

A present invention concerns a polymer compound comprising essentially starch, a softener, a polyolefin, a process for production of a polymer compound, an application for this and also a sheet and a form. Polymer compounds with starch are known, whereby a starch or other polymers also used, preferably on a basis of their biodegradability, their attractive price and their independence of mineral oil products.

Use of biological polymers as a technical synthetic material is described in various patent documents. Ways in which native starch, gelatin or other bio-polymers are modified so that they can be used as technical polymers, are described in EP-011 82 40, EP-28 24 51, EP-32 65 14, GB-22 14 919 and EP-32 75 05. Here this occurs by means of extrusion or kneading of starch or a bio-polymer with aid of water taken up into bio-polymers or starch concerned, or through addition of additional water, where however, even a relatively large water content present is highly undesirable during extrusion of a bio-polymer broken down in this way.

Contrary to this, it is proposed in PCT-W090-05 161, that native starch be converted into a technically usable polymer, that is, into so-termed thermoplastic processable starch, without water and using additives or softeners, such as glycerine for example. Certainly, processability and water-resistance of a starch-polymer concerned is better than that of starch-polymers produced in accordance with a production process described above, however mechanical properties and, in particular, water resistance are still insufficient for many applications, particularly such as production of sheets.

For this reason, it is proposed in a number of patent documents such as EP-040 28 26, EP-040 47 23, EP-40 47 27, EP-40 47 18 and EP-40 73 50, that starch be mixed with thermoplastic synthetic materials such as polyolefins, polyalcohols, ABS copolymers, ethylene-acrylate-copolymers, copolymers of vinyl pyrrolidines, copolymers with amino groups etc, and to produce polymer blends. With this there is however a problem that compatibility of starch concerned and other polymers is insufficient or mixing of phases of individual polymers is poor.

This is shown for example when producing sheets from these materials, where a non-starch content of a polymer present in this mixture produced, by itself, as a sheet, that is, formed with accordingly substantially thinner wall thickness, has better resistance to tearing than a corresponding thicker sheet produced from an overall polymer mixture concerned.

In accordance patent documents EP-40 05 31 and EP-40 05 32, it is proposed that starch concerned, as in W090-05 161, be processed by means of a high-boiling softener, in order to obtain thermoplastically processable starch to then mix with ethylene acrylate and/or polyvinyl/alcohol copolymers. Sheets produced from these starch polymer mixtures have a better resistance to tearing, although they are still adversely affected by moisture.

This also applies to starch-polymer mixtures which are produced in accordance with W090-14 388, where polyethylenes and ethylene-acrylate-copolymers are mixed with glycerine starch.

In EP-A-402 826, starch is used in production of a polar ethylene-copolymer, where starch fibres are worked in in an unmelted state.

Starch fibres are also mixed in with ethylene copolymers as a filler, in an unmelted state, in a temperature range of 100 to 175°C.

A present invention therefore offers a polymer compound, essentially comprising starch, which is particularly suited to production of sheets which, in forms and extruded bodies, such as sheets for example, result in good mechanical qualities and non-susceptibility to moisture.

In accordance with a present invention, this is achieved by means of a polymer compound in accordance with a claim 1 and/or by means of a polymer compound produced in accordance with a process in accordance with claim 4.

A polymer compound comprising essentially starch and a polyolefin obtained by means of substantially water-free mixing, that is, by mixing, with a water content of at most 28%, of thermoplastically processable starch with at least one polyolefin and at least one ethylene-acrylate-monoacid-anhydride-copolymer and, where applicable, a vinyl bond having an anhydride function, as a substitute. Reference is made, in particular, to W090 05 161, for a definition of and production of thermoplastically processable starch.

A copolymer and/or a vinyl bond in a polymer compound proposed in accordance with a present invention act as a phase agent between a starch phase and a polyolefin phase. A copolymer concerned includes both hydrophobic and hydrophilic constituents and thereby penetrates a phase boundary between a starch and a polyolefin concerned.

A polymer compound proposed in accordance with a present invention is obtained by mixing essentially up to 70% thermoplastically processable starch, containing at least one

softener, with 10-90% weight polyolefin and 1-35% weight ethylene-acrylate-monoacid-anhydride-copolymer.

