

The invention presented here concerns a biologically degradable polymer mixture, consisting essentially of starch and at least one hydrophobic polymer, a method of producing a biologically degradable polymer mixture consisting essentially of starch and at least one hydrophobic polymer, as well as a single-layer or multi-layer sheet.

For controlling the problem of waste, plastics are more and more being taken into account as time passes, not least of all because their proportion in the treatment of waste is constantly increasing as a result of their increasing use as materials and/or semi-finished materials or raw materials. In contrast to other materials, such as, for instance, glass or metal, the recycling of plastics, although frequently attempted, is very problematical since it is practically impossible to return the very different types of plastics separately, which in itself would be necessary in order to be able to make again reasonable use of the plastics.

For this reason, it must be assumed that larger and larger amounts of plastic must be disposed of, so that the importance of so-called degradable plastics or polymers is increasing. In this connection, biologically degradable polymers are of particular interest which are degraded under the action of micro-organisms, bacteria, fungi, enzymes or the like, and as low-molecular products scarcely constitute a problem any longer.

The probably most widely used biopolymers are in most cases based on starch, in which connection, to be sure, starch is scarcely suitable as an industrially usable polymer. Polymer mixtures with starch are known, the starch or else other biopolymers being preferably used due to their biological degradability, due to their favorable price and due to the independence from petroleum products.

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The use of biopolymers as industrial plastic is described in various patents. EP-O11 82 40, EP-28 24 51, EP-28 89 20, EP-BO 44 01, EP-32 65 14, GB-22 14 919 and EP-32 75 05 describe such as crystal starch, gelatine or other biopolymers are modified or destructured so that they can be used as industrial polymers. This is done by extruding or kneading the starch or the biopolymer with the aid of the water absorbed in the biopolymer or the starch, or by addition of further water, in which case, however, the relatively high water content present is extremely undesirable, for instance during the extrusion of a biopolymer which has been destructured in this manner.

In contrast to this, it is proposed in PCT/WO90/05161 that crystal starch be converted without water and with the use of additives or softeners or swelling agents, such as, for instance glycerol into an industrially usable polymer, i.e. into so-called thermoplastically processable starch. The processability and water resistance of this starch polymer is, it is true, substantially better than the starch polymers produced in accordance with the methods of manufacture described above, but the mechanical properties and, in particular, the water resistance are still insufficient for many industrial uses, such as, in particular, the manufacture of sheets.

For this reason, it has been proposed in a large number of patents that the starch be treated with further polymers in order to obtain properties which permit industrial use. Thus, CH-644 880, CH-644 881, DE-PS-24 62 802 and DE-24 55 732 propose subjecting the starch first to a surface treatment with some additives and then mixing it with thermoplastic polymers, such as polyethylene, etc. In DE-OS-40 38 732 a material is proposed which has a base of starch with the addition of water and plasticizing agents as well as an aqueous polymer dispersion, formed from a thermoplastic polymer.

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In contrast to the above-mentioned documents, patents such as EP-40 28 26, EP-40 47 23, EP-40 47 27, EP-40 27 28, EP-40 73 50, EP-40 97 88, EP-41 78 28, EP-O 32 802, US-39 52 347, US-50 95 054 and AT-365 619, instead of starting from crystal starch, start from destructured starch, gelatinised starch or plasticized starch, which are mixed with thermoplastic plastics such as polyolefins, polyalcohols, ABS-copolymers, ethylene/acrylic acid copolymers, copolymers of vinyl pyrrolidines, copolymers with amino groups, etc. In the case of all the above-mentioned polymer mixtures, based on starch, the problem arises that the compatibility between starch and the other polymers is insufficient or the phase mixing of the individual polymers is poor. As is known, starch is extremely hydrophilic, while, as a rule, the polymers used for the mixing are hydrophobic. In the final analysis, the biological degradability of all the said polymer mixtures is still insufficient since the degradation time of the polymers used, which generally are synthetic polymers, is much too long, so that one can scarcely speak of biological degradability.

In order to improve the mechanical properties, it is proposed in a number of patents, such as WO90/10671, WO91/02023 and WO91/02025, that the starch be first destructured with a high water content and the water content then be reduced to less than 6% during the production of the polymer mixture in the mixing process with an ethylene copolymer. In WO92/02363 it is furthermore proposed to add a high-boiling plasticizing agent to the polymer mixture, while in WO92/01743 of the same applicant a boron compound is admixed with the polymer mixture. In DE-39 39 721 it is furthermore proposed to add a cross-linking agent in addition to a polyvinyl-alcohol-starch mixture for the production of sheets.

In order to increase the biological degradability, WO88/06609, in turn, proposes admixing an iron compound as well as a fatty acid to a polymer

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mixture consisting of polyethylene and starch or modified starch. EP-282 368, in turn, proposes a biologically degradable mixture prepared from polyurethane, PVC with plasticizer, a carbohydrate such as starch, as well as an aliphatic polyester, polyurethane being suggested inter alia, to be based on polycaprolactone. In all the above-mentioned documents of the state of technology, it is clear that in all cases some properties can be improved by the solution selected while others suffer thereby. Thus, a compromise is always made between the properties, such as water resistance, biological degradability, and mechanical properties in order to be able to improve some of these properties.

Thus, for example, in the production of sheets from a polymer mixture, it is proposed, in accordance with a large number of the above-mentioned documents, that the non-starch part of polymer present in the proposed mixtures, produced by itself alone as sheet, i.e. developed with accordingly a substantially thinner wall thickness, has a substantially better tear strength than the thicker sheets produced in corresponding manner from the entire polymer mixture. The reason for this lies either in the high absorption of water or else in the poor phase mixing between the different polymers.

In accordance with patents EP-40 05 31 and EP-40 05 32, it is proposed that the starch be treated, similar to WO90/05161, by a high-boiling plasticizer such as glycerol, urea or sorbitol, in order to obtain thermoplastically processable starch, which is then mixed with ethylene-acrylic acid and/or polyvinyl-alcohol copolymers. Sheets prepared from these starch/polymer mixtures have, it is true, a better tear strength but are still too sensitive to moisture.

The same is true of starch/polymer mixtures prepared in accordance with WO90/14386, in which glycerol-starch-polyethylene and ethylene-acrylic-acid

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copolymers are admixed.

In W091/16375, in turn, there is proposed for the production of sheets, a polymer blend which uses thermoplastically processable starch in accordance with WO90/05161, together with a polyolefin, as well as a phase or bonding mediator in order to improve the phase mixing between the starch and the polyolefin. Similarly, in the as of yet unpublished PCT/CH92/00091, it is proposed that thermoplastically processable starch be mixed with at least one polyolefin and at least one ethylene-acrylate-maleic anhydride copolymer, the esterification product between the starch and the added copolymer serving as phase mediator between the starch phase and the polymer phase. The advantage of this polymer mixture is that, due to the good mixing of the starch phase with the further polymer phase, such as for instance the hydrophobic polyolefin phase, excellent mechanical properties can be obtained when, for instance, manufacturing sheets.

To be sure, all of these polymer mixtures also have the important disadvantage that their biological degradability can in no way satisfy the demands made today as to such degradability.

In connection with biologically degradable polymers, a direction which is targeted away from starch has therefore been pursued for some time, in the manner, for instance, that aliphatic polyesters such as caprolactone or polyhydroxy-butyric acid hydroxyvaleric acid copolymers (Biopol) have been developed which have excellent biodegradability. The problem with these products, however, resides in the fact that they are very expensive to produce, so that their use as industrial mass-produced plastic is out of question.

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In this connection, reference may be made to an article in the journal Capital 6/92, pg 208, entitled "Miracle Films Reduce Plastic Rubbish", in which such new developments are described. Another great advantage of these newly developed materials resides in the fact that they are hydrophobic and thus water resistant, this in contrast to starch which is very hydrophilic. This difference brings it about, however, that a "stretching" of the said expensive, biologically degradable polymers with starch involves the problem that two phases are present which cannot be mixed. This inability to mix starch with the said hydrophobic, biologically degradable polymers in turn, has the result that mixed polymers produced in this manner have poor mechanical properties, whereby, once again, the problem discussed originally above is present, namely that compromises must be made between water-solubility, biological degradability and mechanical properties.

The task of the present invention is now to propose a solution for the problem discussed above by providing a polymer mixture which has good water resistance, has perfect biodegradability, and, in addition, has good mechanical properties, thus making the use as mass-produced plastic possible. Another prerequisite for the suitability as mass-produced plastic resides, not least of all, also in the price of the polymer mixture proposed being within an acceptable range.

In accordance with the invention, the task proposed above is achieved by means of a biologically degradable polymer mixture in accordance with the text of Claim 1.

Proposed is a biologically degradable polymer mixture consisting essentially of starch and at least one hydrophobic polymer, the hydrophobic polymer being at least substantially biologically degradable and being capable of being

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suitably processed thermoplastically, the mixture furthermore including a polymer phase mediator and/or a macromolecular dispersing agent, the starch being present as disperse phase in the mixture with the hydrophobic polymer as continuous phase and the phase mediator or the dispersing agent being responsible for the molecular coupling of the two phases.

The polymer mixture proposed is thus based on the same principle as that set forth in the as of yet unpublished PCT/CH92/00091 in which, surprisingly, the phase mediators proposed in the said international patent application are also suitable for effecting the molecular coupling between the two phases.

Furthermore, similar to PCT/CH92/00091, one preferably proceeds from thermoplastically processable starch such as proposed, for instance, in W090/05161 or W091/16375. In analogous manner, it is therefore proposed in accordance with the invention that the starch be presented as so-called thermoplastically processable starch (TPS), obtained by mixing crystal starch, substantially free of water, with at least one plasticizing or swelling agent in an amount of 15 to 40 % in weight, relative to the weight of the mixture, the plasticizing or swelling agent used being suitable for at least partially swelling or dissolving the starch or derivative of it.

As suitable swelling or plasticizing agent for the production of the thermoplastically processable starch there are suitable, in particular, among other products, sorbitol, glycerol, hydroxy acids such as, for instance, lactic acid and their salts, as well as polyvinyl alcohol. In addition, however, there are also suitable all swelling or plasticizing agents or else additives such as used in the two above-mentioned international patent applications for the production of thermoplastically processable starch.

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The essential advantage of the polymer mixture produced in accordance with the invention over all known, state-of-the-technology polymer mixtures described, lies in the fact that this industrial "plastic" is based on starch, a thermoplastically processable which is substantially insensitive to water, since the hydrophobic polymer is present as continuous phase or matrix in the mixture and, on the other hand, the polymer mixture is of excellent biological degradability within a reasonable period of time, because the hydrophobic polymer itself is of good biological degradability.

