der er fremstillet af det polymere materiale, har en rivestyrke i henhold til DIN 53455 på 100 til 1000 %, især på 200 til 800 %.

25 **13.** Stivelsesholdigt termoplastisk forarbejdbart polymert materiale, **kendetegnet ved, at**

(a) det polymere materiale indeholder mindre end 3 vægt-%, i forhold til den samlede sammensætning, lavmolekylære substanser og ingen glycerin og/eller sorbitol, hvor lavmolekylære substanser er substanser med en molekylvægt på mindre end 500 g/mol,

(b) det polymere materiales stivelsesandel udgør mindst 34 vægt-%,

(c) en folie, der er fremstillet af det polymere materiale, har en rivestyrke i henhold til DIN 53455 på mindst 200 % og/eller en dart-drop-værdi i henhold til ASTM D-1709 på mindst 5 g/μm,

(d) det polymere materiale indeholder polyester og en epoxidgrupp持idig copolymer med en molekylvægt (M_w) på 1.000 til 25.000.

5 **14.** Polymert materiale ifølge krav 13, **kendetegnet ved, at** det polymere materiales stivelsesandel er mindst 35 vægt-%, især mindst 36 vægt-%, fortrinsvis mindst 37 vægt-%, mere foretrukket mindst 38 vægt-% og mest foretrukket mindst 39 vægt-%.

10 **15.** Polymert materiale ifølge et af kravene 13 eller 14, **kendetegnet ved, at** en folie, der er fremstillet af det polymere materiale, har en rivestyrke i henhold til DIN 53455 på mindst 300 % og/eller en dart-drop-værdi i henhold til ASTM D-1709 på mindst 10 g/ μ m; og/eller at det polymere materiale som yderligere bestanddel indeholder en polyester, fortrinsvis i en mængde på mindre end 70 vægt-%, især på mindre end 65 vægt-%, mere foretrukket på mindre end 60
15 vægt-%, mest foretrukket på mindre end 55 vægt-%.

16. Anvendelse af et polymert materiale ifølge et af de foregående krav til fremstilling af formdele, folier eller fibre.

20 **17.** Formdele, folier eller fibre, indeholdende et polymert materiale ifølge et af kravene 13 til 15.

Effect of starch proportion on tensile strength and elongation at break

(Glycidyl additive content in each case 0.5 wt.%)