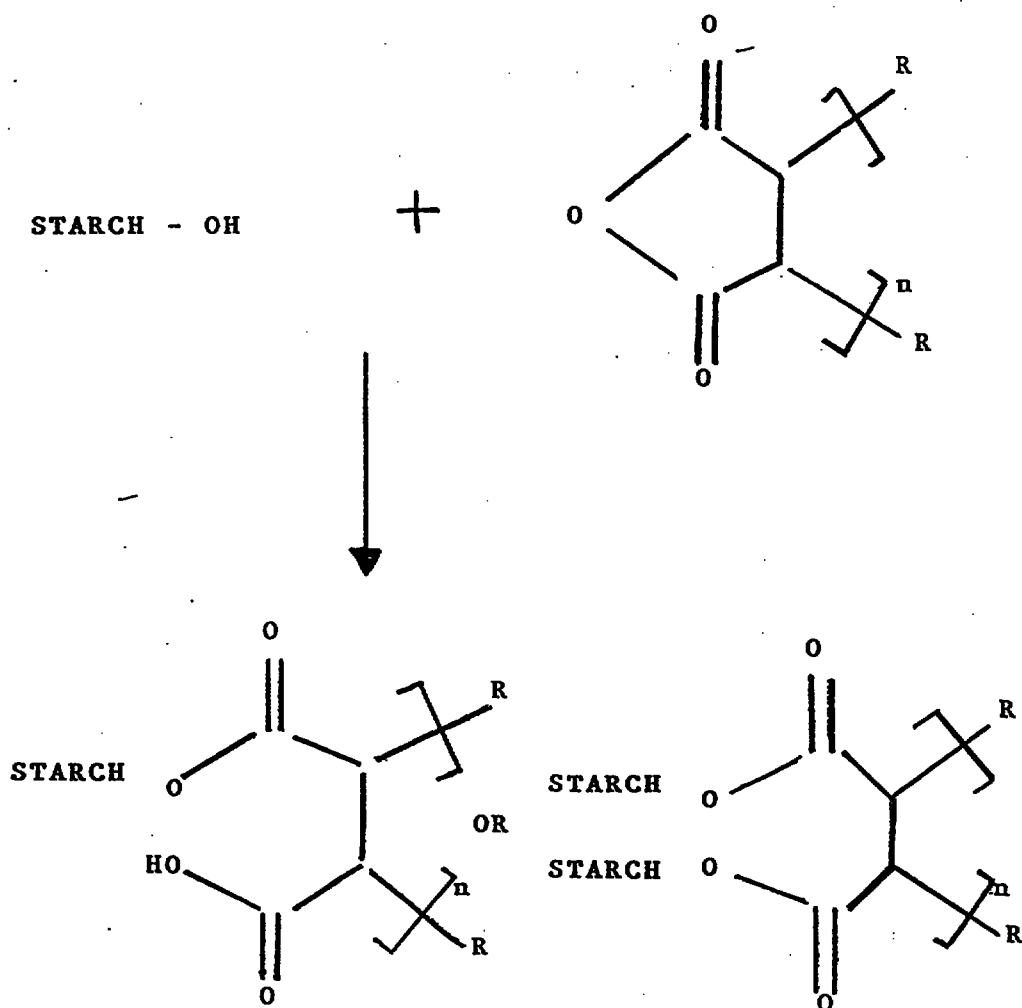
In order to realize both good mechanical values such as solidity of forms and extruded materials such as sheets as well as high sensitivity to moisture, it is proposed, in accordance with a present invention, that 45-70% weight, preferably 50-65% thermoplastically processable starch, containing at least one softener from a series comprising glycerine, urea, an amino-alcohol, sorbitol and/or succinic acid anhydride, be mixed with 10-40% weight, preferably 20-35% polyethylene or polypropylene, and 10-35% weight, preferably 15-25% ethylene-acrylate-monoacid-anhydride-copolymer. Both sensitivity to moisture and also high solidity are influenced by components of polyolefin and of a copolymer concerned, whereby also a too high content of these two constituents in a compound concerned is undesirable for reasons of pricing.

A too high content of these constituents in sheets leads to increase in gas permeability while, with a high starch content, oxygen permeability through such sheets for example is low.

