

European Patent 0 397 819

The invention relates to starch for thermoplastic processing, to a method of manufacturing starch for thermoplastic processing, to a method for manufacturing granules, flakes etc. and moulded bodies, extrudates, films etc. from starch, and to moulded bodies, fillers and carrier materials consisting substantially of starch.

Natural or native starch, such as are obtained by washing and drying the raw starch of, for example, potatoes, cereals, maize etc., has a prominent macromolecular structure, in which the macromolecules do not or barely penetrate one another. This structure means that native starch is very inhomogeneous, and this inhomogeneity is normally at least partly retained even if the starch is melted down.

In the wake of increased use of hydrophilic polymers, which includes starch, as so-called natural plastics materials for a wide variety of applications, it has also been attempted to process starch by the known plastics processing techniques, i.e. by injection moulding and extrusion for example.

Due to the properties of native starch outlined above, however, it has not been possible to manufacture a moulded body from a starch which has adequate mechanical properties, such as strength for example. According to the processing techniques currently known for processing hydrophilic polymers, such as gelatin or cellulose for example, it has been tried to homogenise starch with a specified water content, of the order of 10 % to 20 % relative to the total weight, in a worm extruder of an injection moulding machine, for example, and then to process the starch.

GB 1 014 801 discloses a method according to which a cooled mixture of native starch containing 12 % to 15 % water, or having an insubstantially smaller water content, and a gelatinising promoter are processed to give a plastics-like product. According to the method described, the essential feature is that the

starch has a sufficient water content of at least 12 %.

In EP-A-0 118 240, a starch material and method of manufacturing it are described, the starch being suitable for manufacturing moulded bodies, such as in particular capsules for enclosing pharmaceutical products. In this method, starch is plastified at high temperature and under pressure and with a water content of 5 to 30 % by weight, in order to bring the starch into the processable form required according to the invention.

FR-1 293 184 discloses the processing or plastification of starch derivatives, wherein it is proposed *inter alia* to extrude "hydroxypropyl starch" with 10 % glycerol at 100°C and with a water content of 1-20 %, whereupon the plastified compound is conditioned for 24 hours at 25°C and 20 % relative humidity. The essential feature is that the plastified compound thus manufactured is water-soluble.

DE-OS-37 12 029 discloses a method of pressing moulded bodies from starch, wherein a mixture of native starch containing *inter alia* 0.5 % lubricant and 10-22 % water is melted down in an injection moulding machine in a temperature range of 90°C to 240°C and is then processed. The essence of the invention is that the water content is retained throughout the process.

It has been found that this processing technique only produces an improvement in the mechanical properties of the starch moulded bodies and therefore of the homogenising effect in the molten starch if the water in the intake zone of the worm piston is not driven out of the starch in the form of steam due to the effect of heat, but rather remains in the starch along the entire length of the piston. A further prerequisite is that extremely thorough mixing takes place, as is achieved for example in a kneader or twin-shaft extruder with a correspondingly long piston. The shaft piston or kneader piston in this case forms a virtually sealed chamber, in which case the piston length and temperature control along the piston are critical to the achievement of an adequate homogenising effect.

This procedure for manufacturing homogeneous starch or rather thermoplastically processable starch is obviously complex and critical, but various processing parameters, such as the retention of an adequate water content, temperature, processing method, machine type, worm length etc., are to be maintained precisely. It is therefore not surprising that in the known method according to EP-A-0 304 401 it is recommended to separate the homogenising stage or restructuring stage and the subsequent processing of the molten starch in order to obtain satisfactory properties in the starch moulded bodies. The essence of the process mentioned is that the first stage of the process is carried out in what is known as a sealed system, so that the water cannot escape in the form of steam, for example.

The high water content of 10-20 % required in the process mentioned, as is generally known in plastics processing technology, is not necessarily advantageous either for processing nor for the properties of the moulded bodies to be manufactured. In particular, a water content of the order of 17 % or more for example prevents practical extrusion of the starch, e.g. for the manufacture of films, profiles or tubes. In general, it can be stated that an open method of processing, as is the case with extrusion for example, is rendered impossible due to the high vapour pressure of water of significantly over 1 bar. But if the water content is at least 25 % by weight, the mixture can be processed at 108°C in the "open" system, although the extrudate is sticky and loses its shape at 20°C.