In order for the hydrophilic starch phase and the hydrophobic polymer phase to have good mixing properties or for the starch to be suitably dispersible in the hydrophobic polymer, the phase mediator of the invention or a macromolecular dispersing agent is provided for, the phase mediator on the one hand possibly being a block copolymer which comprises at least two blocks, one of which blocks is at least substantially soluble in the hydrophobic polymer phase while the other block is at least substantially soluble in the starch phase

The phase mediator can, however, also be formed by a reactive additional polymer which is substantially soluble in the hydrophobic polymer phase and comprises groups which are reactive with respect to the starch and react with at least a part of the starch and thus, in the mixture, form the phase mediator which is responsible for the above-mentioned molecular coupling of the two phases.

In accordance with another variant of the invention, in order to form the phase mediator, one can start with a hydrophobic polymer of the above mentioned type which includes, in the molecule chain, ester groups which become reactive at raised temperatures after their disintegration and react, at least in part, with at least a part of the starch or of the thermoplastically processable starch. The

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molecule chains of the hydrophobic polymer which have thus reacted with the starch or the thermoplastically processable starch form, within the mixture, the phase mediator which, in turn, is responsible for the molecular coupling of the two phases.

In connection with the polymer mixture produced in accordance with invention, it is essential, however, that in all cases the thermoplastically processable starch be present as disperse phase, for which reason the starch can be present only up to a maximum proportion in the mixture, namely up to the proportion in which the hydrophobic polymer is still present as a substantially coherent continuous phase. As soon, for instance, as the two phases are present in the same function in the mixture, i.e. both as continuous phase and disperse phase, the water resistance of the polymer mixture is no longer assured. In practice, it has been found that the thermoplastically processable starch can be present in the polymer mixture up to a proportion of at most 70 % by weight, based on the total weight of the mixture, in which case the starch is as still present as a disperse phase. If the proportion of starch selected is too small, the problem again arises that the high price of the hydrophobic, biologically degradable polymer becomes too great a factor. Accordingly, the thermoplastically processable starch is present in the polymer mixture of the invention meaningfully in a portion within the range of 30 to 70 % by weight and preferably 50 to 65 % by weight, based on the total weight of the mixture.

As hydrophobic, biologically degradable thermoplastically processable polymers, the following polymers are, in particular, suited :

- cellulose derivatives with a degree of substitution ≤ 2 , such as cellulose ethers, cellulose esters or cellulose mixed esters;

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- aliphatic polyesters, such as caprolactone, polyhydroxybutyric acid, polyhydroxybutyric acid / hydroxyvaleric acid copolymers, and polylactic acids;
- hydrophobic proteins, such as Zein; and/or
- polyvinyl alcohol, prepared by less than 100 % hydrolyzation of polyvinyl acetate, preferably with a degree of hydrolyzation of approx. 88%.

As example of a cellulose ether, mention may be made of cellulose diethyl ether (CdE), which can be thermoplastically processed, for instance, with diethyl tartrate as plasticizer at about 190° C and is biologically degradable. The maximum water absorption at 20° C in water is only just 0.04 parts by weight.

As example of cellulose esters, mention may be made of cellulose diacetate (CdA) or as mixed ester, cellulose acetate butyrate, which can be thermoplastically processed with plasticizers at 180° C and which are biologically degradable. The maximum water absorption at 20° c in water is only just 0.05 parts by weight.

Both of the above examples of cellulose derivatives are offered today on the market at prices in the region of Swiss Francs 12.--/kg.

Caprolactone can be processed without plasticizer at 120° C; it is partially crystalline, with a melting point of between 60 and 80° C and vitreous solidification at -50° C. The mechanical properties are comparable to those of low-density polyethylene. The maximum water absorption at 20° C is < 0.01

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parts by weight; furthermore, caprolactone is biologically degradable. The prices are in the region of Francs 10.-- to 12.--/kg.

Polyhydroxy-butyrac acid / hydroxyvaleric acid copolymers are thermoplastically processable, have good mechanical properties and a low water absorption of < 0.01 parts by weight and are furthermore readily biologically degradable. Their relatively high price of Francs 30.-- to 50.--/kg, on the other hand, limits the use of these polymers.

The same is true of polylactic acid which, although it can be readily thermoplastically processed, has good mechanical properties and is biologically degradable, is rarely used since its price is in the region of Francs 1000.-- to Francs 3000.--/kg.

As hydrophobic protein, zein is proposed, which is thermoplastically processable, with 0.2 parts by weight of lauric acid or diethyl tartrate at 130° C. Zein is furthermore biologically degradable and its cost is about Francs 20.-- to Francs 30.--/kg. One disadvantage of zein lies in its relatively high water absorption, which lies clearly above 0.1 parts by weight.

Finally, mention may also be made of polyvinyl alcohol, known under the trademark Moviol, the polyvinyl acetate used for the production being advantageously 88% hydrolyzed.

As already mentioned above, it is possible to use two different groups of phase mediators. On the one hand, phase mediators are proposed which are compatible with thermoplastically processable starch and, at the same time, compatible with the hydrophobic polymers. On the basis of the different cohesion energy densities of starch and the hydrophobic polymers, only block

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copolymers enter into consideration, namely those which consist of one block soluble in starch and of one block soluble in the hydrophobic polymer phase. It is, of course, essential in this connection that the phase mediator also be biologically degradable and can be suitably processed thermoplastically. As example of this, a polycaprolactone/polyvinyl alcohol copolymer may be mentioned. Such a phase mediator can be added in an amount of up to 100 % based on the weight of the hydrophobic polymer, but preferably only an amount of 5 to 50 % by weight of such polymer is used for the manufacture of the polymer mixture of the invention.

The other group of phase mediators comprises reaction products between a further biologically degradable polymer with starch which has groups reactive with respect to the starch and is compatible with the hydrophobic polymer phase, these reactive groups possibly comprising, for instance, epoxy groups or else acid anhydride groups. These reactive groups now react with a part of the starch and thus form in the polymer mixture the phase mediator which is responsible for the molecular coupling of the two phases.

Such a phase mediator can, in turn, be present in the polymer mixture in an amount of up to 100% by weight, based on the weight of the hydrophobic polymer, the polymer mixture preferably having a proportion of phase mediator of 5 to 50% by weight, based on the weight of the hydrophobic polymer.

The additional polymer used for the production of this type of phase mediator can be a hydrophobic polymer, taken from the above-indicated list of hydrophobic polymers which are used in the polymer mixture. In this connection, one of the said polymers is provided with reactive groups, such as, for instance, epoxy groups or acid-anhydride groups, which then react with the starch upon the production of the polymer mixture. In principle, it would, of

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course, be conceivable for the hydrophobic polymer to be replaced completely by such an additional polymer, whereby, in the final analysis, the polymer mixture would consist only of thermoplastically processable starch and the phase mediator.

The introduction of the reactive groups is effected in this connection in the manner that the reactive groups are grafted on a hydrophobic polymer, such as, for instance, a polymer in accordance with the above-indicated list, by means of vinyl polymerization or condensation, this being achieved in the case of the epoxy groups by a glycidyl ether and in the case of acid anhydride groups for instance by succinic anhydride. Of course, it is also possible to provide other reactive groups which can react with the starch molecules.

In contrast to this, it is, however, also possible to produce a polymer blend defined in accordance with the invention, during the production of which an externally added phase mediator can be dispensed with, in the manner that the phase mediator forms itself during the production of the polymer mixture. In this connection, it is proposed, in accordance with the invention, that as hydrophobic polymer be used a polymer having ester groups which are built into its molecule chains and which, at raised temperatures, after disintegration, become reactive and thus effect transesterification of the hydrophobic polymer and also, occurring in part as quasi additional polymer, react with a part of the starch or of the thermoplastically processable starch. The reaction products of the molecule chains which thus react with the starch then form the phase mediator which is again responsible for the molecular coupling of the two phases. Naturally, it would theoretically be possible for all molecule chains of the hydrophobic polymer to react with the starch, but it can as a rule be assumed that the transesterification reaction takes preference over the esterification reaction with the starch, whereby only a part of the

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hydrophobic polymer is converted into phase mediator. Again, the phase mediator eventually will be present in the polymer blend in an amount of about 5 to 50 % by weight, based on the total weight of the hydrophobic polymer.

As example of this, mention may be made of polycaprolactone, which contains in the molecule chains ester groups which, for instance, can presumably enter into the above-mentioned transesterification reaction with the starch at a temperature of about 190° C.

Generalizing, this results in particular from what has been stated above that in the polymer mixture of the invention, the phase mediator can be formed of starch or thermoplastically processable starch with aliphatic polyester grafted thereon, obtained for instance by reaction of polycaprolactone with the starch. In this connection, it has been found that the more starch including grafted polyester is present, the more the water resistance of the polymer mixture can be increased.

The polymer mixtures proposed in accordance with the invention can, of course, be provided with any desired additives, additions, fillers, pigments, etc., such as generally known in the case of polymers and, in particular, in the case of thermoplastically processable plastics. Since their addition is strongly dependent on the use intended, and since furthermore, such additions are well known from practice, their use in connection with the polymer mixtures defined in the invention will not be taken up in detail, with the exception of plasticizers. It is self-evident that, in view of the requirement of biological degradability of the polymer mixtures, this property must also be paid the necessary attention during the use of such additions and additives, since otherwise the biological degradability would naturally suffer thereby.

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As additive, mention may be made, in particular, of the admixing of a plasticizer which is compatible with the hydrophobic polymer and preferably reduces its melt viscosity. On the one hand, the advantage of a plasticizer is that the hydrophobic, biologically degradable polymer is made less brittle by the plasticizer and furthermore, that during the production of the polymer blend, the quasi encapsulation of the thermoplastically processable starch by the hydrophobic phase is favoured by the reduction of the viscosity.

A process which is particularly suitable for the production of the above-mentioned biologically degradable polymer mixtures of the invention is described in the text of Claim 16.

Preferred execution variants of the process of the invention are characterised in the dependent Claims 17 to 24.

For the production of the biologically degradable polymer mixture of the invention, one can start either from crystal starch or from thermoplastically processable starch, such as defined, for instance, in international patent application WO90/05161.

In the event that one starts from crystal starch, it must, of course, first of all be rendered soluble with the use of at least one plasticizing or swelling agent, in which connection the crystal starch should have for this rendering soluble a water content of $< 10\%$ and preferably $< 6\%$ by weight. To be sure, a certain water content of the said order of magnitude of up to 6% by weight can definitely be advantageous for the rendering soluble of the crystal starch, for instance with glycerol or sorbitol. Afterwards, the mixture prepared in this manner is melted to form a thermoplastically processable starch and mixed mechanically, in which connection the water content, however, must now be

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reduced to less than 1% by weight, and preferably $< 0.5\%$ by weight, based on the total weight of the mixture, and the mixing then continued until a homogeneous mass is obtained.