For production of above-mentioned polymer compounds in accordance with a present invention, it is proposed that native starch and/or a derivative of this with 15-40% weight of at least one softener, such as glycerine, urea, an amino-alcohol, sorbitol and/or succinic acid anhydride be mixed, substantially free of water, to produce thermoplastically processable starch, whereupon starch produced in this way, in a melted material in a temperature range from 165-210°C, is mixed with a polyolefin, preferably such as polyethylene and/or polypropylene, and an ethylene-acrylate-monoacid-

anhydride-copolymer and/or a vinyl bond having an anhydride function as a substitute.

With this mixing process, monoacid-anhydride groups and/or an anhydride function in copolymers are esterified by free hydroxyl groups in starch in accordance with a following general reaction sequence:



A polyolefin concerned, such as polyethylene or polypropylene for example, forms a type of matrix in which starch is enclosed. In order, however, to produce a strong bond between polyethylene and/or polypropylene and starch and/or both phases, a copolymer concerned and/or a vinyl bond acts, as mentioned above, such that good mechanical values such as solidity are correspondingly realized with forms, and/or sheets produced from a polymer compound concerned.

This bonding on a phase boundary is, as mentioned above, achieved with aid of a copolymer, whereby an above-mentioned esterizing reaction is responsible for this. That a stated reaction occurs on mixing of starch and a copolymer concerned, can be shown from a relevant infra-red spectrum. This evidence in a relevant infra-red spectrum is dealt with below.

Favoured implementation variations of a process in accordance with a present invention, particularly such as production of thermoplastically processable starch and ethylene-acrylate-monoacid-anhydride-copolymer, are characterized by the wording of any one of claims 5 to 8.

It should again be noted here that, concerning production of thermoplastically processable starch, reference should be made to W090-05 161.

Polymer compounds produced in accordance with a present invention are particularly suitable for production of single or multi-layered sheets. In addition, production of a sheet concerned can occur immediately after production of a polymer compound, by extruding a polymer compound melt by means of a fish-tail nozzle or a blast head. It is however also possible to firstly granulate a polymer compound concerned and to subsequently process a granulated material concerned to form a sheet.

In particular, it is also possible to coextrude a polymer compound in accordance with a present invention together with other polymers to form multi-layered sheets, whereby, for example, a three-layered sheet can contain a layer produced from a polymer compound in accordance with a present invention, in each case as an outer layer, while a middle

layer is produced essentially from thermoplastically processable starch.

It is also possible to add a propellant such as sodium carbonate or an organic acid for example, to a polymer compound concerned before it is extruded, whereby an organic acid concerned can be citric acid for example.

Of course, it is also possible to produce forms or extruded materials such as tubes, from polymer compounds proposed in accordance with a present invention, with a composition of a polymer compound concerned being decided, within limits in accordance with a present invention, depending on requirements for a product to be produced.

A present invention is now explained in detail in connection with following examples of implementation and in relation to annexed figures. These figures are as follows:

Fig. 1 Infra-red spectrums of a polymer compound concerned at a start and an end of a mixing process,

fig. 2 a heat-flow diagram of native starch with glycerine,

fig. 3 a heat-flow diagram of thermoplastically processable starch,

fig. 4 a heat-flow diagram for use of thermoplastically processable starch, mixed with an ethylene-acrylate-monoacid-anhydride-copolymer, and

fig. 5 a heat-flow diagram for use of native starch and glycerine, mixed with an ethylene-acrylate-monoacid-anhydride-copolymer.

1. Production of thermoplastically processable starch

Here this is based on dried, native starch, whereby a water-content of starch concerned is preferably less than 1% weight. Native starch is converted with a suitable softener such as glycerine, whereby 25 - 35% weight glycerine, in relation to an overall compound, is added. A starch/glycerine compound is then intensively mixed in an extruder, within a temperature range of 160-190°C, preferably with a high level of shearing, whereby this mixing can of course also occur in a kneader.

Other materials such as urea, sorbitol, succinic acid anhydride, amino-alcohols and such like are also of course suitable as softeners, whereby, here, WO90 05 161, in which a series of appropriate softeners and/or additives are defined, was again referred to.

Further processing of thermoplastically processable starch produced in this way can occur directly in a same extruder, or starch concerned can first be granulated.

2. Ethylene-acrylate-monoacid-anhydride-copolymer

Further details of production of this copolymer are not given here; this involves standard products, and is moreover not part of a present invention.