It is therefore an object of the invention to create a thermoplastically processable starch and a method of manufacturing same without the above-mentioned disadvantages and in order to permit a simpler processing method and problem-free processing of the starch according to the known polymer processing techniques.

This object is achieved according to the invention by means of a method according to the wording of claim 1 and by thermoplastically processable starch according to the wording of claim 22.

A method is proposed for manufacturing thermoplastically processable, homogeneous starch, which has a crystalline content in the starch of less than 5 %. By means of the crystallinity, it can be established whether the starch is adequately homogenised and therefore whether the starch is thermoplastically processable. Whereas native starch is highly crystalline, thermoplastically processable starch has virtually no crystalline content. According to the method, native or natural starch is mixed with at least 10 % by weight of at least one additive, relative to the total weight of the mixture of starch and additive, and is melted down by the application of heat, in which case the additive(s) has or have a solubility parameter of more than $30.7 \text{ (MPa)}^{1/2}$ ($= 15 \text{ (cal)}^{1/2} \text{ cm}^{-3/2}$) and upon mixing with the starch, reduces or reduce its melting point in such a manner that the melting point of the starch/additive mixture is below the decomposition temperature of the starch. The vapour pressure of the additive(s) in the mixture together with the starch is less than 1 bar in the melting temperature range of the homogeneous mixture. Finally, the water content of the starch at the time of mixing with the melt must be reduced to less than 5 %.

For this reason, sufficient additive must be present in the melt, which displaces or replaces the water in order to reduce the water content of the melt to less than 5 % relative to the starch. By adding additive or additives, in particular during melting and mixing, the water content of approx. 17 % naturally occurring in starch is removed.

Preferably the solubility parameter of the additive in a temperature range of 100°C to 300°C is of the order of 30.7 to 51.0 $\text{(MPa)}^{1/2}$ ($= 15 \text{ (cal)}^{1/2} \text{ cm}^{-3/2}$).

In particular, if the melting and mixing of the starch with at least one additive is carried out in an open environment, i.e. not under pressure, the vapour pressure of the additive in the melting range of additive and starch, in which mixing or processing of the thermoplastically processable starch takes place, must be less than one atmosphere in order that the additive does not escape uncontrollably

from the mixture with the starch.

It is further proposed that the at least one additive is so selected that the interfacial energy between the additive and starch is not greater than 20 % of the individual interfacial energies relative to air. If the additive meets this requirement, it is ensured that the interaction between the additive and starch is satisfactory.

The mixing of natural or native starch with the additive can be so effected that the mixture is fed to a plastics processing machine, such as a single or twin-shaft extruder or a kneader for example and the mixture is mixed therein, for example in the shaft piston or kneader piston, to produce an at least almost homogeneous thermoplastic compound. Particularly if the vapour pressure of the additive in the temperature range in which mixing is carried out is smaller than one atmosphere, mixing can be carried out in any open or sealed vessel. Only if the vapour pressure of the additive in the temperature range in which mixing is carried out is greater than one atmosphere does the vessel have to be sealed, so that the additive does not escape from the mixture.

It is further proposed to use at least one of the following substances as an additive: glycerol, formamide or N-methyl formamide.

Preferably, the 10 to 35 % by weight (relative to the total weight) additive(s) is added to the starch for mixing.

It is further proposed to add to the starch/additive mixture a plastifier, in which case it is proposed in particular to add 0.5 to 15 % by weight (relative to the total weight of the starch/additive mixture) of one of the following substances, for example: sorbitol, glycerol, glycerol mono- or diacetate, a polyalkyl oxide or a citrate.

Preferably, mixing and homogenisation of the starch with the additive is carried out in a temperature range of 120 to 220°C.

According to a preferred modified embodiment, the starch is mixed with glycerol in a quantity of 10 to 35 % by weight of the total weight of the mixture and is melted down and then mixed with the melt until an at least almost homogeneous mixture is obtained, in which after cooling the crystalline content of the starch is less than 5 %.

Further preferred embodiments of the method according to the invention are characterised in the dependent claims 2 to 21.

Preferably, the natural or native starch together with the at least one additive and optionally further additives is fed to a plastics processing machine, such as a single- or double-shaft extruder or a kneader, are melted down and are mixed into a homogeneous thermoplastic compound.

It is further proposed to add to the mixture composed of starch and additive at least one further additive, such as for example a filler, a lubricant, a plastifier, a softener, a pigment or other colourant and/or an agent to assist removal from the mould.

