

Single- or multi-layer sheet, partially consisting of starch

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The present invention concerns a single or multiple-layer sheet of substantially reduced gas-permeability, and a method of producing a single-layer or multiple-layer sheet, a polymer blend consisting of a polyolefin and starch, a method of producing the polymer blend, thermoplastically processable starch, a method of producing thermoplastically processable starch, a sheet consisting of a polymer blend, and a shaped body consisting of a polymer blend.

For the packaging of, for instance, oxygen-sensitive materials such as foodstuffs, it is important that the packing means be of low gas-permeability, i.e. have a low oxygen permeability in the example indicated.

Further requirements on such packing materials are that they be insensitive to moisture, have sufficient mechanical properties, are transparent depending on their use and are of low price.

In particular for the packaging of foodstuffs, there are known sheets of PVC and, even of substantially more general use today, sheets of polyvinylidene chloride or PVDC, such as, for instance, "Saran." The gas-permeability of these materials as well as their insensitivity to moisture are excellent. However, these materials have the great disadvantage that the disposal of them is not unobjectionable as a result of their chlorine content, since hydrogen chloride is produced upon burning.

For this reason, these chlorine-containing sheets are being increasingly replaced by so-called sandwich sheets, such as, for instance, multi-layer

sheets consisting of a layer of polyamide and a layer of polyethylene or of a layer of polyethylene and a layer of polyvinyl alcohol. There are no limits on the possibilities of variation of the different sandwich sheets. In order that these different polymer materials adhere well to each other, intermediate layers of so-called block copolymers are for instance proposed which serve as so-called phase mediators.

In these sandwich sheets, the polyamide layer, for example, forms a good barrier to oxygen while, on the other hand, the polyethylene layer is responsible for the impermeability to water. Depending on the properties of the individual polymers and of the required properties of the sheet, the layers can be arranged in various manners. three, four, five or multiple-layer sheets, for instance, are known.

The manufacture of these multi-layer sheets is, however, relatively expensive since, on the one hand, measures must be taken to see to it that there is good adherence between the individual layers and furthermore the polymers selected, such as, for example, polyamide, are relatively expensive raw materials.

Although these polymers are substantially unobjectionable as compared with chlorine-containing polymers such as PVC or PVDC, their disposal is nevertheless not without problems. Plastics consisting of polyethylene, polyamide, polypropylene, etc. are still today incinerated to a substantial extent since they are scarcely, if at all, biologically degradable. Furthermore, the so-called recycling of these plastics is scarcely possible or is possible only with difficulty.

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One object of the present invention is therefore to create a sheet for the packaging of materials which is of low gas-permeability, such as, for instance, oxygen permeability, and which furthermore is substantially insensitive to moisture.

Another object of the present invention is to create a polymer material which is suitable, at least in part, for the production of such a sheet.

In accordance with the invention this problem is solved by a single- or multi-layer sheet with greatly reduced gas permeability in accordance with the text of one of the claims, as in particular in accordance with one of the Claims 1 to 9.

There is proposed a single-layer or multiple-layer sheet of substantially reduced gas-permeability which comprises at least one layer which is made, at least in part, of substantially thermoplastically processable starch. Sheets of starch have the required reduced gas-permeability and furthermore the disposal of starch presents no problem since it is easily biologically degradable.

It is furthermore proposed that said at least one layer be made of a polymer blend, the blend containing a polyolefin in addition to the thermoplastically processable starch. In this way, the sensitivity to moisture of the sheet is greatly reduced.

It is proposed in this connection that said at least one layer consist of a polymer blend which is produced from thermoplastically processable starch with polyethylene and/or polypropylene, as well as a phase mediator or

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bond promoter in order to improve the adherence between the two polymers.

In accordance with the present invention, there is furthermore proposed a single- layer or multiple-layer sheet of substantially reduced gas-permeability which is at least substantially insensitive to moisture, the sheet comprising at least one layer obtained in part from substantially thermoplastically processable starch and preferably having a water content of $< 3.5\%$ by weight, the insensitivity to moisture of the sheet resulting from the fact that said at least one layer furthermore comprises at least one hydrophobic polymer which is mixed with the starch upon the production of said at least one layer and/or that the starch is at least partially cross-linked on the surface of said at least one layer and/or that said at least one layer is covered by at least one additional layer which is at least substantially insensitive to moisture.

In a variant of the sheet in accordance with the invention, the sheet comprises on both sides of said at least one layer at least one further layer consisting of a polyolefin and/or a polymer blend of thermoplastically processable starch with a polyolefin. The polyolefin is preferably polyethylene and/or polypropylene. When very high demands are made on the moisture impervious of the sheet, the other layers consist exclusively of a polyolefin.

Depending on the requirements as to the adherence between the different layers, there is present between said at least one layer and each of said further layers an intermediate layer consisting of a block copolymer as phase mediator or bond promoter between the layers. An intermediate layer consisting of the block copolymer is preferably provided when said at least

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one layer consists substantially exclusively of thermoplastically processable starch and the two other layers consist substantially primarily of the polyolefin. The larger the proportion of thermoplastically processable starch in said each other further layer, the less necessary it is to provide an intermediate layer consisting of the block copolymer.

In accordance with another variant of the sheet of the invention, it is provided that the sheet is provided on at least one side with an aluminum coating and/or a silicon- oxide coating such as, for instance, a silicon monoxide coating. In this connection, the sheet may be a single-layer, double-layer or multiple-layer sheet, as described above.