The thermoplastically processable starch is now mixed in the melt together with at least one biologically degradable hydrophobic polymer which is thermoplastically processable and with a phase mediator or a dispersing agent or another polymer soluble in the hydrophobic polymer phase, which contains groups that are reactive to starch, the water content, before or during the mixing of the said components being reduced to less than 1.0% by weight and preferably $< 0.5\%$ by weight, based on the total weight at the mixture in order to obtain in this way the biologically degradable polymer mixture defined in accordance with the invention, in which connection, in the case of the use of an additional polymer, the polymer mediator in the polymer mixture is formed by reaction of this additional polymer with a part of the thermoplastically processable starch.

It is important that the production of the polymer blend take place essentially with the exclusion of water, since, otherwise, the dispersing of the starch in the hydrophobic polymer under the action of the phase mediator would not take place properly. Thus, for instance, the acid anhydride groups in the presence of water, do not react with the starch to form the phase mediator but, rather, hydrolyze. This on the other hand prevents the formation of the phase mediator, whereby, as mentioned, a dependable dispersing is made impossible.

The presence of a substantially perfect dispersion in the polymer blend is, however, a prerequisite for the good mechanical properties of the mixture desired in accordance with the invention. Furthermore, there is the danger of the formation of bubbles during the processing of the polymer mixture A

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post-drying of the polymer blend after its production is not able to subsequently improve a polymer mixture which has been defectively produced as a result of moisture.

For the preparation of the polymer mixture of the invention, up to 70% by weight, based on the total weight of the mixture of thermoplastically processable starch can be used in order to make certain that, as required above, the hydrophobic polymer is still present substantially as the continuous phase. The remaining portions in the polymer mixture of the invention are taken up, on the one hand, by the hydrophobic polymer and, on the other hand, by the phase mediator which, based on the weight of the hydrophobic polymer phase, can constitute 2 to 100% by weight, and preferably 5 to 50% by weight. Accordingly, during the production of the polymer mixture, either 2 to 100% by weight, based on the weight of the hydrophobic polymer phase, of a phase mediator is added, or the same weight percent of another polymer which comprises the reactive groups in order to form the phase mediator in the polymer mixture by reaction with parts of the starch.

While for the production of the thermoplastically processable starch, the starch is mixed with the swelling or plasticizing agent in a temperature range in the region of 150 to 190° C, the mixing of the thermoplastically processable starch with the hydrophobic polymer and the phase mediator or the further polymer takes places in a temperature range of about 150 to 230° C. The mixing temperature to be selected depends in this connection essentially on the processing temperature of the hydrophobic polymer selected, for which reason, for instance, when using cellulose derivatives, a temperature on the order of magnitude of 190 to 220° C is used, while when using polycaprolactone, the production of the polymer mixture of the invention is preferably effected within a range of about 150° C to 190° C. With regard of the hydrophobic polymers to

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be used, reference is made to the list of suitable hydrophobic polymers given in connection with the characterizing of the polymer mixtures of the invention.

Similarly, as already stated when characterizing the different polymer mixtures of the invention, in principle, polymer mixtures with two different types of phase mediators can be produced. In accordance with a first variant, the thermoplastically processable starch is treated with preferably 5 to 50% by weight - based on the weight of the hydrophobic polymer - of a block copolymer as phase mediator, the phase mediator consisting of at least one block soluble in the starch phase and one block soluble in the hydrophobic polymer phase, such as, for instance, a polycaprolactone/polyvinyl - alcohol copolymer, in which connection, the at least one hydrophobic polymer, such as, for instance, polycaprolactone, is eventually admixed together with the phase mediator. Of course, phase mediators other than the one indicated above can also be used, such as, for instance, partially hydrolyzed polyvinyl acetate or a polyvinyl acetate/polyvinyl pyrrolidone block copolymer; it is essential in this connection that the phase mediator used contains at least two blocks, of which one each is soluble in one of the two phases.

In the other case, the reactive groups are either first grafted on the hydrophobic polymer suitable for the production of the polymer mixture of the invention by means of vinyl polymerization or condensation by reaction with a glycidyl ether of at least one aliphatic di- or polycarboxylic anhydride, such as, for instance, succinic anhydride, in which case the additional polymer thus formed together with the hydrophobic polymer and thermoplastically processable starch are mixed intensively in the melt with a water content of < 0.5 and preferably < 0.1 % or a hydrophobic polymer that has ester groups incorporated in its molecule chains is used; the ester groups becoming reactive after disintegration at raised temperature and thus leading to a transesterification of

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the hydrophobic polymer and also, acting intermediately as additional polymer, reacting in part with a part of the starch or of the thermoplastically processable starch in order to form the phase mediator. In corresponding manner, a hydrophobic polymer having ester groups incorporated in its molecule chains is also intensively mixed with the thermoplastically processable starch in the melt and with the above-mentioned low water content. This mixing is effected, for instance, in a plastic processing apparatus or machine such as a kneader or an extruder, the reactive groups of the said additional polymer or the disintegrating built-in ester groups reacting during this mixing process with a part of the starch or of the thermoplastically processable starch for the production of the phase mediator. It is essential, in this connection, that the use of an additional polymer that includes reactive groups is a polymer which is substantially soluble in the hydrophobic polymer phase or readily mixable with it. When using a polymer with built-in ester groups in its molecule chains, this happens automatically.

For the production of an additional polymer, one can start, for instance, from ethyl cellulose which is mixed with oleic acid or, in general, with an unsaturated fatty acid or a corresponding triglyceride. By means of radical reaction of the vinyl groups, the maleic acid anhydride groups are grafted onto the ethyl cellulose, which, as mentioned above, are capable of reacting with the starch and in this way form the phase mediator.

As example of a hydrophobic polymer with ester groups built into its molecule chains, mention may be made of polycaprolactone, the ester groups of which permit transesterification reactions with the starch from a certain temperature onwards.

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In accordance with another variation of the invention, it is possible to produce a polymer mixture according to the invention by mixing thermoplastically processable starch with a hydrophobic polymer which consists, at least almost exclusively, of macromolecules which have groups that are reactive with the starch. In this case, the hydrophobic polymer and the phase mediator in the polymer mixture of the invention are substantially identical. In this case as well the hydrophobic polymer or the phase mediator has, of course, to be present in such proportion in the polymer mixture that, as required in the invention, the starch is still present as disperse phase, with the hydrophobic polymer or the phase mediator as continuous phase, in which connection the molecular coupling of the two phases is given due to the bonds between the hydrophobic polymer and a part of the starch molecules.

To return to the above-mentioned example of the ethyl cellulose converted by oleic acid, ethyl cellulose is exclusively used, accordingly, for the production of the polymer blend, which has appended maleic anhydride groups. Depending on the selected processing temperature, mixture ratio and processing time, more or less phase mediator is formed, in which connection, as mentioned, it has to be ensured that the starch is still present as disperse phase. From the standpoint that the hydrophobic polymer and the additional polymer are substantially identical, there can naturally also be included the case, as mentioned, in which the hydrophobic polymer contains ester groups built into its molecule chains.

In accordance with the a further variant of the method of the invention, it has been found advantageous if the hydrophobic polymer is treated with a plasticizer before mixing it with the starch or the thermoplastically processable starch. In this connection, it is advantageous if the plasticizer selected is at least substantially compatible only with the hydrophobic polymer, i.e. is soluble

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only in the hydrophobic phase. Furthermore, it has proven advantageous if the selected polymer reduces the melt viscosity of the hydrophobic polymer. This leads to the assumption that the formation of a dispersion with the starch as disperse phase and with the hydrophobic polymer as continuous phase is further favored if the hydrophobic polymer is treated with a plasticizer which reduces its melt viscosity. As a rule, as is known, the phase with the lower viscosity in a dispersion forms the continuous phase.

Also in connection with the method defined in accordance with the invention, the description of filled, colored, reinforced polymers, etc. is dispensed with since the preparation of such polymer mixtures is well known in the plastics processing industry.

The biologically degradable polymer mixtures defined above in accordance with the invention are suitable for both injection molding and extrusion applications, reference being made here, in particular, to the production of single or multi-layer sheets. In this connection, at least one layer of such a sheet consists of a polymer mixture according one of the Claims 1 to 15. Therefore it is conceivable that a single-layer sheet is produced entirely from a polymer mixture of the invention or else, for instance, a three-layer sheet comprising a central middle layer, produced, for instance, exclusively from thermoplastically processable starch while the two outer layers which cover the layer of starch can be prepared from a polymer mixture such as defined in the invention. In this way, it is possible to produce a substantially water-resistant sheet which consists of a total of 80% by weight or even more of thermoplastically processable starch and which, as a whole, satisfies the demands made as to biological degradability.

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The invention will now be described in further detail below, in part with reference to the accompanying illustrations and on the basis of theoretical considerations and practical examples.

- Illustr. 1 in a diagramme shows the morphology of a polymer mixture in accordance with the invention;
- Illustr. 2 in a diagramme shows the mechanics of the phase mediation in a polymer mixture according to the invention;
- Illustr. 3 in a diagramme shows a representative stress-strain diagramme for the dermination of the mechanical properties for test bodies prepared by means of the polymer mixture of the invention;
- Illustr. 4 show molecular weight distributions of polycaprolactone, not
and 5 pre-treated and pretreated by means of esterification;
- Illustr. 6 shows the biological degradability of a polymer mixture in accordance with the invention in comparison with cellulose;
- Illustr. 7 the biological degradability of cellulose in comparison to various so-called biodegradable polymers.

First of all, referring to Figs. 1 and 2, the basic problem or object of the present invention which has led to the preparation of the polymer mixtures defined in the invention will be briefly discussed.

The incompatibility of the thermoplastically processable starch with hydrophobic polymers can be used, as shown diagrammatically in Illustr. 1, in

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order to disperse them in a matrix consisting of a hydrophobic material. With this structure, it is to be expected that the swelling of the thermoplastically processable starch during storage under water or the water vapor absorption can be effectively limited. The diagramme of the morphology of a polymer mixture in accordance with the invention shows, on the one hand, the thermoplastically processable starch 1 as disperse phase and the hydrophobic polymer 2 as continuous phase.