The following materials are suitable as fillers: a polysaccharide, a cellulose derivative, a synthetic polymer which is at least almost soluble in an additive for starch, and/or a gelatin phthalate.

It is proposed to add 0 to 50 % by weight filler, preferably 3 to 10 % by weight, relative to the total weight of the mixture of starch and additive.

It is further proposed that magnesium oxide is added to the starch/additive mixture in a concentration of 0.02 to 3 % by weight, preferably 0.02 to 1 %, of the total mixture.

Suitable plastifying agents are in particular: a polyalkyl oxide, glycerol, glycerol monoacetate or diacetate, sorbitol or a citrate, which are added in a

concentration in the range from 0.5 to 15 % by weight, preferably 0.5 to 15 % by weight, of the total weight of the starch/additive mixture.

To colour the starch/additive mixture, in particular organic or inorganic pigments are suitable, with a concentration of the order of 0.001 to 10 % by weight, preferably 0.5 to 3 % by weight.

To improve the flow properties, an animal or vegetable fat and/or lecithins, preferably in hydrogenated form, are used, these fats and other fatty acid derivatives preferably having a melting point of more than 50°C.

In order to reduce the hydrophilic properties, and therefore the water permeability of the thermoplastically processable starch during and after its processing, it is further proposed to add to the starch/additive mixture a cross-linking agent or an agent such as alkyl siloxane, for example, in order to modify the starch chemically.

As cross-linking agents, the following substances are particularly suitable: divalent and polyvalent carbonic acids and/or their anhydrides, acid halides and/or acid amides of divalent or polyvalent inorganic acids, epoxy resins, formaldehyde and/or urea derivatives, divinyl sulphones, isocyanates, oxo-compounds, such as acetone formaldehyde or multivalent oxo-compounds and/or cyanamide. If acid amides of carbonic acids are used, an acid group should be available as a free carboxyl group.

The processes proposed above for manufacturing thermoplastically processable starch are suitable in particular for manufacturing granules, flakes, pills, powder, tablets or fibres from thermoplastically processable starch.

The thermoplastically processable starch manufactured according to the process described previously can be further processed direct according to the conventional, known plastics processing methods. However, it should be ensured particularly in the extrusion of tubes, films and the like that the additive

has a vapour pressure at the processing temperature of less than one atmosphere in order to prevent foaming of the starch. If the water content is too high, for example, the formation of bubble films, tubes etc. is not possible. By adding a sufficient quantity of additive, the absorption of water which is a natural property of starch is at least partly prevented.

Furthermore, thermoplastically processable homogeneous starch is proposed which has a crystalline content in the starch of less than 5 % and which is obtainable by the homogeneous mixing of starch and/or a starch derivative with at least 10 % by weight, relative to the total weight, of at least one additive, wherein the additive(s), when mixed with the starch, reduces or reduce the melting point in such a manner that the melting temperature of the starch/additive mixture is below the decomposition temperature of the starch, and has or have, in the mixture with the starch in the melting temperature range of the mixture, a vapour pressure which is less than 1 bar. During mixing in the melt, the water content of the starch must be reduced to less than 5 %.

It is proposed that the molar mass of the starch used is in a range of greater than 1 million, preferably in a range of 3 million to 10 million.

The solubility parameter δ , as is known, is composed substantially of the three components, in particular a polar component δ_p , a component δ_H corresponding to the hydrogen bridge-ring structures, and a dispersion component δ_d , or is a function of these three dimensions. According to the invention, it is proposed that the component δ_p corresponding to polar interactions and the component δ_H corresponding to hydrogen bridge-ring structures are larger than the component δ_d of the solubility parameter δ of the at least one additive corresponding to the dispersion forces. Preferably, δ_p and δ_H are twice as large as the dispersion component δ_d .

Further embodiments according to the invention of thermoplastically

processable starch are characterised in the dependent claims 23 to 25.

The thermoplastically processable starch may take the form of granules, flakes, pills, tablets, powder or fibres.

The thermoplastically processable starch manufactured according to the process described above is particularly suitable as a filler or as a formulation agent for adding to thermoplastic or duroplastic polymers. Its suitability as a filler or formulation agent arises particularly from the fact that the properties of the thermoplastically processable starch are controllable via the molar mass or molar mass distribution of the starch, which is relatively narrow.

The thermoplastically processable starch is furthermore suitable as a carrier material, for example, for active ingredients, for example pharmaceutical active ingredients, and reagents, such as flaking agents for effluents.