The aluminum or silicon oxide coating is applied in an order of magnitude of 100 to 400 Å. Silicon oxide, such as preferably silicon monoxide, is selected as coating for the sheet when the transparency of the sheet is to be substantially retained. The coating of the sheet with aluminum or silicon oxide is preferably effected by vapor deposition on the sheet in a high vacuum.

In accordance with another variant of the sheet of the invention, it is proposed that, at least on one side, the sheet have a siloxane coating which is at least partially cross-linked with itself and/or with the starch. This again may be a single-layer or multiple-layer sheet, as described above. The siloxane coating of the sheet is obtained in the manner that a siloxane monomer, such as, for instance, an alkyl siloxane, is applied to at least one side of the sheet and the siloxane is then treated with an electron gun, whereby the siloxane is cross-linked to itself and in part to the starch on the surface of the sheet. By the addition of a photosensitizer to the siloxane monomer the cross-linking to the starch can be additionally increased.

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The coating of the sheet with the siloxane monomer is effected preferably by means of so-called dip coating in which the sheet is dipped into a bath which contains the siloxane monomer, and the siloxane film is then produced by means of a doctor blade. The depth of penetration upon the cross linking is about 7 to 10 μ , depending on the energy selected in the UV source or in the electron beam.

The sheet can be coated with the siloxane on one or both sides.

As alkyl siloxanes, diethoxydimethylsilane or tetra-ethoxysilane is particularly suitable. The application of the siloxane monomer is preferably effected in a thickness of 1 μ .

Instead of applying a coating to the sheet it is possible, in accordance with another variant, to treat the sheet on its surface with a UV source or an electron gun in if, such a manner that the starch is at least partially cross-linked on the surface of the sheet.

The cross-linking has the result that the water resistance of the starch is increased. The cross-linking can be further increased by adding a photosensitizer to the starch.

In accordance with another variant of the sheet of the invention it is proposed that borax, Mg^{2+} ions and/or Ca^{2+} ions or other polyvalent cations be added to the thermoplastically processable starch. This is done in the manner that, upon the production of the thermoplastically processable starch, it is treated with borax, magnesium sulfate or calcium

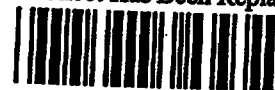


carbonate. The advantage of these additions is that the water sensitivity of the starch can be reduced thereby.

The abovementioned single-layer or multiple-layer sheets can be produced by the known, customary methods of producing sheets. Thus, for instance, said at least one layer of sheet which consists essentially of thermoplastically processable starch can be produced by slot extrusion or by blowing thermoplastically processable starch or a polymer blend consisting of thermoplastically processable starch with a polyolefin, such as preferably polyethylene or polypropylene. The blowing or extrusion conditions depend in this connection on the melting point of the polymer selected.

In analogous manner it is possible to produce, for instance, a three-layer sheet by slot backing or blow coextrusion of at least three layers, said at least one layer, consisting substantially of thermoplastically processable starch, being covered on both sides by a further layer which is prepared from a polyolefin and/or a polymer blend of a thermoplastically processable starch and a polyolefin, such as preferably polyethylene or polypropylene. Depending on the requirements, it is furthermore possible to provide an intermediate layer consisting of a block copolymer between said at least one layer and said further layers in order to increase the adherence between the layers.

Also in the present case, the extrusion or blowing conditions depend on the melting ranges of the polymers or polymer blend selected, in which connection the extrusion conditions for the thermoplastically processable starch should not substantially exceed 210° C since otherwise degradation of the starch can be noted.



There is furthermore proposed a polymer blend consisting of a polyolefin and starch which is particularly suitable for the production of a sheet in accordance with the invention which has been described above. This polymer blend is obtained by mixing a polyolefin such as, for instance, polyethylene or polypropylene, with thermoplastically processable starch having a water content of $< 3.5\%$ by weight, in which the percentage of starch in the total mixture must not exceed 70% by weight. The proportion of thermoplastically processable starch is preferably 30 to 70% of the total weight of the polymer blend.

In particular, the polymer blend is obtained in the manner that the polyolefin, such as polyethylene or polypropylene, is mixed with the starch in a kneader or extruder within a temperature range of 150°C to 200°C , and preferably 160°C to 190°C , the temperature range depending on the melting range of the polyolefin selected.

A phase mediator is furthermore preferably added, it being a block copolymer which is customarily used in the production of multiple-layer sheets as intermediate layer or else in the production of polymer blends from polar and non-polar polymers.

For the production of such a polymer blend with starch it is essential that thermoplastically processable starch be used. There are known, for instance, polymer blends of polyethylene with 40% of an at least partially destructured starch, the destructuring being effected substantially by the use of water. Shaped bodies produced from such polymer blends are brittle and the production of sheets is substantially out of the question. This is due, not least of all, also to the high water content of the destructured starch.



As compared with this, it is possible with the abovementioned polymer blends of the invention, with the use of preferably 30 to 70 % by weight of thermoplastically processable starch, to produce excellent sheets and shaped bodies the mechanical and physical properties of which do not differ substantially from those of polyolefin. In this connection, the amount of the thermoplastically processable starch used depends on the desired moisture insensitivity of the polymer blend, sufficient insensitivity to moisture still being obtained with the use of 70% starch. Thus, for instance, such a sticky polymer blend become on its surface only when exposed to 100% air humidity. On the other hand, this polymer blend can be stored without problems at 40 % air humidity and room temperature.