The boundary surface 3 present in this connection is shown greatly enlarged, diagrammatically, in Illustr. 2. The disperse distribution of the thermoplastically processable starch 1 in the hydrophobic polymer 2 is made possible under the action of the phase mediator 4, which phase mediator 4 comprises a segment 6 which is mixable with the thermoplastically processable starch 1 and a segment 5 which is mixable with the hydrophobic polymer 2. The phase having the lower viscosity in this connection, as a rule, forms the continuous phase, for which reason it may be indicated to add a viscosity-reducing additive, such as, for instance, a plasticizer, to the hydrophobic polymer. In this connection, it is advantageous for this plasticizer to be compatible only with the hydrophobic phase in order in this way to effect a reduction of the viscosity specifically in the hydrophobic phase.

The exact particle size of the individual phases, as shown in Illustr. 1, is determined by the rheological behavior of the individual phases, the nature of the mixing process, and the interfacial energy. Based on the thermodynamically caused incompatibility of the thermoplastically processable starch with the hydrophobic polymer, only a slight intermixing of the two polymers takes place at the phase boundary, which as a rule leads to an impairment in the mechanical properties of a mixture of the two substances. For this reason, it is necessary that a sufficient mechanical coupling of the two phases or a low

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interfacial energy be obtained, which can be achieved by the use of the block copolymer or phase mediator shown diagrammatically in Illustr. 2. This phase mediator penetrates through the phase boundary 3. As a rule, these phase mediators consist of two blocks each sufficiently compatible with one of the two polymers respectively.

The preparation of polymer mixtures defined in accordance with the invention will now be explained in further detail on the basis of the following examples, in which connection the above-indicated fundamental theoretical considerations are taken into consideration in order to obtain the good properties desired in accordance with the object of the invention for a thermoplastically processable, biologically degradable polymer mixture.

1. Polymer mixture of cellulose acetate butyrate and thermoplastically processable starch

As cellulose ester, cellulose acetate-butyrate (ZAB) was mixed together with thermoplastically processable starch (TPS) in a Brabender kneader at 160° C with different mixture ratios. As TPS there was used a starch which is reacted with 30% by weight glycerol, this being done in accordance with the processing conditions disclosed by way of example in W090/05161 or in W091/16375. Tenite Sutryate 525 of the company Eastman Kodak was used as cellulose acetate-butyrate-mixed ester.

The two polymers were first mixed without any additives in the range of parts by volume of ZAB to 80 parts by volume of ZAB, the balance being TPS, and on basis of pressed plates prepared therefrom, the swelling in water was investigated and tensile tests carried out on test specimens. In this



connection, it was found that as from about 55 percent by volume of ZAB the swelling was only slight and furthermore that the test specimens had experienced an increase in weight, leading to the conclusion that the TPS phase could no longer be extracted from the test specimens.

The values for elongation at rupture and rupture work are shown in Table 1.1 below. In this connection it can be noted that, as a function of the percentage by volume of the ZAB, the rupture work and the elongation at rupture pass through a minimum at about 50 to 60 by volume percent of ZAB the rupture work increasing approximately twenty times at 80 percent by volume. It can be concluded from this that in this range the transition from TPS to ZAB is present as continuous phase. Upon the simple mixing of TPS and ZAB, there is thus obtained merely a drastic impairment in the mechanical properties; this is undoubtedly due to the insufficient dispersion of the TPS phase in the ZAB matrix and to very poor mechanical coupling of the phases.

Table 1.1

Percent by Volume ZAB (% V/Vges)	Elongation at Rupture (%)	Rupture Work (KJ/mm ²)
30 %	10 %	10
40 %	10 %	37
50 %	8 %	35
60 %	4 %	28
70 %	6 %	66
80 %	37 %	800

Rupture work and elongation at rupture of TPS/ZAB blends as a function of the percent by volume of EAB; prepared at kneading temperature of 160° C; tensile tests carried out on 0.3 mm pressed plates.

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Since, in the case of incompatible polymer mixtures, the continuous phase is formed by the component having the lower viscosity, as in our case the hydrophobic polymer or the ZAB, a plasticizer which is only compatible with the ZAB phase and thus selectively reduces its viscosity was now added to the mixture. In this way, a better dispersion of the TPS phase was to be obtained. As plasticizer, acetyl triethyl citrate (ATE) was used because of its biological degradability. Mixtures were prepared with an amount of TPS of 40% by volume, with variation of the volumetric ratio of ATZ to ZAB, the mechanical properties obtained being set forth in Table 1.2 below:

Table 1.2

Percent by Volume ZAB (% V/Vges)	Elongation at Rupture (%)	Rupture Work (KJ/mm ²)
8.3 %	91.7 %	670
20 %	80 %	620
25 %	75 %	450
33 %	67 %	270
42 %	58 %	160

Rupture work and elongation at rupture of TPS / ZAB / ATZ blends as a function of the percent by volume of ATZ in the ATZ / ZAB phase. Mixtures prepared at a kneading temperature of 160° C; tensile tests carried on 0.3 mm pressed plates.

In the case of 8.3 ATZ in the ZAB phase a twenty-fold increase in the rupture work is already achieved as compared with a specimen without ATZ but otherwise the same amount of TPS (40 Vol.%), in which connection the material can be elongated up to 70%. On the basis of a scanning electron microscope

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photograph of the polymer mixtures containing a proportion of ATZ of 25* by volume in the ZAB phase, it could be shown that the desired morphology had been achieved and that ZAB forms the continuous phase. To be sure, it could be noted from the photograph of the polymer mixture that the size of the TPS microphases was still considerable and the dispersion obtained is insufficient. This is also shown in Table 1.2, where the mechanical properties with a percentage by volume of 75% ZAB are insufficient.

A further improvement in the mechanical properties was now obtained by incorporating a phase mediator in the polymer mixture as proposed in accordance with the invention. Upon the preparation of the polymer mixture of ZAB and TPS in accordance with the invention, epoxidized soybean oil was added, it serving at the same time as plasticizer for the ZAB phase. The mechanical properties measured for specimens with 40 % by weight TPS are set forth in Table 1.3.

Table 1.3

Vol. ant.ESO (% V/Vges)	Vol. ant. ZAB (%) V/Vges)	Elongation at Rupture (%)	Rupture Work (KJ/mm2)
8.3 %	91.7 %	20 %	600
20 %	80 %	53 %	620
25 %	75 %	92 %	880
33 %	67 %	93 %	790
42 %	58 %	94 %	600

Rupture work and elongation at rupture of a blend of (1) 40% V/Vges TPS, (2) 60% V/Vges ZAB/EOS. the volumetric percentages in the table refer to the ZAB/EOS phase, rupture work and elongation were determined on 0.3 mm pressed plates, blend prepared at 160° C in a Brabender kneader.

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From this table it can be noted that by the addition of epoxidized soybean oil, the rupture work can be clearly increased as compared with ATZ. A scanning electron microscope photograph of the polymer blends thus prepared shows furthermore that the microphases of the TPS are substantially smaller and still have a size of only about 3 to 4 μm , in contrast to the TPS microphases in blends containing ATZ, where the size of these phases is in part 15 μm . As compared with the blends with ATZ as plasticizer, a reduction in the diameter of the dispersed TPS microphases by a factor of 3 to 4 can thus be obtained with the use of epoxidized soybean oil. This, in turn, means an increase in the total boundary surface between the two phases by the same factor of 3 to 4. Since even with an optimal selection of the melt viscosities of two incompatible blends, a mechanical dispersion on this length scale can scarcely be obtained, it has to be assumed that the epoxidized soybean oil, in addition to its function as plasticizer of ZAB, has also effected a reduction in the interfacial energy between the two phases. This can have been obtained only in the manner that the epoxy groups reacted in part with starch molecules and thus produced the phase mediator claimed in accordance with the invention.

The best mechanical properties were obtained with a blend consisting of 40% TPS, 15% epoxidized soybean oil, and 45% ZAB (percentage by volume), the determination of the degree of swelling based on pressed plates of a thickness of 0.3 mm after storage at 24° in water showed stable behavior, i.e. the plates do not fall apart. The swelling amounted to merely 9%, whereby the goal was obtained that TPS has been included in a matrix of a hydrophobic polymer.

the polymer blend produced in this manner can be produced practically 100% from renewable growing raw materials, whereby a material has been developed, the components of which are substantially biologically degradable.

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Upon the preparation of polymer mixtures from cellulose acetate-butyrate mixed ester and thermoplastically processable starch, it could therefore be shown that, with the selection of a suitable phase mediator, blends of good mechanical properties are obtained, the required morphology, i.e. an encapsulating of the TPS phase in the ZAB matrix, being achieved. Moulded parts made from this material remain stable upon storage in water and exhibit only very limited swelling. Particularly with epoxidized soy oil, it was possible to produce a blend having excellent properties. In this connection, a morphology was obtained which is characterized by a size of the TPS microphases of less than 2 to 3 μm . As mentioned above, it is therefore to be assumed that the epoxidized soybean oil not only influences the viscosity of the ZAB phase but also effects a certain reduction in the interfacial energy between the two phases. A chemical reaction (ether formation) of the epoxy groups with the starch is therefore to be assumed. A chemical modification of the starch at the phase boundary has thus been obtained, whereby a certain compatibility with the ZAB phase has been brought about.

2. Polymer blend prepared from thermoplastically processable starch and polycaprolactone

Polycaprolactone (PCL) has proven suitable for the preparation of polymer blends with thermoplastic starch (TPS) - Polycaprolactone is a homopolymer of E-Caprolactone and, according to the manufacturer (Union Carbide), is completely biologically degradable and non-toxic and suitable for the preparation of sheets and as polymer additive.

For the preparation of different polymer blends, three different types of TPS were used, designated below as glycerol-TPS, standing for a thermoplastically processable starch containing 20% by weight glycerol; as TPS-LSM 1 standing

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for a thermoplastically processable starch containing 15 % by weight glycerol and 15 % by weight sorbitol; as well as TPS-LSM2 standing for a thermoplastically processable starch containing 30% by weight sorbitol.

All three types of TPS were extruded, together with caprolactone, in a ratio of 1:1, the two types PCL 5 787 and PCL 767E of Union Carbide being used for the tests carried out.

In order to provide conditions which were as free as possible of water during the extrusion, the thermoplastically processable starch was atmospherically degassed before the addition of the polycaprolactone, whereby the water content was clearly reduced to less than 0.5% by weight. The extrusion was carried out on a Theysoim twin-screw extruder, specimens having different temperature profiles being produced for each mixture. On average, approximately the following temperature profile was selected in the extruder:

80 to 160° / 160 to 170° / 180 to 190° / 150 to 180° / 130 to 140° / 130° / 100 to 140°.

The throughput of the different polymer mixtures was varied between 20 kg/hour and 40 kg/hour. The speed of the extruder was selected within a range of 170 to 300 rpm. The energy introduced thus gave a value of about 270 to 440 W per kg of polymer mixture. The measured water content was 0.26 to 0.6% by weight H₂O.