In the same way, thermoplastically processable starch is suitable for bonding water in a water-deprived environment and/or to a water-permeable substrate. The starch is extruded, for example, to form large-area films or meshes and is laid on the substrate, consisting for example of sand or gravel. Due to hydrophilia, the starch bonds to water, whereby for example irrigation can be carried out more efficiently in desert-like regions.

The process according to the invention will now be explained further by means of a few main research results with reference to tables.

Table I shows the effect of additives on the melting temperature of native starch.

Table II shows the homogenisation process with different additive quantities and different homogenising conditions and their effects on the molar mass and crystallinity of the starch.

Table III, selected mechanical values of homogenised and insufficiently

homogenised starch, and

Table IV, the dependence of the shear viscosity on the homogenisation temperature and composition of the starch.

In order to examine the effect of additives on native starch, it is necessary to remove the water content of approx. 17 % naturally present in starch. This is carried out on the one hand by adding additives, in particular in the melting down operation and in mixing, and on the other hand by the conventional drying methods. According to the properties required in the moulded body to be produced, such as in particular thermal and mechanical properties, preferably approx. 10 to 25 % additive is mixed with the native starch, and thereby the water content of the starch is reduced by the addition of the additives. The melting temperature of the starch can also be substantially influenced thereby, which has an effect on the processing of the starch on the one hand and on the hot-forming strength of the moulded bodies on the other hand.

This effect has been examined more closely by adding five different additives. First, the native starch was completely dried in order to exclude the effect of water. Then to the dried starch was added 10 % by weight in each case of additive, and the mixture was slowly heated, the supply of heat being carried out accurately. Thus the thermal transformation could be precisely followed, and the temperature range at which the mixture is completely molten could be deduced. As additives, DMSO, glycerol and ethylene glycol, and as a comparison test, propylene glycol and butylene glycol were used. The thermal transformation ranges measured, and therefore the effect of the additives on the melting temperature of the starch are compiled in Table I. Finally, it should be noted in this case that the lower start of a peak is associated with brittle temperature, whereas melting takes place in the range at the upper end of the peak.

Of the additives used, ethylene glycol lowers the melting point of starch the most, whilst the use of butylene glycol produces a relatively high melting range

of approx. 200°C. Also investigated was the addition of propylene carbonate, in which case the starch decomposed before melting. Lowering of the melting temperature is obviously associated with the effect of the molecular structure in the native starch, but this effect has not been fully investigated before.

If the mixture composed of starch and additive is processed further, in the homogenising operation, i.e. during mixing of the starch/additive melt, attention must be paid to the resulting melting temperature.

Thus for example mixtures of propylene glycol and native starch with a propylene glycol content of 10 to 20 % were fed to a kneader and then mixed at 175°C. According to the quantity added, the dwell time of the mixture in the kneader was 40 to 100 sec., and by mixing in more additive, the processing temperature could be lowered in order to achieve sufficient homogeneity in the melt. In another example, glycerol was added, and accordingly it was possible to reduce the processing temperature in the kneader. From experience, it has been found that the addition of 1 % additive produces a reduction in the melting range of approx. 10°C, or that at the same shear velocity, the same viscosity of the mixture at 1 % more additive is achieved even at a temperature which is approx. 10°C lower.

The average power in the kneader for the above-mentioned tests was approx. 10 kW per 100 kg mixture of starch and additive. The homogeneity of the melt was tested by manufacturing test bodies and subjecting these to strain/stress tests. In the range where the measured mechanical properties, i.e. tensile strength or tear-resistance could not be further substantially improved, accordingly it could be deduced that the melt was sufficiently homogeneous. On the basis of this strain/stress test, sufficient reference data can be processed to be able to make deductions concerning the appropriate dwell time in the extruder or kneader based on a specified composition of the starch/additive melt.

Table III shows the homogenisation of starch, carried out under different homogenising conditions, and their effects on the homogeneity of the resulting thermoplastic starch.

Potato starch is used, in which case the potato starch P_3 together with 15 % additive covers a melting range of approx. 180°C, and potato starch P_4 together with 15 % additive covers a melting range of approx. 195°C.

In column A the composition of the starch/additive mixture is indicated, the value A = grammes additive per (gramme starch + gramme additive). A value of $A = 0.15$ therefore means 15 grammes additive to 100 grammes mixture consisting of starch and additive. As an additive, a mixture of the previously mentioned, preferred additives is used, which contains a solubility parameter of 20 cal. $^{1/2}$ cm $^{-3/2}$ at 150°C.