In the case of the sheets of the invention mentioned above or for the said polymer blend, there is proposed the use of thermoplastically processable starch which is obtained by mixing starch and/or a starch derivative with at least 20 % by weight of an additive, by feeding thermal or mechanical energy and by at least partially removing the naturally bound moisture in the starch, the additive comprising at least one of the following substances :

- glycerol,
- an amino alcohol,
- DMSO,
- N-methylacetamide,

The thermoplastically processable starch preferably has a water content of < 3.5 % and in particular < 1 % by weight.

In order to produce the thermoplastically processable starch, it is proposed that the starch and/or a starch derivative be mixed with at least 20 % by



weight, and preferably 25 to 45 % by weight, of an additive with the feeding of mechanical energy in the form of deformation energy on the order of magnitude of 0.25 to 0.5 kWhr/kg of starch / additive mixture, the mixture being heated at least to a temperature such as to permit a mixing of the components so as to form a homogeneous mass and said at least one additive comprising at least one of the abovementioned substances.

In contrast to the methods of destructuring crystal starch which have been customary up to the present time, in which the destructuring is effected substantially with the aid of water, there is obtained, in accordance with the method proposed herein, a thermoplastically processable starch which can be worked without problems by the known extrusion and injection molding methods and by means of which shaped bodies and extruded bodies which have excellent mechanical properties can be produced. In particular the thermoplastically processable starch, in contrast to starch which is destructured with water, has an excellent stress-strain behavior which does not deteriorate even upon aging.

Thus, shaped bodies made of thermoplastically processable starch are flexible within limits, while shaped bodies made from starch which has been destructured with water are substantially brittle, particularly after a certain period of aging.

In accordance with a variant of the method proposed above, starch is mixed with 25 to 40 % by weight, and preferably 32 to 38 % by weight, of an aminoalcohol, such as aminoethanol, aminopropanol and/or trishydroxylethylaminomethane, the mixture being processed, depending on the nature of the additive and the amount thereof, within a temperature



range of 60°C to 120°C in an extruder or kneader with the feeding of deformation energy of 0.3 to 0.36 kWhr/kg of starch/aminoethanol mixture so as to form a homogeneous mass. The natural moisture of the starch is in this connection removed either before the mixing with the amino alcohol by drying or else during the mixing, for instance in the kneader or extruder, in accordance with known methods, for instance by aspiration.

In accordance with another variant, the starch or starch derivative is mixed with 30 to 45 % by weight, and preferably 34 to 40 % by weight, glycerol and worked, depending on the amount of addition substance, within an temperature range of 120°C to 180°C in an extruder or kneader while feeding a deformation energy of 0.3 to 0.36 kWhr/kg of starch-glycerol mixture so as to form a homogeneous mass. The natural moisture of the starch is substantially withdrawn by aspiration in the extruder or kneader.

In order to reduce the sensitivity to moisture of the thermoplastically processable starch it is advantageous to replace up to 20 % by weight, and preferably about 10 % by weight, of the additive by borax, magnesium sulfate or calcium carbonate upon the production of the thermoplastically processable starch.

The abovementioned thermoplastically processable starch as well as the polymer blend are particularly suitable for the production of one or more layers in the abovementioned foils of the invention. Of course, these materials can also be used for the production of extruded products or injection moldings.

The invention will now be explained in further detail below with reference to the accompanying figures and on basis of examples.



Figs. 1 to 5 show, on basis of examples, possible variant constructions of foils in accordance with the invention.

Fig. 1 shows a single-layer sheet which comprises one layer 1. This one layer consists of a polymer blend in accordance with the invention, prepared from a polyolefin and thermoplastically processable starch. In this connection, the proportion of thermoplastically processable starch can be 30 to 70 % by weight, based on the total weight of the polymer blend. The proportion of thermoplastically processable starch depends on the requirements as to the moisture sensitivity of the film. The oxygen barrier in this film is determined essentially by the proportion of thermoplastically processable starch, while the water impermeability can be adjusted by the proportion of polyolefin, such as for instance polyethylene.

Fig. 2 shows a single-layer sheet covered on both sides by a coating 3. In the example shown, the layer consists of thermoplastically processable starch, while the coatings 3 may be an aluminum coating, a silicon-oxide coating, or a siloxane coating. While in the case of aluminum or silicon oxide, the layer thickness is 100 to 400 Å, the layer thickness of the siloxane coating is on the order of magnitude of 1 μ . In case of the use of aluminum, the sheet shown has excellent imperviousness to oxygen and its resistance to water is also excellent. The advantage of the use of silicon oxide, such as for instance silicon monoxide, is that the sheet is still transparent. On the other hand, the water resistance and oxygen resistance are not as outstanding as when aluminum is used.

The advantage of the siloxane coating lies in the excellent water resistance of the sheet.



In the example shown in Fig. 3, a three-layer sheet is shown, it consisting of a central layer 1 and two peripheral layers 5. The central layer 1 consists of thermoplastically processable starch while the two peripheral layers 5 consist of polyolefin, such as for instance polyethylene. In between the layers 1 and 5 an intermediate layer of a block copolymer can be arranged, as is customary in the production of multiple-layer sheets.

In the example shown, the central layer 1 is responsible for the oxygen barrier, while the two polyethylene layers assure the water impermeability of the sheet. The layer thickness in this connection can be selected as required, i.e., for example, the two layers 5 may each be 1 μ while the central layer 1 is 7 μ . It is, however, definitely also possible for the two outer layers 5 to be 30 μ in thickness while the central layer is 60 μ .