Copolymers appropriate for a present invention preferably have a composition as follows:

contents by weight

ethylene	80-95% weight
acrylate methyl ester	5-15% weight
monoacid-anhydride	0.2-1% weight

In a following example of a polymer compound produced in accordance with a present invention, a copolymer with following contents by weight was used:

ethylene	88.0% weight
acrylate methyl ester	9.0% weight
acrylate ethyl ester	2.5% weight
monoacid anhydride	0.5% weight

3. Production of a starch-ethylene-copolymer compound

After production of a thermoplastically processable starch in accordance with point 1., a homogenous compound of polypropylene and a copolymer in accordance with point 2. was added to a starch melt in a same extruder, at a start of a second mixing zone at a temperature set for an extruder concerned of 170°C. A mass temperature at this point was approx. 190 to 200°C. Starch-polyethylene-copolymer compound was then mixed into this second mixing zone with intensive shearing, whereby this shearing was produced by means of kneading blocks and backwash elements. Preferably, a co-kneader or double-shafted extruder is used for mixing concerned. A total input of mechanical energy was approximately 0.4 KWh/Kg.

Quantities of added polyethylene and a copolymer concerned are summarized in a following table.

A high-density polyethylene produced by BASF was, furthermore used as polyethylene. A softener content and/or a content of glycerine in a thermoplastically processable starch used is likewise shown in a following table.

Sheets as stated in a following table, were produced with polymer compounds in accordance with a present invention, which were tested for tensile stress and extension. Measurements accordingly recorded are likewise given in a following table.

Starch-polyethylene-copolymer compounds produced in accordance with a present invention

Water content	softener (% weight)	TPS/P/K*	tensile strength	tensile strength at flow limit	extension %
2.8	18.6	50:20:30	18.2	-	95.0
0.5	25.7	15:10:40	15.9	-	43.0
0.5	25.7	50:25:25	12.2	-	168.0
0.5	25.7	65:21:14	12.0	-	78.0
0.5	25.7	50:15:35	16.6	-	59.0
0.5	25.7	55:32:13	16.2	-	53.0
0.8	19.1	55:13:32	17.5	-	30.0
0.8	17.3	50:15:35	16.7	-	26.5
0.8	17.3	60:12:28	15.7	-	14.0
0.5	12.0	50:15:35	20.5	21.0	290 (longitudinal direction)
0.5	12.0	50:15:35	20.5	21.0	290 (longitudinal direction)

* TPS - thermoplastically processable starch, P - copolymer, K - polyethylene

Concerning tensile strength, it is clear that a selected mixing ratio between separate constituents exerts only a relatively weak influence. By contrast, however, with extension, contents of polyethylene and a copolymer have a relatively large effect, whereby both a relatively low polyethylene content and a low copolymer content lead to a relatively low level of extension in a sheet.

4. Estering reaction

During implementation of a process of mixing thermoplastically processable starch, polyethylene and ethylene-acrylate-monoacid-anhydride-copolymer in an extruder, there is an esterification reaction of monoacid-anhydride groups in a copolymer with hydroxyl groups of starch. Such an esterification reaction is moreover also possible between monoacid-anhydride groups and glycerine which has been added to starch as a softener; this reaction is nevertheless relatively uncommon.

As evidence of this reaction, samples were taken from a polymer compound concerned at a start and end of a mixing stretch in an extruder concerned and corresponding infra-red spectrums were recorded which are shown in fig. 1. In addition, fig. 1 also shows that infra-red-active molecule oscillations of anhydride groups occur at a $1,780\text{ cm}^{-1}$ point. Alongside this, infra-red-active oscillations of ester groups can be seen at $1,740\text{ cm}^{-1}$.

Curve 1 shows an infra-red spectrum at a start of a mixing process and curve 2 shows an infra-red spectrum after an end of a mixing process.

In addition, infra-red spectrums of samples along a mixing-stretch showed that intensity of peaks of anhydride groups decreases with increasing duration of mixing while intensity of ester oscillations increases.

Figs. 2 and 3 show heat-flow diagrams of native starch and glycerine and/or of thermoplastically processable starch.

Figs. 4 and 5 record an esterification reaction in a heat-flow calorimeter, with a heat-rate of $10^{\circ}/\text{min}$. In addition, a course of an exothermic reaction is shown, with a range of from 165°C to 207°C , with an observable maximum peak at 190°C .

Fig. 4 is based on thermoplastically processable starch with addition of ethylene-acrylate-monoacid-anhydride-copolymer and fig. 5 is for native starch and glycerine.