The temperatures T_3 to T_6 represent temperature reference values of the adjusted temperatures of the individual zones of the homogenising apparatus. As homogenising apparatus a kneader is used.

T_E is equal to the temperature of the compound upon discharge from the kneader.

B is equal to the speed of rotation of the kneader shaft in rpm.

C is equal to the power applied to the compound in the form of mechanical work in (kW).

D is equal to the compound flow in the kneader, i.e. output of the melt through the kneader in (kg/h).

E is equal to the limit viscosity of the thermoplastic starch after leaving the kneader, measured in solution in 0.1 nKOH at 60°C after a dissolving time of

one hour at 110°C in the Ubelhoder capillary viscometer, measured in (cm³ per gramme). E is a measure of the molar mass (M) of the thermoplastic starch in (g/Mole). The associated correlation is equal to:

$$E = 0.2 \times M_G^{0.4} \text{ (} M_G = \text{mean weight of molar mass).}$$

E of native untreated starch is 260, which results in a value for M_G of native untreated starch of 6×10^7 .

F means the crystalline content as a percentage. From the crystallinity of the starch, it can be established whether sufficient homogenisation has taken place and therefore whether the starch is thermoplastically processable. Native starch is highly crystalline, whilst thermoplastically processable starch has virtually no crystalline content left.

Measurement of crystalline content:

Method of measurement: X-ray diffraction on powder,

Unit of measurement: intensity of scattered radiation as a function of the scatter angle,

Native potato starch: sharp reflexes at the scatter angles (degrees) 6, 14, 17, 20, 22, 24, 26,

Measure of crystallinity:

F_x = surface content of the scatter intensity - scatter angle function for the sharp reflexes of the treated starch,

F_n = surface content as above for native untreated starch.

$$F = \frac{F_x}{F_n} \cdot 100 \text{ (\%)}$$

The F-values of the treated starch in the homogeneous thermoplastic state are less than 5 %.

Commentary on Table II:

Criteria for evaluating how well or badly homogenisation of the starch has succeeded is represented by the value F for the crystalline content. Values of between 0 and 5 are optimal, whilst even values greater than 5 % indicate unsatisfactory homogeneity of the thermoplastic starch.

The values found for E, i.e. for the limit viscosity, are within a rational range, but even the lowest value found for E produces an average molar mass M_G of 1.5 million.

If the various values for A are compared, i.e. for the composition of the starch mixtures with P_3 and P_4 , it becomes clear that the values in a range from 0.25 to 0.3 pass through an optimum. Thus for example mixtures from the starch P_3 having A-values of 0.35 and 0.4 after homogenisation still yield a high crystalline content, whereas values for A of 0.3 and 0.25 have virtually no detectable crystalline content left. The same picture is obtained furthermore for starch mixtures from P_4 potato starch with additive. This statement obviously cannot be generalised, but the homogenising effect does also depend not insignificantly on the composition or properties of the additive(s).

An essential criterion for homogenisation is the power applied, since it is clear from the experiments that the higher the power consumption of the kneader, the better the quality of homogenisation of the starch. This can be deduced, for example, from samples 3a, 3b and 3c, where homogenisation takes place virtually at the same temperature range and where the composition of the starch mixture is also equal, in particular with a value for $A = 0.35$. An identical effect can also be derived from a comparison of samples 9 and 10, where sample 10

produces adequate homogeneity with a higher power consumption of the kneader, whereas sample 9 has a crystalline content of 25 %.

In order to achieve adequate homogeneity in the thermoplastic starch, the choice of temperatures in the homogenising apparatus is also essential, as can be seen for example from a comparison of the samples 5a and 5b. Thus, for example, sample 5b produces a better homogeneity, even though less power is supplied to the kneader. The improved homogeneity in this case results largely from the significantly higher temperatures selected in the kneader.

The readings cited in Table II show clearly, however, that no generalisation can be made about the composition, selected temperatures in the kneader and power supplied. It is therefore an object in any starch/additive mixture selected to optimise the execution of the process in order to obtain a thermoplastic starch. Finally, an essential criterion is whether it is desired to set a high or a low molar mass. The answer to this question is ultimately determined by the requirements as to whether the thermoplastic starch is to be used for injection moulding or for extrusion. As is known, the more viscous polymers are more suitable for extrusion, whereas the less viscous polymers are more suitable for injection moulding.