The example shown in Fig. 4 is practically identical to the sheet of Fig. 3. It only the two peripheral layers 5 consist of a polymer blend which has been produced from a polyolefin with thermoplastically processable starch. In this case, the water resistance of the two peripheral layers 5 depends on the polyolefin content of the polymer blend. This sheet can always be selected when the requirements as to water imperviousness are not too high. The advantage of this sheet lies on the one hand in its price, since the starch is considerably cheaper than polyethylene and, on the other- hand, starch is biologically very easily degradable upon disposal, while polyethylene must be incinerated.



Fig. 5, finally, again shows a three-layer sheet similar to Fig. 4, coated on both sides by a coating 3. The coating 3 can be selected similar to the coating 3 in Fig. 2, i.e. it may consist of aluminum, silicon oxide or silane.

The examples of a sheet in accordance with the invention which are shown in Figs. 1 to 5 can, of course, be varied in numerous ways. thus, of course, two-, four-, five- or multiple-layer sheets can be produced. Furthermore, it is possible, for instance, to coat a sheet only on one side.

The production of thermoplastically processable starch, of polymer blends, and of sheets in accordance with the invention will now be described in further detail on the basis of examples, with reference to Figs. 6 to 11.

A. Production of thermoplastically processable starch

First Example : Glycerol Starch

Potato starch and 36 % by weight glycerol, based on the total weight of glycerol/starch, were introduced into a twin-shaft extruder. The mixture was intensively mixed in the extruder at about 160° C with the addition of deformation energy of 0.32 kWhr/kg of starch/glycerol mixture, the melt being at the same time degassed in order to remove the water from the starch. As a result of the mixing of the two components a homogeneous melt is obtained which can then be withdrawn and granulated. The water content of the thermoplastically processable starch which has been homogenized in this manner is about 0.3 % by weight.

By the mixing and homogenizing of the crystal starch with glycerol, all crystallites and crystal structures of the crystal starch are broken up and the



starch is substantially amorphous in the thermoplastically processable starch. In contrast to this, destructured starch which has been produced by known methods from crystal starch by destructuring with water higher temperatures still has a certain crystallinity. The difference between thermoplastically processable starch and destructured starch can be shown, for instance, on the basis of the water vapor absorption isotherms.

Fig. 6 shows in this connection a water-vapor absorption isotherm for thermoplastically processable starch as well as for destructured starch.

The water-vapor absorption isotherm 11 shows the water absorption of thermoplastically processable starch prepared in accordance with Example 1. The essential feature of this isotherm is that it does not have any point of inversion. It can furthermore be noted that the desorption isotherm is identical to the absorption isotherm. Graph 12 shows the water-vapor absorption isotherm of destructured starch which has been destructured with 25% water at 125° C. In contrast to the isotherm 11, graph 12 shows two points of inversion.

Graph 13 furthermore shows the desorption isotherm of destructured starch, which is not identical to the water-vapor absorption curve. The desorption is obviously delayed as compared with the absorption.

The isotherms in Fig. 6 were furthermore measured at 20° C. Another difference between thermoplastically processable starch in accordance with the present invention and destructured starch is that, even in the event of advanced aging, the water-vapor absorption isotherm of thermoplastically processable starch remains substantially the same while that of destructured starch changes with aging.



Thermoplastically processable starch differs furthermore from water-destructured starch by a different glass transition point. The glass transition point or GT of thermoplastically processable starch is below room temperature while the glass transition point of the destructured starch having a water content of $< 18\%$ by weight is always above 40°C , as a result of which the material is brittle. With more than 18% by weight water, the starch is sticky, as a result of which the material always has a certain flexibility. This feature is retained even upon aging of thermoplastically processable starch, while in the case of destructured starch the glass transition point increases with aging in such a manner that the material becomes brittle after a certain period of time.

Another feature of thermoplastically processable starch resides in its extremely low water content, which is normally $< 3.5\%$ by weight and preferably $< 1\%$ by weight.

Second Example: Thermoplastically Processable Starch with an Amino Alcohol

2.1 Ethanolamine

Crystal starch was dried at 100°C for two days in a drying oven. Two mixtures were then prepared with ethanolamine, namely one mixture with 30% by weight ethanolamine referred to the total weight of the starch/ethanolamine mixture and a second mixture with 34% by weight ethanolamine.



Both mixtures were then homogenized in a kneader at 100° C, the moment of rotation of the kneader being so selected in the case of the first mixture as to introduce a deformation energy of 0.3 kWhr/kg of starch/ethanol mixture, while 0.34 kWhr/kg of starch/ethanol mixture were added to the second mixture by adjustment of the moment of rotation. Thereupon, plates were pressed with the two homogenized compositions for 15 minutes at 100° C. No undigested starch granules could be noted any longer in the two plates under a microscope. The two plate specimens were thereupon subjected to bending tests, the first specimen, containing 30 % by weight ethanolamine breaking immediately as the result of high brittleness while the second specimen, containing 34 % by weight ethanolamine, was bendable due to a certain flexibility.

It was furthermore also found that the water sorption of the first sample was substantially greater than the water sorption of the second, flexible specimen.

2.2 3-Amino-1-Propanol

Once again, crystal starch was dried for two days in a drying oven at 100° C. Again two mixtures were prepared, namely in one case with 32 % by weight of 3-amino-1-propanol referred to the total weight of the mixture and in the other case with 36 % by weight of 3-amino-1-propanol, referred to the total weight of the mixture.

The two mixtures were thereupon again homogenized at 100° C in a kneader, the moment of rotation of the kneader being so selected that in the first case a deformation energy of 0.29 kWhr/kg of mixture and in the second case a deformation energy of 0.32 kWhr/kg of mixture were fed.