Polymer compounds, defined above, in accordance with a present invention, comprising thermoplastically processable starch, a polyolefin, such as, for example, above-mentioned polyethylene, and also an ethylene-acrylate-monoacid-anhydride-copolymer are suitable for production of any form or extruded material. Polymer compounds in accordance with a present invention are specially suited to production of sheets, whereby this can be a single-layer sheet, whereby, for its production, a polymer compound defined by a present invention can be coextruded together with thermoplastically processable starch.

It furthermore needs to be mentioned that instead of ethylene-acrylate-monoacid-anhydride-copolymer any vinyl bonds can be used which carry an anhydride function as a substitute.

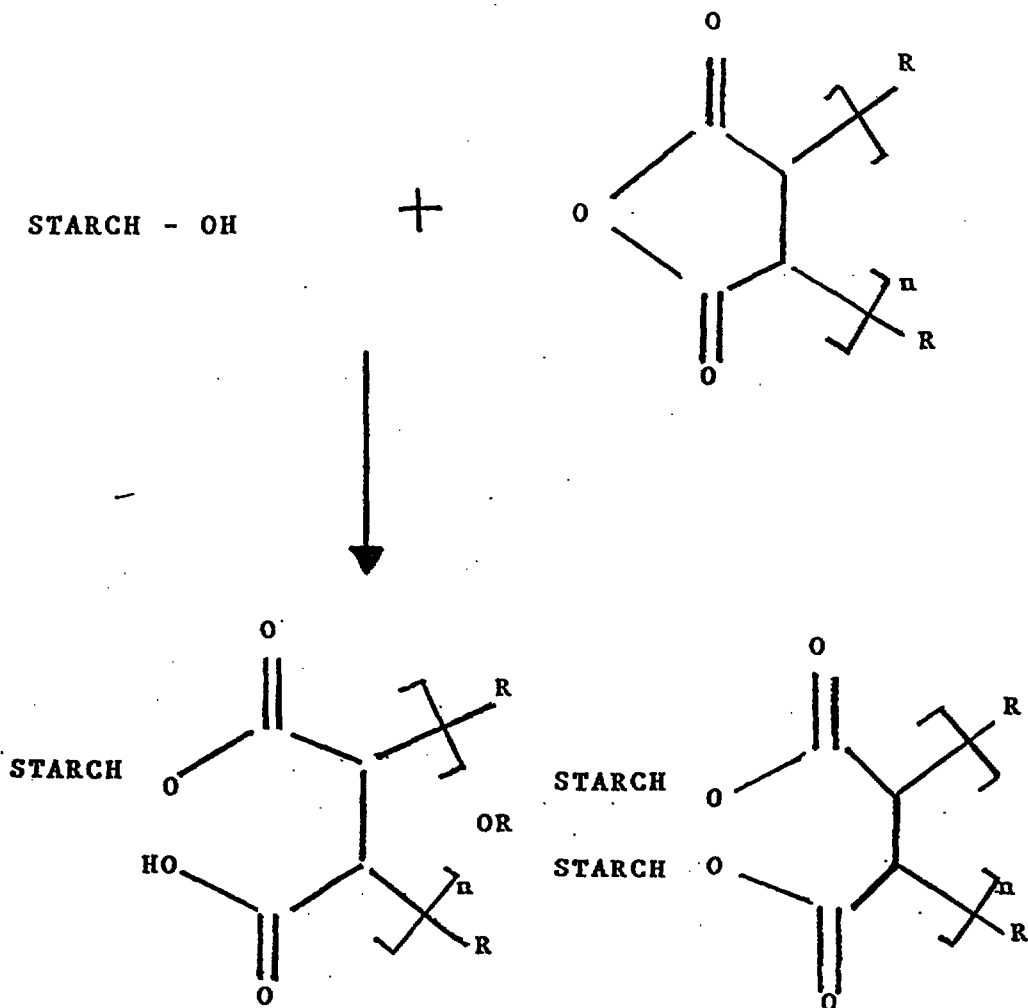


Patent claims

1. Polymer compound essentially comprising a starch, a softener, a polyolefin, an ethylene-acrylate-monoacid-anhydride-copolymer and/or a vinyl bond, having the function of an anhydride, functioning as a phase agent between a starch phase and polyolefin phase, and also starch-monoacid-ester-monoacid-anhydride-ethylene-acrylate-copolymers from an esterification product, obtainable by mixing up to 70% of overall weight of a thermoplastically workable starch, which at least contains a softener, with 10 to 90% of overall weight polyolefin and 1 to 35% of overall total weight ethylene-acrylate-monoacid-anhydride-copolymers and a vinyl bond, functioning as an anhydride, with a water content of, if necessary, a maximum of 2.8%.
2. Polymer compound in accordance with claim 1, obtainable by combining 45 to 70% of overall weight thermoplastically workable starch containing at least one softener from the range, glycerine, urea, an amino-alcohol, sorbitol and/or succinic acid anhydride, 10 to 40% of overall weight polyethylene or polypropylene and 10 to 35% ethylene-acrylate-monoacid-anhydride-copolymer.
3. Polymer combination in accordance with claim 2, obtainable by mixing 50 to 65% of overall weight thermoplastically workable starch, 20 to 35% polyethylene or polypropylene and 15 to 25% of overall weight ethylene-acrylate-monoacid-anhydride-copolymer.



4. Process for producing a polymer combination containing starch and a polyolefin in accordance with any one of claims 1 to 3, wherein native starch is mixed with at least one softener amounting to 15 to 40% of overall weight, to produce thermoplastically workable starch with a water content of < 1%, whereupon up to 70% of overall weight of this is mixed in a melt, at a temperature of 165 to 210°C, with 10 to 90% overall weight polyolefin and 1 to 35% of overall weight ethylene-acrylate-monoacid-anhydride-copolymers and, where applicable, a vinyl bond, having an anhydride function, and a water content totalling a maximum 2.8%, whereby monoacid groups are esterified in copolymers concerned by means of free hydroxyl groups in a said starch in accordance with a following general reaction:





5. Process in accordance with claim 4, wherein glycerine, urea, an amino-alcohol, sorbitol and/or succinic acid anhydride are used as softeners.
6. Process in accordance with claim 4 or claim 5, wherein thermoplastically workable starch accounting for 70% of overall weight is mixed in an extruder or kneader with 10 to 40% overall weight polyethylene and/or polypropylene and 10 to 35% overall weight ethylene-acrylate-monoacid-anhydride-copolymer, whereby processing or operating conditions are used concerning an extruder or kneader such that total input of mechanical energy for a mixing process amounts to 0.4 kWh/kg and whereby an extruder or kneader of a type in which kneading blocks and backwash elements are provided in order to obtain thorough mixing of a melt concerned, is used.
7. Process in accordance with any one of claims 4 to 6, wherein native starch with a water content of less than 1% is homogenized with a softener at a temperature of from 160 to 190°C in an extruder or kneader with shearing, whereupon mixing with polyethylene and/or polypropylene and copolymers occurs, in a further extrusion stage or in the same, in an ensuing zone.
8. Process in accordance with any one of claims 4 to 6, wherein native starch is initially mixed with a softener at room temperature or raised temperature, whereupon the said starch quills and forms dry granulated material which is then used for further processing and for mixing with polyethylene and/or polypropylene and co-polymers concerned.
9. Process in accordance with any one of claims 4 to 8,



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wherein an ethylene-acrylate-monoacid-anhydride-copolymer is used which is obtained by processing 80 to 90% of overall weight ethylene, 1 to 15% of overall weight methyl acrylate and/or ethyl acrylate and 0.1 to 15% monoacid anhydride.

10. Use of a polymer mixture in accordance with any one of claims 1 to 3 for producing at least a layer of a single or multi-layered sheet, wherein a said polymer mixture is processed by means of fishtail extrusion or blast extrusion or co-extrusion to form a sheet.
11. Use in accordance with claim 10, wherein a mixture with pure thermoplastically workable starch including a softener, is extruded into a double- or multi-layered sheet.
12. Use of a polymer mixture in accordance with any one of claims 1 to 3 to produce a foam-like sheet, wherein a polymer mixture has a propellant added to it before extrusion.
13. Use in accordance with claim 12, wherein sodium carbonate or an organic acid, preferably acetic acid is used as a propellant.
14. Sheet with at least one layer comprising essentially a polymer mixture in accordance with any one of claims 1 to 3.
15. Form of extruded material essentially comprising a polymer mixture in accordance with any one of claims 1 to 3.