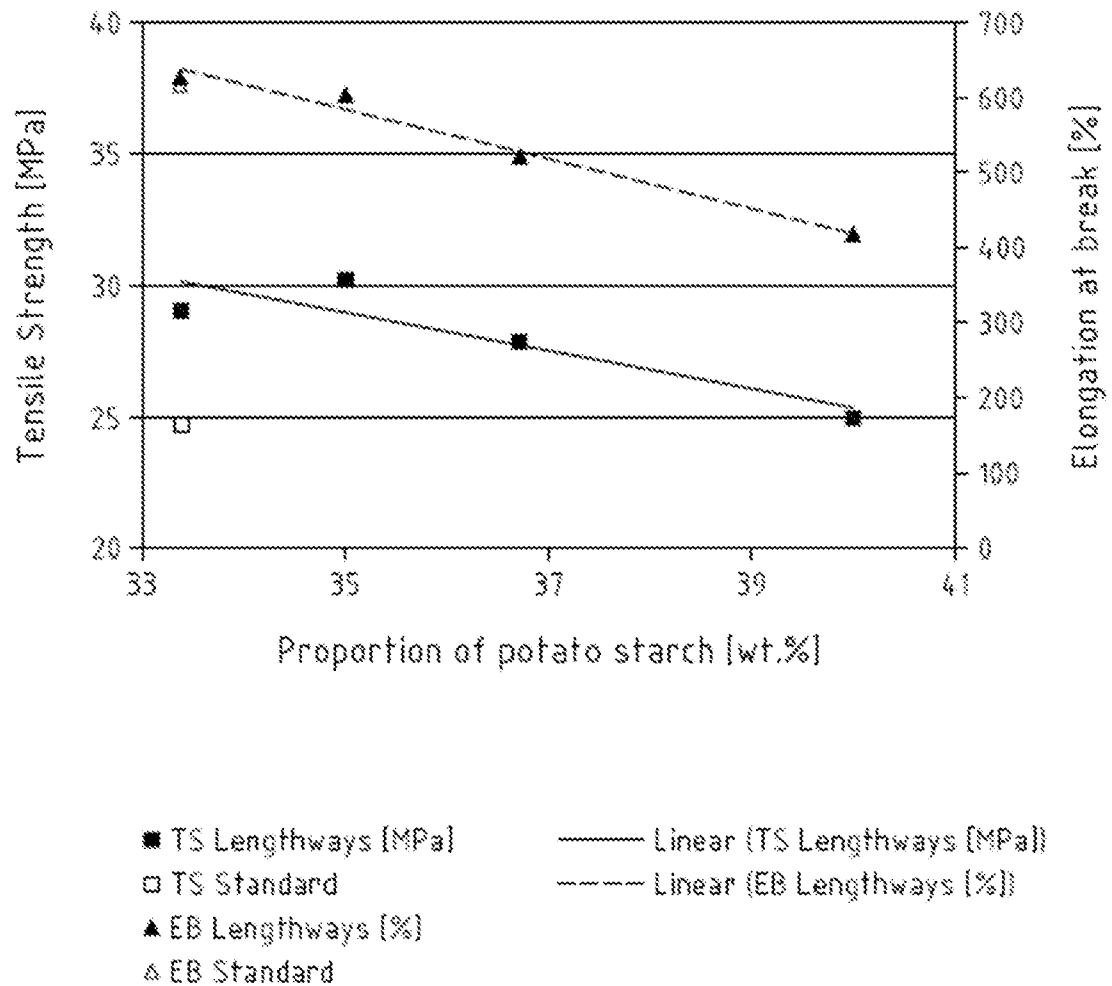


Fig.1

Effect of starch proportion on MFR and dart drop
(Glycidyl additive content in each case 0.5 wt.%)