After homogenization of the compositions, plates were again formed by pressing, again for 15 minutes at 100° C.

Subsequent bending tests showed that the plate of the first mixture was relatively brittle and broke already upon the slightest bending, while the second sample showed increased flexibility and broke only after strong bending. Again, the first specimen showed greater water sorption as than the second.

Of course, the mixtures and processing conditions indicated above in the first and second examples are to be considered merely examples and of course crystal starch may be thermoplastically processable also with a different content of the additive and at other processing temperatures. It was, to be sure, found that upon the use of glycerol the amount of addition is ideally 36 to 38 % by weight, referred to the weight of the total mixture.

Upon the addition of aminoethanol or ethanolamine, the amount of additive is ideally 35 % by weight, upon the addition of aminopropanol ideally 34 to 36 % by weight, and upon the addition of trishydroxyethylaminomethane ideally 34 to 36 % by weight. For the added deformation energy, an ideal value of 0.32 kWhr/kg of starch/addition mixture was found, in which connection deviations from this value also led to the goal.



B. Production of a Polymer Blend

Third Example : Polymer Blend of Polyethylene and Thermoplastically Processable Starch

We started from thermoplastically processable starch or glycerol starch such as prepared in Example 1.

A mixture of 50 % by weight low-density polyethylene (LDPE), 40 % by weight C glycerol starch, and 10 % by weight of a block copolymer (Orevac 18211 of Ato Chemie) were mixed and introduced together into a kneader. The mixture was compounded at a temperature of 160° C with the introduction of 0.2 kWhr/kg of mixture and then granulated.

With this polymer blend, containing 40 % by weight thermoplastically processable starch, standard bodies were produced and the water absorption on the one hand and the stress/strain behavior on the other hand measured.

The shaped bodies were stored for 10 hours in boiling water after which a water absorption of at most 2% could be noted.

The stress/strain behavior was measured by means of a simple elongation test at 20° C. The curve obtained is shown in Fig. 10 and bears the reference number 21. The stress/strain curve will be discussed later.

Thereupon another mixture, containing 70 % by weight of thermoplastically processable starch, 20 % of polyethylene, and 10% block copolymer was worked in the kneader to form the corresponding polymer blend. The



compounding conditions were the same as indicated above. Standard bodies were again made from this polymer blend in order to measure the water resistance. The standard bodies were stored for 10 hours at 70% relative humidity and room temperature without noting any deformation on the surface.

On the other hand, with 100% relative humidity, and therefore in contact with liquid water, it was found that the surface of the standard bodies had become sticky.

On the basis of the two polymer blends produced it can be concluded that the amount of addition of the starch, referred to the total weight of the polymer blend, is to be selected in accordance with the requirements as to water resistance, but that a value of 70 % by weight should not be exceeded. Evidently, sufficient polyethylene must still be present in the polymer blend to form a coherent structure of the polyethylene in the blend. If good water resistance is necessary, the proportion of thermoplastically processable starch in the polymer blend should not exceed 50 % by weight.

Referred to the phase mediator or the block copolymer, it may be stated that an amount of addition of 2 to 5 % by weight already gives good phase mixing of the two polymers. As phase mediator other materials can, of course, also be used such as, for instance, Lotader of CDF Chemie, Novatec of Mitsubishi Chemicals, Surlyn of DuPont, Lonply of Mitsui Toatsu, etc. Said block copolymers are products which are customarily used in the compounding of two-phase polymer blends.

Figs. 7 to 9 show the effect of the amount of phase mediator added on the one hand on the stress at the yield point, on the relative elongation at the



yield point and on the modulus of elasticity. We started from a polymer blend of 50 to 60 % by weight polypropylene, 40 % by weight thermoplastically processable starch in accordance with Example 1, and 10 to 0 % by weight added phase mediator Lotader 3318.

Figs. 7 to 9 show the effects of different added quantities of phase mediator. In Fig. 7 the stress at the yield point is shown, it passing through an optimum at about 3 % by weight added phase mediator, and then assuming a more or less constant value as from 5 % by weight.

The same can be noted in connection with the relative elongation at the yield point from Fig. 8, where the value also remains more or less constant as from 5% added phase mediator.

As compared with this, the modulus of elasticity decreases linearly with the amount of phase mediator added.

Fourth Example : Polymer Blend from Thermoplastically Processable Starch and Polypropylene

We again started from glycerol starch, as prepared in Example 1. 40 % by weight of the glycerol starch was mixed with 50 % by weight of polypropylene and 10 % by weight of Lotader 2400 of CDF Chemie and introduced into a kneader. The polypropylene used, had a meltindex (MFI) of 20g/10sec at 190° C and a load of 5.61 kg. The mixture was mixed in the kneader at 190° C and 0.2 kWhr/kg of mixture and then granulated. Again standard bodies were extruded and the stress/strain behavior measured by means of strain tests at 20° C .



The corresponding stress/strain curve is also shown in Fig. 7 and bears the reference number 22.

Discussion of Fig. 10

Fig. 10 shows a stress/strain diagram in which different test bodies were subjected to elongation tests at 20°C.

For this purpose, standard bodies, prepared from polymer blends with polyethylene and polypropylene as mentioned above, were compared with standard bodies prepared from pure thermoplastically processable starch. Graph 21 shows the stress/strain behavior of a polymer blend with polyethylene and 40% by weight of thermoplastically processable starch and Graph 22 shows a polymer blend with polypropylene and 40 % by weight of thermoplastically processable starch.