Sheets were then formed by blow molding from the polymer mixtures prepared with the three types of TPS and the two types of PCL, in which connection, due to the low melting point of the PCL (about 60° C), the take-up

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rolls had to be cooled or, even better, the sheets were produced by pulling up. Tensile tests were carried out with the sheets produced in this manner in order to measure inter alia the tear strength and rupture energy. In this connection, the sheets were tested both after conditioning for 24 hours at room temperature and after 24 hours stored in water.

In order better to interpret the measured values of the tensile test set forth below in Table 2.1, reference is made, first of all to Illustr. 3, in which a stress-strain diagram is shown. The abbreviations used in said Illustr. are defined in the following list:

RS	Yielding point
As	Relative elongation at the yielding point
Rm	Maximum stress
Am	Relative elongation at maximum stress
Rr	Tear stress
Ar	Relative elongation at rupture

Furthermore, the abbreviations in Table 2.1 have the following meaning :

d	Thickness of the sheet
b	Width of the sheet for all sheets evaluated = 15.0 mm
SO	Cross section of the sheet (reference value for the tension)
W	Rupture work (proportional to surface area under the graph in. acc. with Illustr. 3)
N	Identification of the sheet sample measured

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Herein is :

- N = 1** Sheet produced from glycerol-TPS and PCL, the measured values shown in Table 2.1 each being an average value averaged over the values measured for different specimens, prepared, on the one hand, with the two PCL types 787 and 676 E and under the above-indicated different extrusion conditions.
- N = 2** Samples from glycerol TPS and PCL, after storage in water for 24 hours.
- N = 3** Samples of TPS, LSM 1 and PCL, conditioned for 24 hours at room temperature.
- N = 4** Specimens from TPS, LSM 1/PCL after storage in water for 24 hours.
- N = 5** TPS, LSM 2 and PCL, conditioned at room temperature for 24 hours, and
- N = 6** TPS, LSM 2 and PCL after storage in water for 24 hours.

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Table 2.1

N	Rs N/mm2	As %	Rm N/mm2	Am %	Rr N/mm2	Ar %	d μm	SO mm2	W J/m2	E-Mod. N/mm2
1	10.4	25.5	25.7	781	25.7	782	47	0.72	5.3	220
2	13.5	5.8	14.1	5	14	6	45	0.68	0.11	630
3	15.4	7.9	19.2	607	19.2	607	22.3	0.35	4.35	693
4	18.6	10.2	20.1	290	17.9	317	19.9	0.32	3.17	359
5	19	10.3	21.7	615	20.7	685	92.2	1.38	6.52	717
6	12.7	13	22.4	675	18	785	90.7	1.21	7.08	468

As can be noted from Table 2.1, the glycerol blend in dry state has a tear strength of about 25N/mm2 and a rupture energy of about 5J/m2. After 24 hours in a water bath, the tear strength, however, decreases to about 14N/mm2 and the rupture energy even clearly to below 1J/m2. This great decrease in the mechanical values may be due to the washing out of glycerol.

As compared with this, the sheet prepared from TPS LSM 1 and PCL in its dry state has a tear strength of about 19 N/mm2 and a rupture energy of about 4J/m2. Even in "soaked" state, the corresponding measured values differ only insignificantly from the values indicated; only the rupture energy drops to about 3J/m2.

The sorbitol sheet tears at about 2E/mm2 with a rupture energy of about 6,5 N/mm2. These values do not change even after 24 hours in a water bath, i.e. they tend rather to increase.

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By way of comparison, it may furthermore be mentioned that sheets prepared from pure polycaprolactone have a tear strength of about 18 to 20 N/mm² and a rupture energy on the order of magnitude of 7 to 9 J/m².

The polymer mixtures prepared with thermoplastic starch and polycaprolactone in a ratio of 1:1 on a twin-shaft extruder are suitable both for injection molding, flat-sheet extrusion, and the blowing of sheets. In particular, the polymer mixtures prepared with the sorbitol starch show excellent mechanical properties, so that, based on the above-indicated theoretical considerations concerning polymer mixtures containing two different phases, it must be assumed that a mechanical coupling of the two phases is established at the boundary surfaces.

It was therefore to be assumed that the ester groups in the polycaprolactone which are installed in the molecule chains enter into esterification reactions with the thermoplastic starch, whereby the molecule chains which thus react again form with the starch the phase mediator mentioned in accordance with the invention. This assumption was confirmed by the fact that transesterification reactions take place in the polycaprolactone starting from a given temperature, which it was possible to verify by molecular-weight distributions. This circumstance will be explained in further detail with reference to the molecular weight distributions shown in Figs. 4 and 5.

Illustr. 4 shows a differential molecular weight distribution of poly-epsilon-caprolactone P787 of the Union Carbide Corporation which was not subjected to prior treatment. The average molecular weight obtained is in this connection 213,500, the minimum measured molecular weight 212,400, and the maximum molecular weight ascertained was 218,600.

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The polycaprolactone used for the determination of the curve in Illustr. 4 was then heated to 190° C and then cooled. The molecular-weight distribution was again measured, it being now shown in Illustr. 5. Already on basis of the showing in Illustr. 5, it can clearly be noted that the molecular weight distribution is considerably broader, whereby it already is clear that an internal rearrangement of the molecule chains has taken place. Due to the ester groups present in the molecule chain, a transesterification reaction has taken place.

The values determined on the basis at the distribution of Illustr. 5 gave the following picture.

Weight average of the molecular weight	280,000
Maximum molecular weight:	538,400 and
Minimum molecular weight:	146,300.-

Since the internal transesterification reaction of the molecule chains in the polycaprolactone are in competition with corresponding esterification reactions within the starch, it is clear that, in this way, during the processing of the polycaprolactone with the thermoplastic starch, a part of the polycaprolactone reacts with the starch, as a result of which, as required in accordance with the invention, the phase mediator is formed which is responsible for the molecular coupling of the two phases. The presence of reaction products between polycaprolactone molecule chains with the TPS could finally be proven on basis of a heat-flow diagram, whereby the above-indicated assumption could be finally proven.

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3. Measurement of the biological degradability or compostability of a polymer mixture prepared by way of example in accordance with the invention

The polymer mixture in accordance with the invention which is used in Example 2, consisting of a 1:1 mixture of polycaprolactone and thermoplastically processable starch, the latter having been destructured with 30% sorbitol, was subjected to a composting test and the determination of the biological degradability. In comparison with this, the biological degradability of cellulose was also measured.

The corresponding degradability results are shown in Illustr. 6, the progressive degradation being measured as a function of the percentage conversion of carbon into CO₂. The diagram of Illustr. 6 therefore shows, on the one hand, the composting of the caprolactone/TPS mixture, which is represented by the curve 10. In comparison with this, the degradability of cellulose is represented by the curve 11. While the PCL/TPS mixture is completely degraded within only thirty days, the degradation of cellulose is not yet completed in thirty days. The measurement of the degradability was carried by the Organic Waste System Inc. of Ghent, Belgium, and the US standard AETM D5338 was used as method of measurement.

In order further to document the excellent degradability of the polymer mixture prepared in accordance with the invention, the biological degradability of cellulose as compared with various, so-called biologically degradable polymers available in the market is shown in Fig. 7. In it, the curve 11 again shows the degradation of cellulose while the curve 12 refers to a first sample, namely to a material of the Novomont Company known as "Chart BI". This material is a mixture of about 50% thermoplastically processable starch with an ethylene

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vinyl acetate copolymer having a hydrolysis content of about 75% and a partial content of polyethylene as copolymer. The thermoplastically processable starch contains, inter alia, urea, sorbitol, and glycerol as plasticizing agent.

Graphs 13 and 14 refer to Samples 2 and 3, comprising materials bearing the designation "Material BI" of the Novomont Company, these materials again containing 50% thermoplastically processable starch, about 40% polyvinyl acetate (hydrolyzed to the extent of about 85% to polyvinyl alcohol) and about 10% polyethylene as copolymers.

Finally, graph 15 refers to a fourth sample of the Novon Company, which is a foamed material consisting of about 80% starch and about 20% polyvinyl acetate, the latter being hydrolyzed to the extent of about 85 % to polyvinyl alcohol.

Samples 1 to 4 comprise, as a whole, materials which are available in the market as so-called biologically degradable polymers. As can be clearly noted from Fig. 7 however, the biological degradability is in part substantially poorer than that of cellulose, the degradability of which itself is, in its turn, as shown in Fig. 6, poorer than the biological degradability of a polymer mixture prepared in accordance with the invention.

The graphs of Fig. 7 were also obtained by the OWS Institute of Ghent, Belgium, in accordance with the AFTM Standard D5338.

The fact that the excellent biological degradability of the PCL/TPS polymer mixture prepared in accordance with the invention is not obtained at the expense of the mechanical properties is shown by the values in Table 3.1 below. In that table, the mechanical properties of a PCL/TPS mixture are set

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forth as compared with the properties of Samples 1 and 2 of Fig. 7. In this connection, the tensile stress upon rupture, the elongation upon rupture, and the energy density upon rupture of the three materials is shown for "dry" materials and as well as materials which have been stored for 40 hours in water.

In this connection Sample 6 is the TPS/FCL polymer mixture prepared in accordance with the invention, the biologically degradability of which is shown in graph 10 in Fig. 6

Table 3.1

Change in the mechanical strength of blown-extruded sheets, 'dry' and after storage in water

	Tensile stress at rupture (MPa)	Elongation at rupture (%)	Energy density due to rupture (MJ/m ³)
Sample 1	31	174	4.9
Sample 1 after 40 hr storage in water	27	255	6.2
Sample 2	16	176	2.3
Sample 2 after 40 hr storage in water	48	6	0.2
Sample 6	21	650	6.5
Sample 1 after 40 hr storage in water	19	850	8.0

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From Table 3.1, it is clearly evident that Sample 2 is hydrolyzed relatively strongly upon storage in water and that the material has relatively poor resistance to water. In contrast to this, Samples 1 and 6, i.e., in particular the polymer mixtures prepared in accordance with the invention, show excellent resistance to water. The mechanical properties themselves are also substantially the same, those of Sample 6, however, being even better than those of Sample 1.

Furthermore, a specimen of sample 4 was also included in the series of tests, but storage in water was not possible since the Novon material dissolved completely within only a few minutes. Measurement of the mechanical properties was, accordingly, not possible.

As conclusion of the measurements in accordance with Example 3, it is evident that the biological degradability of the polymer mixture prepared in accordance with the invention is excellent and substantially better than the corresponding degradability of so-called biologically degradable polymers offered today in the market. Furthermore, it was possible to show that this excellent compostability was not obtained at the expense of the mechanical properties or the resistance to water.