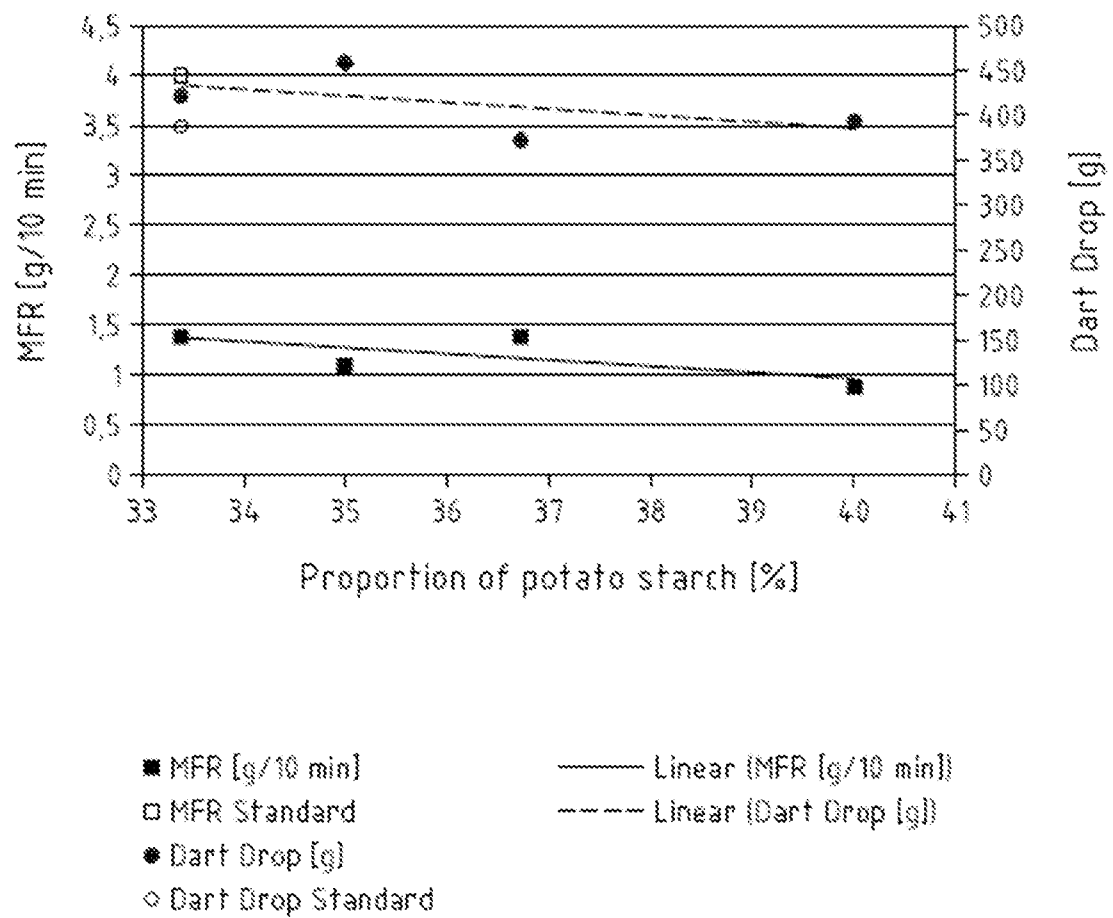


Fig.2

Effect of different glycidyl additives on the tensile strength