By way of comparison, two stress/strain graphs of samples of starch are also included in Fig. 10, they being designated by 23 and 24.

Graph 23 shows the stress/strain graph of a thermoplastically processable starch with 30 % by weight glycerol, to which 0.32 kWhr/kg of starch/glycerol mixture had been added in the kneader upon production.

Finally, Graph 24 refers to the thermoplastically processable starch as prepared in Example 1 i.e. with 36 % by weight glycerol.



Upon comparison of the four graphs it is clear that sample 23 has the lowest strength.

As compared with this, sample 24 has increased strength but cracks occur already upon a relatively short elongation of about 12%.

The stress/strain behavior of samples 21 and 23 is approximately the same, while samples 22 and 24 have a high tensile strength with a particularly high yield point.

It can be concluded from this that upon the production of polymer blends, particularly with polyethylene, the tensile strength is approximately comparable to that of pure thermoplastically processable starch. Since Graph 24, in particular, even has a higher tensile strength than Graph 21, it is assumed that by the incorporation of thermoplastically processable starch in polyethylene the mechanical properties, referred to pure polyethylene, are not impaired. A prerequisite for this, to be sure, is that the plasticization of the starch takes place in accordance with the processing conditions required in the invention.

In addition, it could also be noted that the cracking of the samples from the two polymer blends takes place at a substantially higher elongation than in the case of the pure starch samples.



C. Production of Sheets

Fifth Example : Production of a Single-Layer Starch Sheet

We proceeded from a thermoplastically processable starch having a glycerol content of 35.6 % by weight and a water content of 0.5 % by weight, based on the total weight of the starch mixture.

The starch was melted in a single-shaft extruder with an L/D ratio of 30 and within a temperature range of 180°C to 200°C, operated with a speed of rotation of 110 rpm and a pressure of 90 to 120 bar. As temperature of the compound value of 212° C was measured. A clear transparent sheet was extruded in a slot nozzle at a temperature of 170°C, the speed of withdrawal being up to 12 m/min and the draw-off rolls being cooled to 15°C. In the single-shaft extruder there was furthermore used a screen with different filter screens in order to increase the homogeneity of the melt and keep impurities away from the nozzle.

Upon the production of the sheet it was found that a dwell time of the starch in the extruder of 3 minutes should not be exceeded. With a dwell time of more than 3 minutes in the extruder the starch was obviously degraded and the sheet obtained was brown in color. Furthermore, it is important that the starch granulate does not stand too long (for more than 5 hours) in air before the extrusion since it will otherwise absorb water and thus vapor bubbles can be produced in the sheet. By varying the speed of withdrawal it was possible to produce layer thickness' of the starch sheet of 9 to 270 μ



Sixth Example : Three-Layer Sheet

A three-layer sheet was produced, consisting of low-density polyethylene / starch / low-density polyethylene. As starch, the thermoplastically processable glycerol starch produced in the First Example was used, it having a water content of 0.3 % by weight.

In addition to the single-shaft extruder used in the Fifth Example, another single- shaft extruder having a compression of 1:3 and an L/D ratio of 28 was used. The temperatures on this other extruder were set from 180 ° C to 190° C and we operated with a pressure of 180 bar and a speed of rotation of about 40 rpm, whereby a temperature of the polyethylene composition of 230° was obtained. The throughput was 10 kg/hour.

The three-layer sheet was withdrawn by means of a blow head and in the present example we dispensed with an intermediate layer of a block copolymer. Of course, it is advantageous to use an intermediate layer of a block copolymer in order to obtain excellent adherence between the three layers. All block copolymers, such as already mentioned in Examples 2 and 3, are suitable. Other adherence improving methods are also possible, such as, for instance, corona treatment, ozonizing, etc.

The sheets prepared in Examples 5 and 6 were used on the one hand, to determine the gas-permeability and the moisture permeability, the values of which are compiled in Table. 11. Furthermore, these sheets were provided with coatings in accordance with the following examples.



D. Vapor Deposition on the Starch Sheets

Seventh Example : Vapor Deposition of Aluminum

A starch sheet with a layer thickness of 50μ , prepared in accordance with the Fifth Example, was treated in a high vacuum with aluminum. An aluminum vapor pressure atmosphere of 6×10^{-4} mm Hg was selected, the coating of the starch sheet being carried out on both sides for 20 minutes. The layer which built up during this time amounted to 400 nm each, or a total of 800 nm or 0.8μ .

Another starch sheet was vaporized with aluminum under the same conditions on both sides for 24 minutes, thereby obtaining in each case a layer of 500 nm or, a layer of a total of 1000 nm.

The two starch sheets which had been vapor treated with aluminum in this manner were then subjected to gas- permeability and moisture-permeability tests, the values of which are set forth in Table 11.

Eighth Example: Vapor Deposition. with Silicon Oxide

Similar to the above example, a starch sheet of a thickness of 80μ was used, which had been prepared in accordance with the Fifth Example. The starch sheet was vapor treated with silicon oxide in a high vacuum on both sides, silicon being vaporized by an arc in an oxygen atmosphere of 4×10^{-4} mm Hg. The coating of the starch sheet was effected for 100 minutes, at the end of which a layer of 400 nm had built up on both sides of the sheet.



With a coating time of 150 minutes under the same vapor deposition conditions, a layer thickness of the silicon oxide layer of 600 nm each was obtained.

Again, gas-permeability and moisture-permeability tests were carried out on the starch sheets which had been vapor deposited with silicon oxide, the values thereof being given in Table 11.