Returning to the subject of homogenisation of the starch, it should also be mentioned that obviously the dwell time of the material in the homogenising apparatus or kneader may affect the homogeneity of the material.

Commentary on Table III:

Table III shows the homogeneity or crystallinity of the thermoplastic starch on mechanical properties with reference to the illustration given by way of example of the effect on the stress and elongation at breaking point of the starch.

Sample I is a test body composed of thermoplastic starch material which is adequately or almost ideally homogenised, and which is accordingly

thermoplastically processable. Sample II is a starch sample which is unsatisfactorily homogenised and accordingly has too much crystallinity.

The column "module" shows the module of elasticity of the two materials, which is conveniently virtually the same for both materials. Column A shows the composition of the samples, column E, as in Table II, shows the limit viscosity of the samples, and column F the value for the crystalline content.

G signifies the relative elongation of the material at break in (%), and H stands for the energy input applied to the material until the breaking point of the material was reached. The dimension of H is (kJ/m^2).

Column I shows a compilation of the values of various measurements for samples I, which have a crystalline content of the order of 0 to 5 % max.. These are therefore materials which are almost ideally homogenised and are accordingly perfect for thermoplastic processing.

Correspondingly, various measurements are compiled in column II for materials which are inadequately homogenised.

From column G, it can be clearly deduced that the starch materials from column II are considerably more fragile than the materials in column I. The starch materials in column I further require a higher energy input according to column H in order to be elongated to breaking point.

On the basis of the strain/stress tests, which are illustrated numerically in Table III, the improvement in mechanical properties of thermoplastically processable starch can be clearly deduced. Due to the reduction in crystallinity of the material to less than 5 %, starch materials are obtained having adequate to good mechanical properties. These mechanical properties can obviously be further improved by the quantity of the additive and an appropriate choice of additives.

Since, obviously, shearing forces in the molten starch/additive mixture are responsible for the homogenising effect and therefore lead to a material with lower crystallinity, the association between the shear viscosity of the melt and the shearing effect of the homogenising apparatus needs to be explored more fully. To this end, the intrinsic viscosity of the starch melt, i.e. the dependence of the shear viscosity on the shear velocity, is examined in a capillary rheometer.

As a correlation between the two values, the following equation was found:

$$\eta = K \cdot \dot{\gamma}^{(1-m)}$$

In this case η represents the shear viscosity of the melt in (Pa x sec) and $\dot{\gamma}$ the shear velocity in (sec⁻¹). K is a material constant, which is occasionally also called consistency. K is calculated from the following equation:

$$K = \exp \left[\frac{E_A}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) - a (A - A_0) \right]$$

For the term E_A/R , the value of 5.52×10^4 (degrees Kelvin) was found, where R = the gas constant; and E_A = thermal activation energy of the place-exchanging process of the molecules as the melt flows.

T represents the temperature of the melt (in degrees Kelvin), and T_0 a reference temperature of 458 degrees Kelvin.

a also represents a constant having the value 2.76×10^2 , and A , as is known, represents the composition of the starch/additive mixture. A_0 represents the composition of a reference mixture having the value $A = 0.1$.

It then becomes clear that the term m is a function of the temperature of the melt

and the composition of the starch/additive mixture.

Table IV shows values of m as a function of T (degrees Kelvin) and of A , these values being obtained by the corresponding adjustment of the shear viscosity in the measuring apparatus to the predetermined γ , i.e. the shear velocity. For m , therefore, a function having the general formula: $m = (g(T) + f(A) + r(T, A))$ is obtained.

The values from table IV underline the already suspected fact that at increased temperature of the melt the shear velocity can be reduced in order to obtain the same shear viscosity in the melt, and with increased additive content the temperature of the melt can be reduced in order to obtain the same shear viscosity in the melt.

The starch thus homogenised, or rather thermoplastic starch, can then be further processed direct according to the conventional plastics processing methods, such as injection moulding, extrusion, film-blowing extrusion, injection blow-moulding, deep-drawing etc.. In this case, however, particularly in extrusion, film-blowing extrusion, injection blow-moulding, etc., it should be ensured that the additive has a vapour pressure which is significantly below 1 bar at the temperature at which the melt leaves the extrusion nozzle. The same applies with reference to the water content in the melt, which must not be too high. It should therefore also be ensured that sufficient additive is present in the melt to displace or replace the water. If the water content is too high or an additive is used having a vapour pressure which is too high, the material foams as it leaves the nozzle.