(Glycidyl additive content in each case 0.5 wt.%)

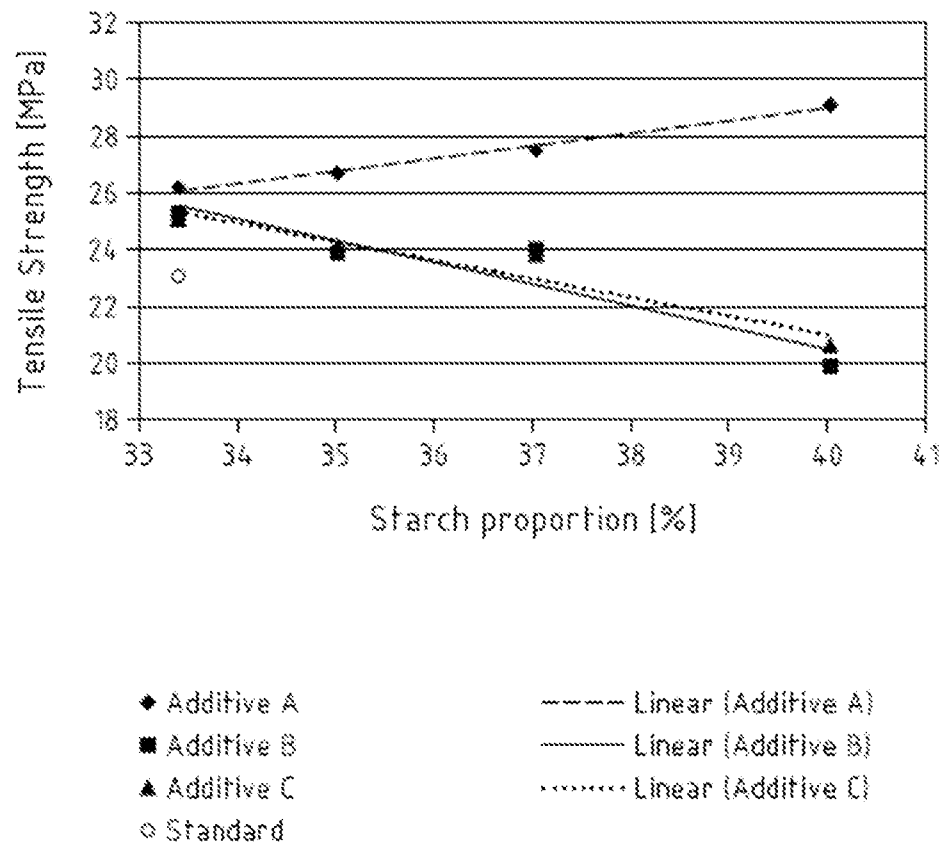
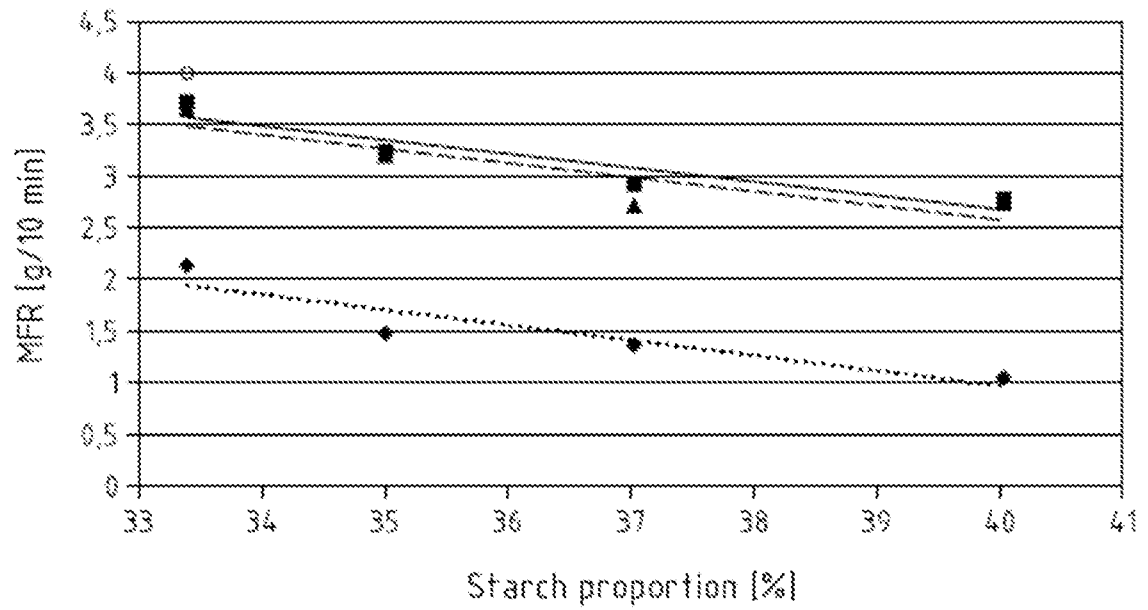