Discussion of Table 11

For Table 11, the oxygen gas-permeability as well as the permeability of water vapor were measured for different sheets which had been produced in accordance with the invention.

As comparison for the sheets of the invention, sheets of cellulose acetate, cellulose hydrate, polyvinylidene chloride (PVDC) and PVC were also included in the experiment.

With regard to the measurement of the water-vapor permeability, it should furthermore be pointed out that this was done at 23° C and the relative humidity in the case of the aluminum coating was 100% relative humidity, in the case of silicon oxide 75% relative humidity, and in the case of cellulose acetate, cellulose hydrate and polyethylene, 90% relative humidity.

With reference to the gas-permeability, the oxygen permeability was measured.



Discussion of the Gas-Permeability

As reference values, there are to be considered the values for the PYDC and PVC sheets which, as is known, find far greater use as a result of their low oxygen permeability. As compared with this, the value of the polyethylene sheet shows a very high oxygen gas-permeability, while the three-layer sheet with a starch intermediate layer has an oxygen permeability which is comparable to that of the PVDC sheet.

The oxygen permeability of the aluminum-coated starch sheets is less by a factor of 10 than that of the PVDC sheet or the said three-layer sheet. As compared with this, the oxygen gas-permeability of the starch sheets vapor-treated with silicon oxide is somewhat poorer than that of the three-layer sheet, which is possibly due to a non-optimal coating of the starch sheet. In itself, the value should agree approximately with that of the three-layer sheet which has a starch intermediate layer.

Discussion of the Water-Permeability

As reference, there is to be considered here the value of the polyethylene sheet since, as is known, polyethylene represents an excellent moisture barrier. It is then also found that only the three-layer sheet in accordance with the Sixth Example, which has a starch intermediate layer, has the same excellent value as pure polyethylene.

As compared with this, the water-vapor permeability of the starch sheets coated with aluminum or silicon oxide is considerably poorer, but, to be sure, still considerably better than cellulose hydrate and cellulose acetate.



From the values in Table 11, it is clear what sheet construction is to be referred for what use. To be sure, it should also be pointed out that starch sheets coated with aluminum or silicon oxide have the advantage over the three-layer sheet with polyethylene that they are biologically completely and rapidly degradable, since aluminum is converted upon disposal to aluminum oxide and silicon oxide to sand.

The advantage of the starch sheets coated with silicon oxide is that they are transparent.

The aspects of the invention shown in Figs. 1 to 11 and Examples 1 to 8 refer, in each case, to examples which can be varied or modified in numerous ways. It is essential in all cases here that the starch used be substantially completely thermoplastically processable and no longer have any crystalline regions.

Claims :

1. Single or multi-layer foil with having substantially lower gas permeability, characterised by the fact that the foil comprises at least one layer, which consists at least partially essentially of thermoplastically processable starch.
2. Foil, preferably in accordance with one of the claims, as in accordance with Claim 1, characterised by the fact that at least one layer consists of a polymer blend, which is obtained by mixing of thermoplastically processable starch with a polyolefin.
3. Foil, preferably in accordance with one of the claims, as in accordance with one of the Claims 1 or 2, characterised by the fact that the said at least one layer consists of a polymer blend, the blend being obtained by mixing thermoplastically processable starch with polyethylene and/or polypropylene as well as a phase or bonding agent between the at least two polymers.
4. Single or multi-layer foil, preferably in accordance with one of the claims, as in accordance with one of the Claims 1 to 3, with substantially reduced gas permeability, that is at least nearly moisture-insensitive, characterised by the fact that the foil comprises at least one layer, which is obtained at least partially starting from essentially thermoplastically processable starch with a water contents of $< 3.5\%$ by volume, and characterised by the fact that the moisture insensitivity is the result of the fact, that the at least one layer comprises at least one hydrophobic polymer, which, during the production of the at least one layer, is mixed with starch and/or the fact that the starch is at least partially crosslinked at the surface



of the at least one layer and/or the fact that the at least one layer is covered by at least one more layer that is at least nearly moisture insensitive.

5. Foil, preferably in accordance with at least of the claims, as in accordance with one of the Claims 1 to 4, characterised by the fact that the foil comprises on both sides of the at least one layer at least one more layer each, that consist of a polyolefin and/or a polymer blend of thermoplastically processable starch with a polyolefin.

6. Foil, preferably in accordance with at least one of the claims, as in accordance with Claim 5, characterised by the fact that between the at least one layer and each of the at least one additional layer, an intermediate layer of block polymer is provided for as phase or bonding agent between the layers.

7. Foil, preferably in accordance with one of the claims, as in accordance with one of the Claims 1 to 6, characterised by the fact that the foil at least on one side has an aluminium or silicium oxide, such as preferably a silicium monoxide coating.

8. Foil, preferably in accordance with at least one of the claims, as in accordance with one of the claims 1 to 6, characterised by the fact, that the foil at least on one side has a siloxane coating that is at least partially crosslinked with itself and/or with the starch.

9. Foil, preferably in accordance with at least one of the claims, as in accordance with one of the claims 1 to 8, characterised by the fact that the thermoplastically processable starch includes borax, magenesium-2+ions and/or calcium-2+ions and/or other polyvalent cations.



10. Process for the manufacture of a single or multi-layer foil, particularly in accordance with one of the Claims 1 to 9, characterised by the fact that at least one layer of the foil is produced by slit extrusion or by blowing of thermoplastically processable starch or a polymer blend, obtainable from thermoplastically processable starch and a polyolefin, such as preferably polyethylene or polypropylene.