The examples described above cover, of course, only a small selection of the many possibilities for the preparation of a polymer blend in accordance with the invention. In principle, it is, of course, possible to mix any hydrophobic, thermoplastically processable and biologically substantially degradable polymer with thermoplastic starch, in which case, however, it is essential that in order to obtain sufficient mechanical properties of the polymer mixture produced in this manner, a phase mediator must be present in order to reduce the interfacial energy at the phase boundary. It is furthermore essential that the

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hydrophobic polymer in the mixture forms a matrix in which the starch is contained encapsulated.

Furthermore, it was found that it is essential for the invention that the production of the polymer blend take place substantially with the exclusion of water in order not to disturb or prevent the manner of functioning or the formation of the phase mediator.

A list of possible biologically degradable polymers available today in the market is in addition given below:

Zein (Zein F 4000) of Fenzian AG, CH-6002, Lucerne,

Ethyl cellulose (Ethyl Cellulose N SO) of Aqualon East BV, NL-2298 ER Rijswijk,

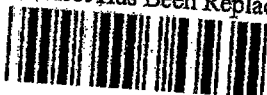
Poly-E-caprolactone of TONE Polymers (Union Carbide Corporation),

Poly-L-Lactid of PURAC biochem, NL-4200 AA, Gorinchem,

Cellulose diacetate (with unknown plasticizer)
(BIOCETA) of TUBIZE PLASTICS, B-1480 Tubize.

The above list sets forth only a few examples of biologically degradable polymers and is, of course, incomplete. All, for instance, synthetically produced hydrophobic polymers are, of course, suitable for the production of a polymer mixture in accordance with the invention, provided that they are biologically degradable: As example of this polyhydroxy-butyric acid may be mentioned.

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Finally, it should also be added that a large number of possible biologically degradable polymers are advantageously used with a plasticizer for the production of a polymer blend in accordance with the invention, since, on the one hand, these polymers are very brittle without plasticizer and, furthermore, the use of a plasticizer has proven advantageous, not least of all in order to reduce the melt viscosity. Thus it is, for instance, almost impossible to process zein without plasticizer since this material is very brittle. With the use of plasticizers it is of course advantageous that they themselves also be biologically degradable. It should furthermore be noted that, if the plasticizer is hydrophilic, the amount of additive should not exceed a certain value since, otherwise, the resistance to water of the entire polymer mixture will be decisively impaired.

The following substances; among others, constitute suitable plasticizers for the different biologically degradable hydrophobic polymers:

- for zein	palmitic acid
	glycerol monostearate
	sorbitol
	triacetin
	Carvon
	1,2-dodecanediol
	lauric acid
	ethyl levulinate
	dibutyl tartrate
	sebacic acid
	diethyl tartrate
	butyl lactate
	polyethylene glycol

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E- caprolactam
 levulic acid
 E - caprolactone
 glycerol
 triethylene glycol

- for ethyl cellulose epoxidized soybean oil

triacet in
 castor oil
 tributyl citrate
 acetyl tributyl citrate
 bis (2-ethylhexyl) phthalate
 bis (2-ethylhexyl) sebacate
 dibutyl adipate
 palmitic acid
 lauryl alcohol
 diethyl tartrate
 triglyceride

- for cellulose

acetate/butyrate acetyl - tri - ethyl citrate
 epoxidized soybean oil
 triglyceride
 oleic acid derivatives

The aliphatic polyesters are as a rule processed without plasticizer.

The above list of suitable plasticizers is intended to give a number of possible examples by which biologically degradable hydrophobic polymers can be

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plasticized. Of course, part of the plasticizers indicated for a polymer are suitable also for other biologically degradable hydrophobic polymers, in the same way, for instance, as a number of plasticizers suitable for ethyl cellulose are also suitable for the plasticizing of cellulose acetate-butyrate mixed ester. Although the present invention has been described in relation to particular embodiments thereof, many other variations and modifications and other uses will become apparent to those skilled in the art. It is preferred, therefore, that the present invention be limited not by the specific disclosure herein, but only by the appended claims.

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Claims

1. A biologically degradable polymer mixture consisting essentially of starch and at least one hydrophobic polymer, characterized by the fact that the hydrophobic polymer is at least essentially biologically degradable and thermoplastically processable and that the mixture contains a phase mediator or a macro molecular dispersing agent, starch being present in the mixture as the disperse phase with the hydrophobic polymer as the continuous phase and the phase mediator or dispersing agent being responsible for the molecular coupling the two phases.
2. A biologically degradable polymer mixture, preferably in accordance with at least one of the claims, as in accordance with Claim 1, characterized by the fact that the starch is present as so-called thermoplastically processable starch (TPS), obtained by substantially water-free mixing of crystal starch including at least one melting or swelling agent in the range of 15 to 40 % in weight, preferably 20 to 36 % in weight of the total mixture, with crystal starch or a derivative of it; the melting or swelling agent being suitable to at least partially swell or dissolve the starch or the derivative.
3. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with claim 2, characterized by the fact that the thermoplastically processable starch contains a swelling or melting agent at least one of the following substances : Sorbitol, glycerine, a hydroxy acid, such as lactic acid and/or its salt and/or poly vinyl alcohol.
4. Polymer mixture, preferably in accordance with one of the claims, as in accordance with the Claims 1 to 3, characterised by the fact that the phase

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mediator is a block copolymer, consisting of at least two blocks; one of the blocks being at least to the greatest extent soluble in the hydrophobic polymer phase and the other block being at least to the greatest extent soluble in the starch phase.

5. A polymer mixture, preferably in accordance with one of the claims, as in accordance with one of the Claims 1 to 3, obtained by essentially water-free mixing of starch or thermoplastically processable starch with the one hydrophobic polymer of the kind stated, together with a further polymer which is reactive towards the starch; the polymer being at least to the greatest extent soluble in the hydrophobic polymer phase and which includes groups that are reactive towards the starch; these groups reacting at least partially with a part of the starch or the thermoplastically processable starch and in that way in the mixture form the phase mediator which is responsible for the coupling of the two phases.

6. A polymer mixture, preferably in accordance with one of the claims, as in accordance with one of the Claims 1 to 3, obtained by essentially water-free mixing of starch or thermoplastically processable starch with a hydrophobic polymer of the kind stated, comprising ester groups built into the molecule chain, which become reactive under raised temperatures after disintegration and react at least in part with at least a part of the starch or the thermoplastically processable starch, which in this way, together with molecule chains of the hydrophobic polymer that have reacted with starch or with thermoplastically processable starch, form the phase mediator that is responsible for the molecular coupling of the two phases.

7. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 1 to 6, characterized by the fact

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that the phase mediator is formed by starch or thermoplastically processable starch with aliphatic polyester grafted thereon.

8. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 1 to 7, characterized by the fact that the proportion of starch or thermoplastically processable starch amounts to up to 70% in weight based on the total weight of the mixture.

9. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 1 to 8, characterized by the fact that the proportion of starch or thermoplastically processable starch amounts to 30 to 70 % in weight, preferably 50 to 65 % in weight, based on the total weight of the mixture.

10. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 1 to 9, characterized by the fact that the proportion of phase mediator amounts to from 2 to 100% by weight based on the weight of the hydrophobic polymer, preferably 5 to 50 % in weight. .

11. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 1 to 10, characterized by the fact that at least one of the following polymers is present as hydrophobic polymer in the mixture:

- a cellulose derivative having a degree of substitution ≤ 2 , such as a cellulose ether, a cellulose ester or a cellulose-acetate-butyrate-mixed ester;

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- an aliphatic polyester, such as polycaprolactone, polyhydroxybutyric acid, a polyhydroxy butyric acid, hydroxyvaleric acid copolymer and/or polylactic acid and;
- a hydrophobic protein, such as Zein and/or
- polyvinylalcohol, not 100% hydrolised.

12. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with the Claims 1 to 4 to 8 to 11, characterised by the fact that a polycaprolacton polyvinylalcohol-copolymer is provided for as phase mediator.

13. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with Claims 3 to 5 or 5 to 11, characterized by the fact that the mixture contains as the phase mediator a reaction product of starch or thermoplastically processable starch and another polymer with epoxide-, ester- or acid-anhydride groups which are reactive with the starch.

14. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with Claim 13, characterized by the fact that the additional polymer for the formation of the reaction product with groups reactive with starch consists essentially of a polymer in accordance with Claim 11, onto which the reactive epoxide-, ester-, or acid-anhydride groups are grafted by vinyl polymerisation or condensation.

15. A polymer mixture, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 1 to 14, characterized by the fact that the hydrophobic phase and the hydrophobic polymer respectively include a softener which is preferably compatible only with the hydrophobic phase and selectively reduces its melting viscosity.





16. A process for the production of a biologically degradable polymer mixture consisting essentially of a mixture of starch and at least one hydrophobic polymer, characterized by the fact that starch together with at least one biologically degradable hydrophobic polymer and a phase mediator or dispersing agent or one of the other polymers which are soluble in the hydrophobic polymer phase is mixed in the melt with groups that are reactive with starch; the water content being reduced to $< 1.0\%$ by weight based on the total weight of the mixture before or during the mixing and the additional polymer forming the phase mediator through reaction with the starch.

17. A process, preferably in accordance with at least one of the claims, as in accordance with Claim 16, characterized by the fact that crystal starch or derivatives thereof are rendered soluble with at least one plasticizing or swelling agent and are mixed into the melt for the formation of thermoplastically processable starch; the water content being reduced to $< 1\%$ by weight before or upon the mixing and thereupon up to 70 % by weight of this resulting thermoplastically processable starch being mixed with the hydrophobic polymer and 2 to 100 % by weight, preferably 5 to 50 % by weight, based on the weight of the hydrophobic polymer, of a phase mediator or an additional polymer.

18. A process, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 16 or 17, characterized by the fact that the mixing of starch or of thermoplastically processable starch with the hydrophobic polymer and the phase mediator or the additional polymer takes place within a temperature range of 150°C to 230°C ; at least one of the following materials being used as hydrophobic polymer :

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- a cellulose derivative having a degree of substitution ≤ 2 , such as a cellulose ether, a cellulose ester or a cellulose-acetate-butyrate-mixed ester;
- an aliphatic polyester, such as polycaprolactone, polyhydroxybutyric acid, a polyhydroxy butyric acid, hydroxyvaleric acid copolymer and/or polylactic acid and;
- a hydrophobic protein, such as Zein and/or
- polyvinylalcohol, not 100% hydrolised.

19. A process, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 16 to 18, characterized by the fact that the starch or the thermoplastically processable starch are mixed with 5 to 50 % by weight based on the weight of the hydrophobic polymer of a block copolymer as phase mediator, consisting at least of one block which is soluble in the starch phase and one block which is soluble in the hydrophobic polymer phase, such as, for example, polycaprolacton/polyvinylalcohol-copolymer and said at least one hydrophobic polymer.