By adding further additive, as described above, the properties of the moulded bodies and extrudates can be further substantially affected. Thus, for example, by adding inorganic fillers, such as magnesium oxide, aluminium, silicon etc., the transparency can be reduced or eliminated altogether. Additives of plant or animal fats improve the flow properties of the melt and improve removal of the starch from moulds. However, modifying the properties is not the primary

subject of the invention, so that this matter is not described more fully here.

A further essential aspect is the adding of cross-linking agents to the starch, since moulded bodies and extrudates of pure starch are not water-resistant due to their hydrophilic property. By the addition of cross-linking agents and other chemical modifying agents, parts composed of starch are rendered at least partially or almost fully water-resistant and can therefore be used in practice without problems. The choice and addition of one of the cross-linking agents mentioned above substantially depends on the additive and the quantity to be added to the native starch, in which case the additives may also play a role. Temperature and dwell time in the extruder, i.e. during melting, homogenising and processing, are therefore the essential criteria for the type of cross-linking agent to be selected. In principle, during the processing of the starch, cross-linking must not progress so far that the thermoplasticity of the starch is affected in such a manner as to make subsequent processing of the starch problematic; but this situation is well known in practice from processing partially cross-linkable thermoplasts, from the manufacture of powder coatings etc., so that there is no need to go into further detail here.

The previously mentioned additives and processing conditions used by way of example were only intended to illustrate the invention more fully and can be varied in any manner by the use of other materials and processing conditions according to requirements. The essential point is that by adding an additive to the native starch and mixing these two materials in the melt, a thermoplastically processable starch can be created. It is also essential that the additive has a cohesion energy density which permits the additive to modify the molecular structure of the native starch in such a manner as to render the starch thermoplastically processable. Finally, a further requirement is that the vapour pressure of the additives, at least in open processing, is less than 1 bar in the processing temperature range.



Claims

1. Process for manufacturing homogeneous starch having a crystalline content of less than 5 % and capable of being subjected to thermoplastic processing, characterised in that native or natural starch is mixed with at least 10 % by weight of an additive, compared to the total weight of the starch/additive mixture, and is formed into a melt by the application of heat, wherein the additive has a solubility parameter of more than $30.7 \text{ (MPa)}^{1/2}$ ($= 15(\text{cal}^{1/2} \cdot \text{cm}^{-3/2})$) and when mixed with the starch lowers its melting point so that the melting temperature of the starch/additive mixture is below the decomposition temperature of the starch, and the vapour pressure of the additive(s) in the mixture together with the starch is less than 1 bar in the melting temperature range of the homogeneous mixture, and in that the water content of the starch in the melt is reduced to less than 5 %.
2. Process according to claim 1, characterised in that the water content of approx. 17 % naturally occurring in the starch is removed by the addition of an additive or additives during melting and mixing.
3. Process according to claim 1 or 2, characterised in that the starch is completely dried before mixing with at least one additive.
4. Process according to one of claims 1 to 3, characterised in that at least one of the following substances is used as an additive: glycerol, formamide or N-methyl formamide.
5. Process according to one of claims 1 to 4, characterised in that the starch is mixed with additive in a quantity of 10 to 35 % by weight of the total weight of the



mixture, is melted down and then mixed until the melt is homogeneous.

6. Process according to one of claims 1 to 5, characterised in that mixing and homogenisation of the starch melt with the additive is carried out in a temperature range of 120 to 220°C.
7. Process according to one of claims 1 to 6, characterised in that the starch is mixed with glycerol in a quantity of 10 to 35 % by weight of the total weight of the mixture and is melted down.
8. Process according to one of claims 1 to 7, characterised in that the starch is mixed with at least one additive and melted down, the additive having a solubility parameter in a temperature range of 100 to 300°C of 30.7 to 51.0 (MPa) ($= 15-25(\text{cal}^{1/2} \cdot \text{cm}^{-3/2})$) and its interfacial energy relative to the starch is not greater than 20 % of the individual interfacial energies of the starch and additive relative to air.
9. Process according to one of claims 1 to 8, characterised in that the natural or native starch and at least one additive are fed together into a plastics processing machine, such as a single- or twin-shaft extruder and a kneader, are melted down and are mixed into a homogeneous thermoplastic compound.
10. Process according to one of claims 1 to 9, characterised in that as a plastifier, a polyalkyl oxide, glycerol, glycerol monoacetate or diacetate, sorbitol or a citrate is used in a concentration in the range of 0.5 to 15 % by weight of the total weight of the mixture.
11. Process according to one of claims 1 to 10, characterised in that at least one of the following materials are added as a filler to the starch/additive mixture:
 - another polysaccharide,
 - a cellulose derivative,