Fig.3

Effect of different glycidyl additives on the MFR course

(Glycidyl additive content in each case 0.5 wt.%)



- ◆ Additive A
- Additive B
- ▲ Additive C
- Standard
- Linear (Additive A)
- Linear (Additive B)
- Linear (Additive C)
- Linear (Standard)

Fig.4

Effect of different proportion of glycidyl additive
on the MFR course

(190 °C, 5 kg)

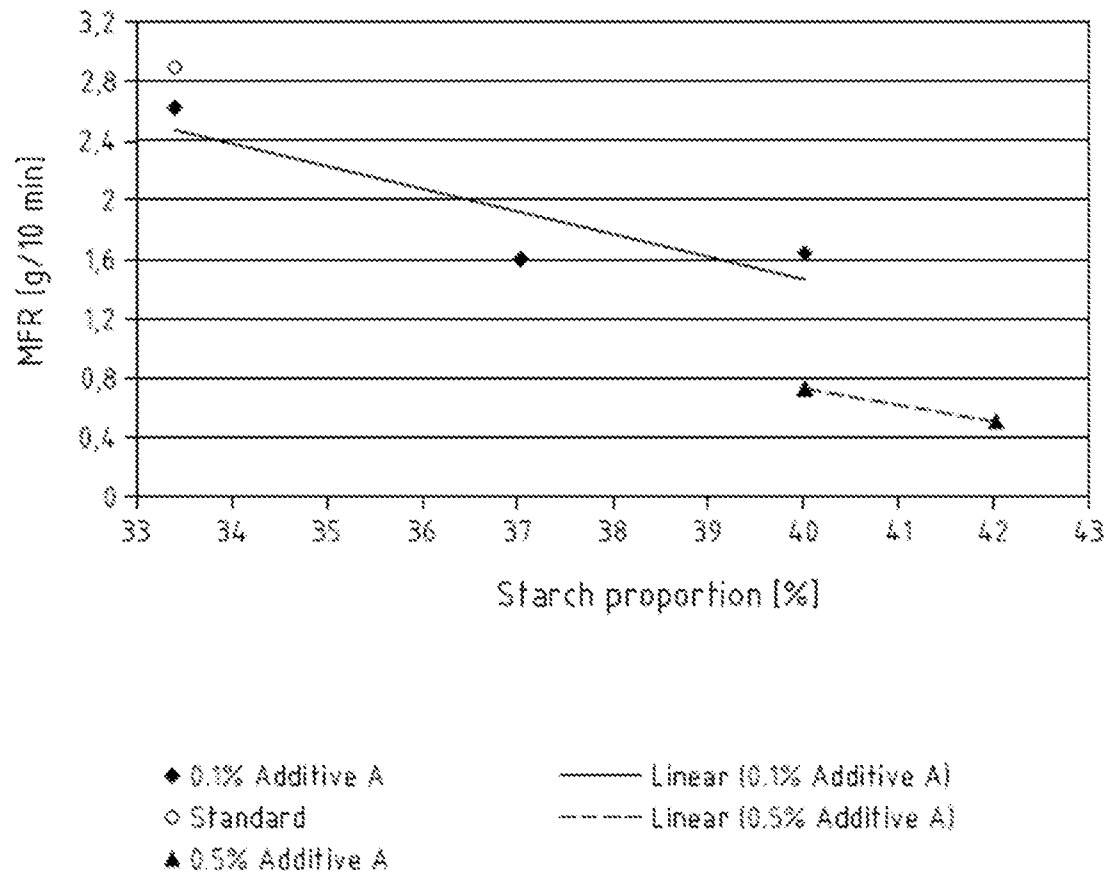


Fig.5

Effect of different proportions of glycidyl additive on elongation
at break and tensile strength