20. A process, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 16 to 18, characterized by the fact that the reactive groups are grafted on the hydrophobic polymer by means of vinyl polymerization or condensation by reaction with a glycidyl ether or at least one aliphatic di- or polycarboxylic anhydride, such as , for example, succinic acid anhydride, in order to produce the additional polymer, and thereafter the additional polymer thus produced and the hydrophobic polymer are intensively mixed in the melt with the starch or the thermoplastically processable starch at a water content of < 0.5 % by weight, preferably < 0.1 % by weight, for example in a plastic-processing device or machine such as a kneader or an extruder.

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21. A process, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 16 to 18, characterised by the fact that a polymer, into the molecule chains of which ester groups have been built, is used as hydrophobic polymer; the ester groups becoming reactive at raised temperatures after disintegration and effecting transesterification of the hydrophobic polymer as well as posing intermediary-wise as additional polymer; the ester groups in part reacting with a part of the starch or thermoplastically processable starch in order to form the phase mediator; the hydrophobic polymer containing the built-in ester groups, such as, for example, polycaprolacton, being intensively mixed with the starch at a water content of < 0.5 % by weight, preferably < 0.1 % by weight, in the melt, for example by a plastic-processing device or machine, such as a kneader or an extruder.

22. A process, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 16 to 21, characterised by the fact that crystal starch or derivatives thereof with a water content of a maximum of 6 % by weight, preferably 1 to 4 % by weight, are rendered soluble with 25 to 35 % by weight, based on the weight of the mixture, of a plasticizer or a swelling agent, such as Sorbitol or glycerine; and afterwards being brought to a temperature of approx. 170° C to 190° C while at the same time reducing the water content to < 0.5 % by weight, then being mixed for the production of thermoplastically processable starch; afterwards approx. 30 to 45 % by weight of the hydrophobic polymer and 5 to 15 % by weight of the phase mediator or 5 to 20 % by weight of the additional polymer, based on the total weight of the mixture inclusive of the starch, being admixed and then being mixed in the melt at a temperature range of approx. 150° C to 230° C at a moisture content of < 0.5 % by weight, preferably < 0.1 % by weight.

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23. A process, preferably in accordance with at least one of the claims, as in accordance with Claims 16 to 18 or 20 to 22, characterised by the fact that the hydrophobic polymer and the additional polymer are essentially identical.

24. A process, preferably in accordance with at least one of the claims, as in accordance with one of the Claims 16 to 23, characterised by the fact that the hydrophobic polymer, before the mixing with the starch or the thermoplastically processable starch, is treated with a softener, the softener being compatible preferably only with the hydrophobic phase or not being mixable with it and the softener reducing the melting viscosity of the hydrophobic polymer.

25. Single or multi-layer sheet, characterised by at least one layer consisting of a polymer mixture in accordance with one of the Claims 1 to 5.

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Abstract :

A biologically degradable polymer mixture is proposed which consists essentially of starch and at least one hydrophobic polymer. The hydrophobic polymer in this connection is to be at least substantially biologically degradable and thermoplastically processable and the mixture with the starch is to include a polymer phase mediator or a macromolecular dispersing agent so that the starch is present in the mixture as disperse phase with the hydrophobic polymer as continuous phase, and the phase mediator or the dispersing agent is responsible for the molecular coupling of the two phases. As starch there is preferably used thermoplastic starch which has been prepared substantially with the exclusion of water by means of sorbitol or glycerol. The production of the biologically degradable polymer mixture is also carried out substantially with the exclusion of water.

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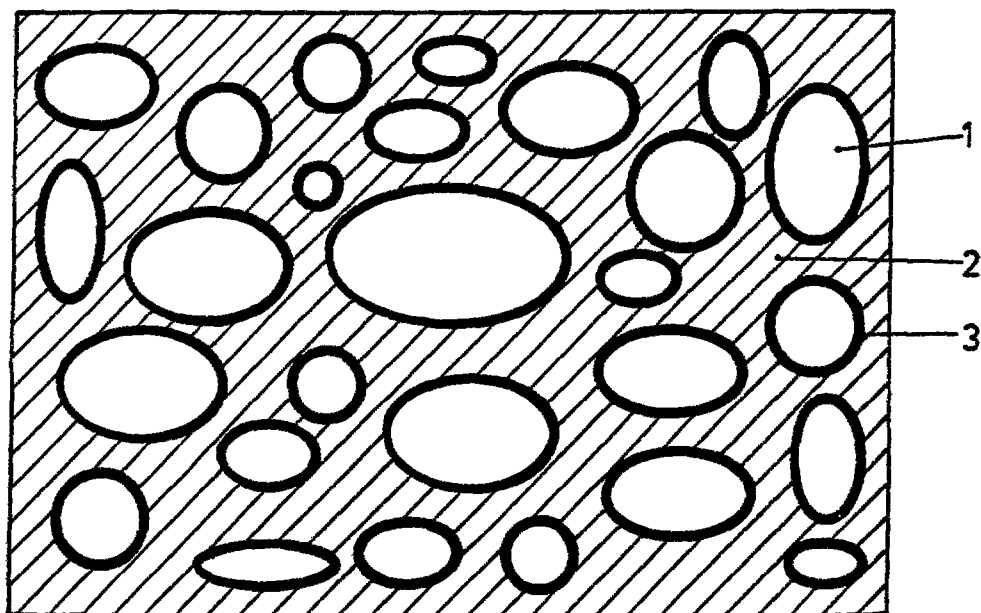


FIG. 1

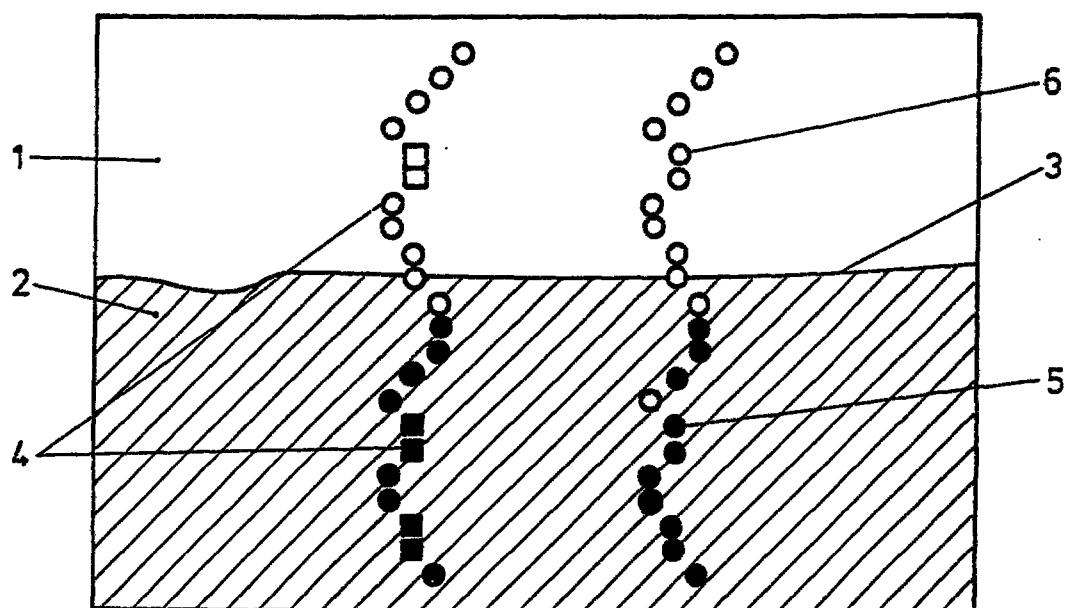
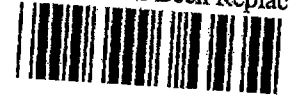