- a synthetic polymer soluble in an additive for starch,
- a gelatin phthalate,

more than 0 to 50 % by weight relative to the total mixture of a filler being added to the starch/additive mixture.

12. Process according to claim 11, characterised in that filler is added to the starch/additive mixture in a proportion of 3 to 10 % by weight of the total mixture.

13. Process according to one of claims 1 to 12, characterised in that at least one inorganic filler is added to the starch/additive mixture in a concentration of 0.02 to 3 % by weight of the total mixture.

14. Process according to one of claims 1 to 13, characterised in that magnesium oxide is added to the starch/additive mixture in a proportion of 0.02 to 3 % by weight of the total mixture.

15. Process according to one of claims 1 to 14, characterised in that an organic or inorganic pigment is used in a concentration of the order of 0.001 to 10 % by weight relative to the total weight.

16. Process according to one of claims 1 to 14, characterised in that an organic or inorganic pigment is used in a concentration of the order of 0.5 to 3 % by weight relative to the total weight.

17. Process according to one of claims 1 to 16, characterised in that, as a means of improving the flow properties, an animal or vegetable fat, a lecithin, preferably in hydrogenated form, is used, these fats and other fatty acid derivatives having a melting point of more than 50°C.

18. Process according to one of claims 1 to 17 for the manufacture of at least partly cross-linked starch, characterised in that at least one cross-linking agent is added to the starch/additive mixture.



19. Process according to one of claims 1 to 18, characterised in that as a cross-linking agent at least one of the following substances is used:

- a divalent or polyvalent carbonic acid and/or an anhydride thereof,
- a halide and/or an acid amide of a divalent or polyvalent carbonic acid,
- a derivative of a divalent or polyvalent inorganic acid,
- an epoxy resin, such as a multivalent glycidyl ether,
- formaldehyde and/or a urea derivative,
- an isocyanate,
- an oxo-compound, such as acetone formaldehyde or a multivalent oxo-compound,
- cyanamide.

20. Process for manufacturing granules, flakes, pills, powder, tablets or fibres from homogeneous starch capable of being subjected to thermoplastic processing, using the process according to one of claims 1 to 19.

21. Process for manufacturing moulded bodies, extrudates or films from homogeneous starch capable of being subjected to thermoplastic processing, using the process according to one of claims 1 to 20, characterised in that the homogeneous starch/additive melt is processed direct.

22. Homogeneous starch having a crystalline content of less than 5 % and



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capable of being subjected to thermoplastic processing, obtainable by means of a process according to one of claims 1 to 21.

23. Starch capable of being subjected to thermoplastic processing according to claim 22, characterised in that the limit viscosity mean of the molecular weight of the starch is in the range of 3 million to 10 million.

24. Starch capable of being subjected to thermoplastic processing according to claim 22 and 23, characterised in that it is present in the form of granules, flakes, pills and/or tablets, or as a powder, or in the form of fibres.

25. Starch capable of being subjected to thermoplastic processing according to one of claims 22 to 24, characterised in that the component δ_p , corresponding to polar interactions, and the component δ_H , corresponding to the hydrogen bridge-ring structures, of the solubility parameter δ of the at least one additive are larger than the component δ_d of the solubility parameter δ of the at least one additive.

26. Moulded body composed of homogeneous starch capable of being subjected to thermoplastic processing according to one of claims 22 to 25.

27. Use of the starch capable of being subjected to thermoplastic processing according to one of claims 22 to 25 as a filler for filling and/or formulating thermoplastic or duroplastic polymers.

28. Use of the homogeneous starch capable of being subjected to thermoplastic processing according to one of claims 22 to 25 as a support material for receiving additives and/or reagents.

29. Use of the homogeneous starch capable of being subjected to thermoplastic processing according to one of claims 23 to 25 for bonding water in a water-depleted environment and/or to a water-permeable substrate,



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wherein the starch is used in the form of a film, a mesh or other extrudate.