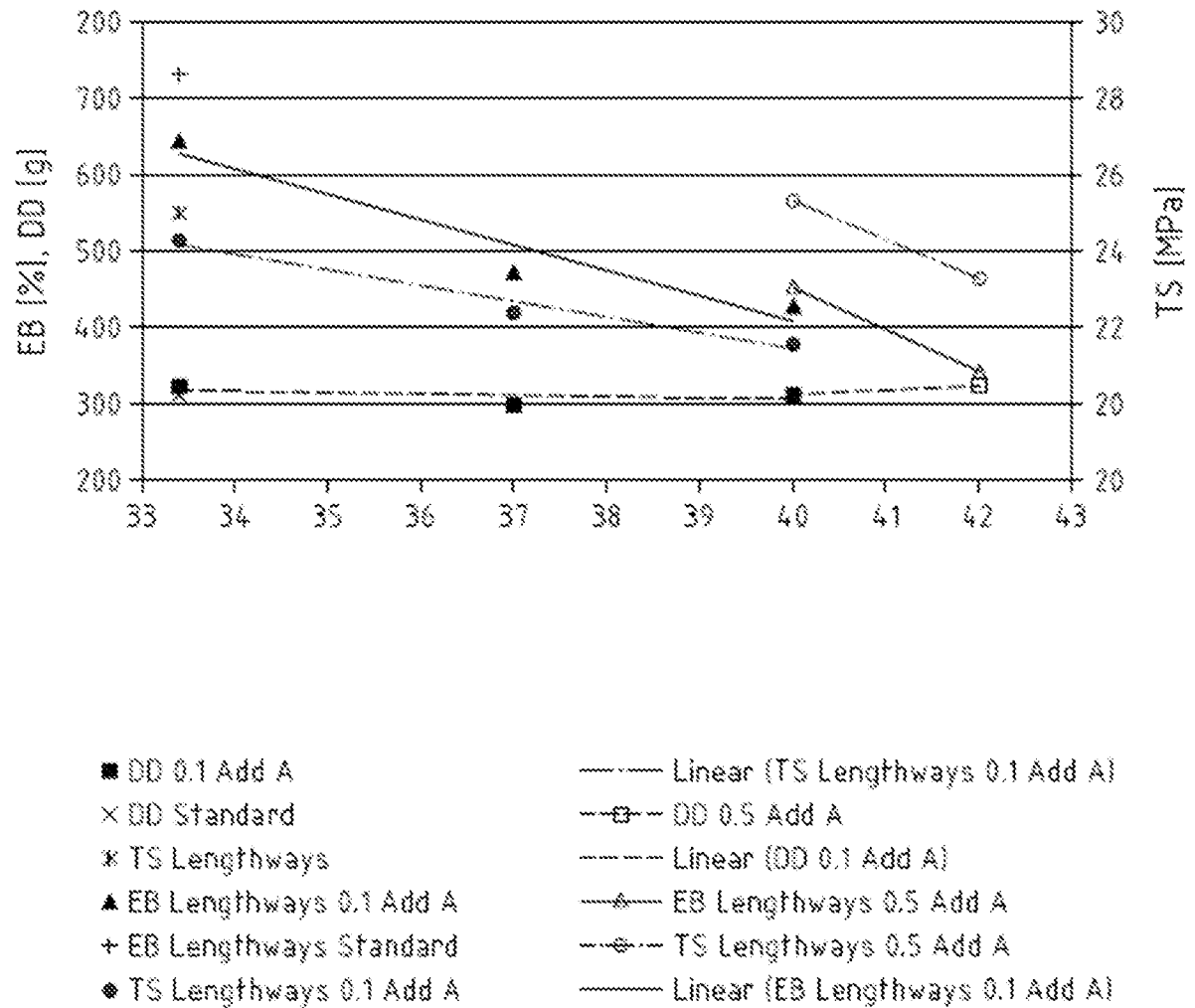


Fig.6

Comparison of different glycidyl additives with
equivalent glycidyl proportions

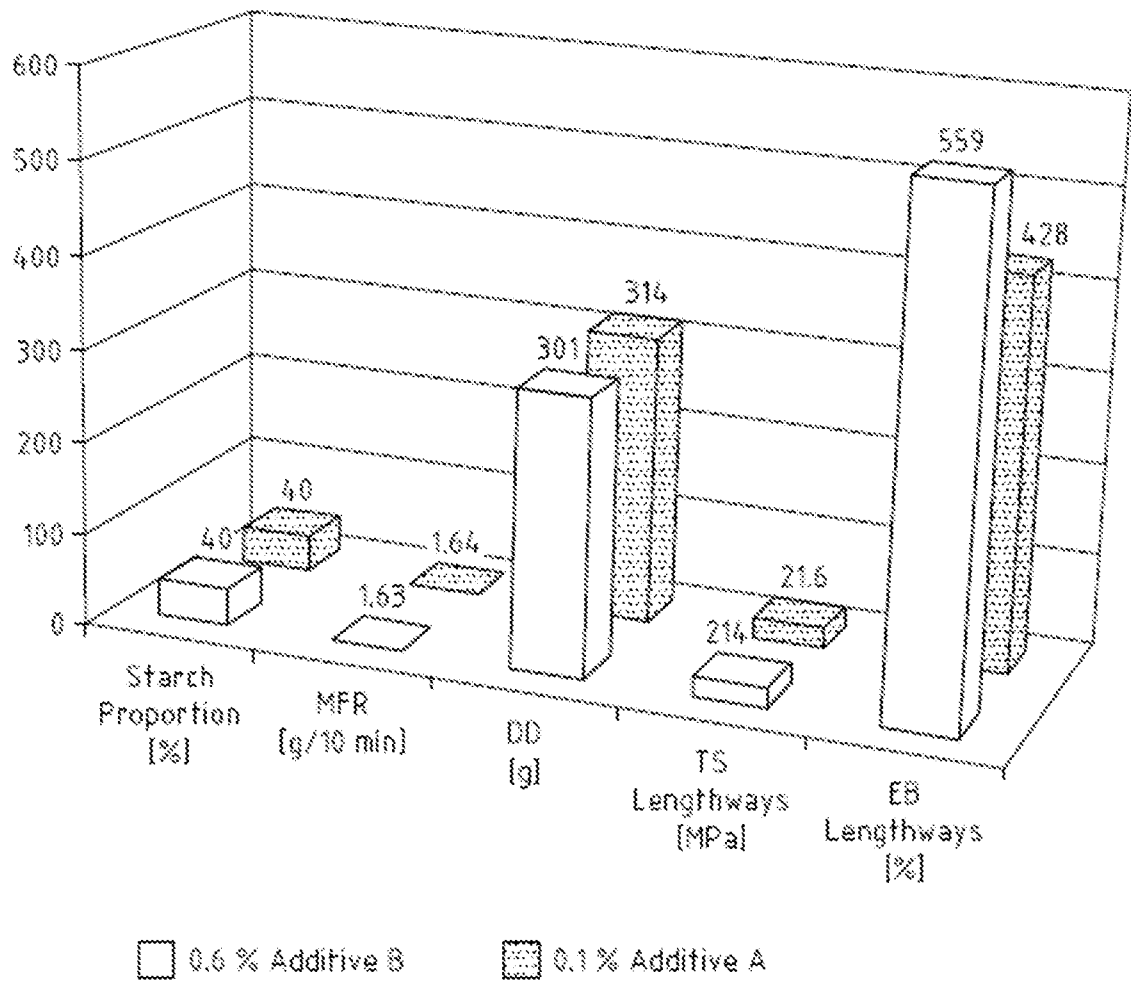


Fig.7