11. Process, preferably in accordance with at least one of the claims, as in accordance with Claim 10, characterised by the fact that the foil is produced by the slit laminating or blowing extrusion of at least three layers, whereby the at least one layer is covered on both sides by one more layer each, consisting of a polyolefin and/or a polymer blend of thermoplastically processable starch and a polyolefin, such as preferably polyethylene or polypropylene.

12. Process, preferably in accordance with one of the claims, as in accordance with one of the Claims 10 or 11, characterised by the fact that the foil on both surfaces is treated with a UV source or an electron beam gun in such way that the starch is at least partially crosslinked.

13. Process, preferably in accordance with at least of the claims, as in accordance with one of the Claims 10 or 11, characterised by the fact that the foil is coated on at least one side with a siloxane monomer, such as alcylosiloxane and that it is afterwards treated with an electron beam gun, whereby the siloxane is crosslinked with itself or partially with the starch on the surface of the foil.



14. Process, preferably in accordance with at least one of the claims, as in accordance with one of the claims 10 or 11, characterised by the fact that the foil is vapour-deposited in a high vacuum with aluminium or a silicium oxide.

15. Polymer blend, consisting of a polyolefin and starch, in particular for a foil, preferably in accordance with one of the Claims 1 to 9, obtainable by mixing a polyolefin, such as polyethylene or polypropylene, with thermoplastically processable starch with a water content < 3 % by volume, in which the share of the starch amounts to up to 70 % in weight of the total mixture.

16. Polymer blend, preferably in accordance with one of the claims, as in accordance with Claim 15, obtainable by mixing the polyolefin, such as polyethylene or polypropylene with starch, in which the share of the starch amounts to 30 to 70 % in weight of the total mixture and by further mixing it with a phase agent that is a block copolymer.

17. Process for the manufacture of a polymer blend, in particular as in accordance with Claim 15 or 16, characterised by the fact that a polyolefin, such as preferably polyethylene or polypropylene, is processed with 30 to 70 % in weight of thermoplastically processable starch, in reference to the total weight of the mixture, in a kneader or extruder within a temperature range of 150 to 200° C, preferably 160 to 190° C, depending on the melting range of the selected polyolefin, a phase mediator, a block copolymer, preferably being added to the mixture.

18. Thermoplastically processable starch, in particular for foils, preferably in accordance with one of the Claims 1 to 9, and/or for a polymer blend,



preferably in accordance with one of the Claims 15 to 17, obtainable by mixing starch and/or a starch derivative with at least 20 % in weight of an additive, by feeding of thermal and/or mechanical energy as well as by an at least partial drawing off of the naturally bound moisture in the starch, the additive comprising at least one of the following substances :

- Glycerine
- an aminoalcohol
- DMSO (Dimethylsulfoxide)
- N-methylacetamide
- Urea.

19. Thermoplastically processable starch, preferably in accordance with at least one of the claims, as in accordance with Claim 18, characterised by the fact that the water content is < 3.5 % in weight, preferably < 1 % in weight.

20. Process for the manufacture of thermoplastically processable starch, as in particular in accordance with one of the Claims 18 or 19, characterised by the fact that the starch and/or a starch derivative is mixed with at least 20 % in weight, preferably 25 to 45 % in weight, of an additive while feeding mechanical energy in the range of 0.25 to 0.5 kWh/kg starch/additive mixture, during which the mixture is heated to at least a temperature allowing a mixing of the components into a homogenous mass and in which the at least one of the additives includes at least one of the following substances :

- Glycerine
- an aminoalcohol

- DMSO (Dimethylsulfoxide)
- N-methylacetamide
- Urea.



21. Process for the manufacture of thermoplastically processable Starch, preferably in accordance with at least one of the claims, as in accordance with Claim 20, characterised by the fact that the starch is mixed with 25 to 40 % in weight, preferably 32 to 38 % in weight, of an aminoalcohol, such as amino ethanol, amino propanol and/or trishydroxyl ethylene amino ethane; and that it is processed into a homogenous compound, depending on the additional substance and the quantity of the additive, within a temperature range of 60° C to 120° C in an extruder or kneader while at the same time being fed deformation energy of 0.3 to 0.36 kWh/kg of starch-aminoethanol mixture; the natural moisture of the starch to the greatest extent either being drawn off before the mixing with the aminoalcohol or during the mixing with the aminoalcohol by degassing in ways that are known.

22. Process, preferably in accordance with at least one of the claims, as in accordance with Claim 20, characterised by the fact that the starch and/or the starch derivative is mixed with 30 to & in weight, preferably 34 to 40 % in weight, glycerine; and that it is processed into a homogenous compound, depending on the additional substance and the quantity of the additive, within a temperature range of 120° C to 180° C in an extruder or kneader while at the same time being fed deformation energy of 0.3 to 0.36 kWh/kg of starch-glycerine mixture; the natural moisture of the starch or the starch derivative to the greatest extent being drawn off during the mixing in ways that are known.



23. Process, preferably in accordance with at least one of the claims, as in accordance with Claims 20 to 22, characterised by the fact that up to 20 % in weight, preferably approx. 10 % in weight, of the additive is replaced by borax, magnesium sulphate or calcium carbonate.
24. Film or sheet, consisting essentially of a polymer blend, as in particular in accordance with one of the Claims 15 or 16.
25. Shaped body, produced by injection moulding or extrusion of a polymer blend, in particular as in accordance with one of the Claims 15 or 16.