FIG. 2



Tension-Elongation Behaviour

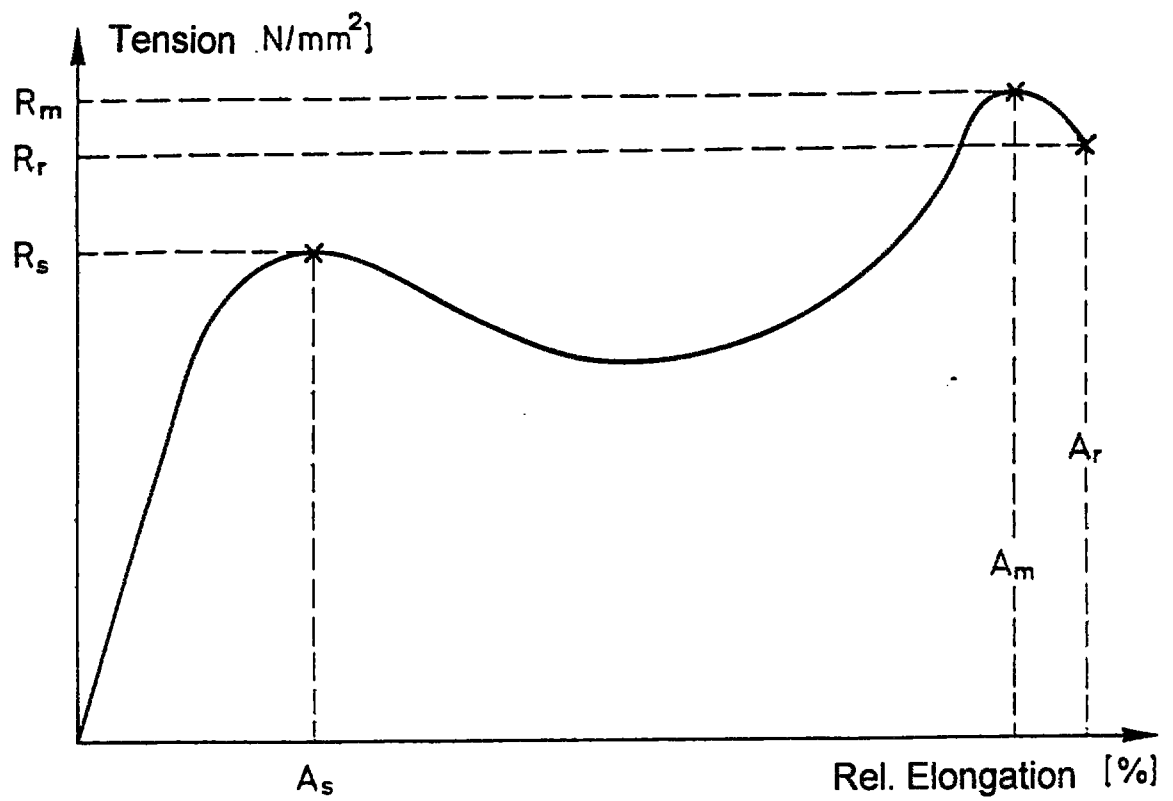
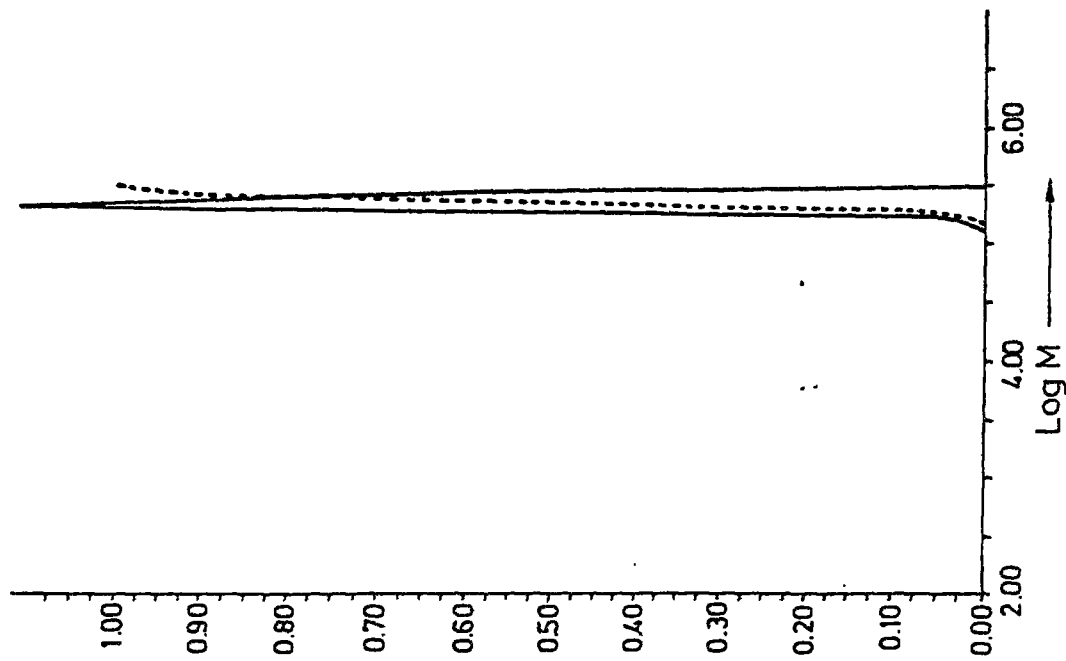
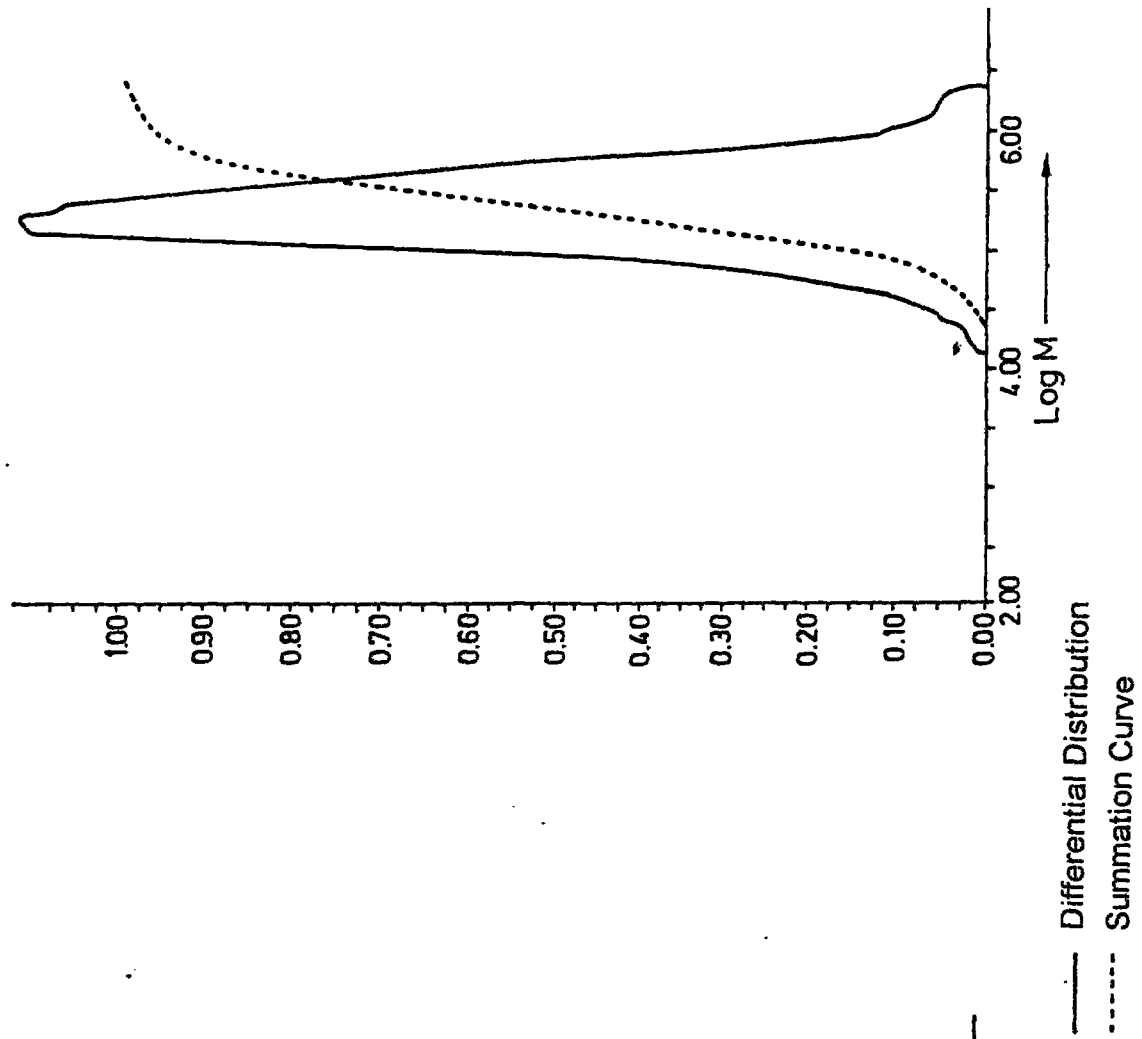


FIG.3



BIOLOGICAL DEGRADATION OF A TPS/PCL BLEND
AS COMPARED WITH CELLULOSE

CONVERSION OF CARBON INTO CO₂ (%)

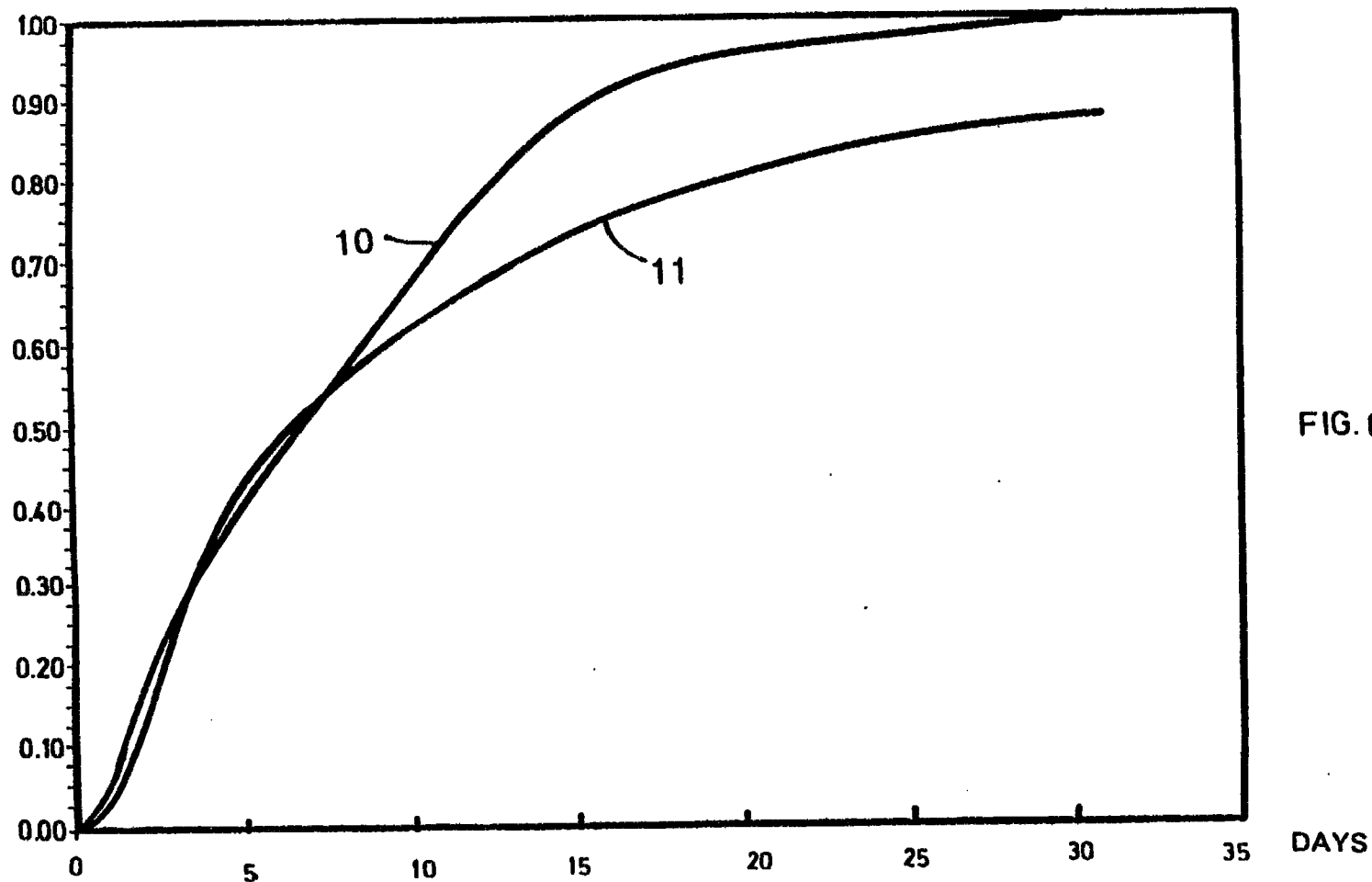


FIG. 6

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BIOLOGICAL DEGRADATION OF CELLULOSE AS COMPARED WITH
BIOLOGICALLY DEGRADABLE POLYMERS

CONVERSION OF CARBON INTO CO₂

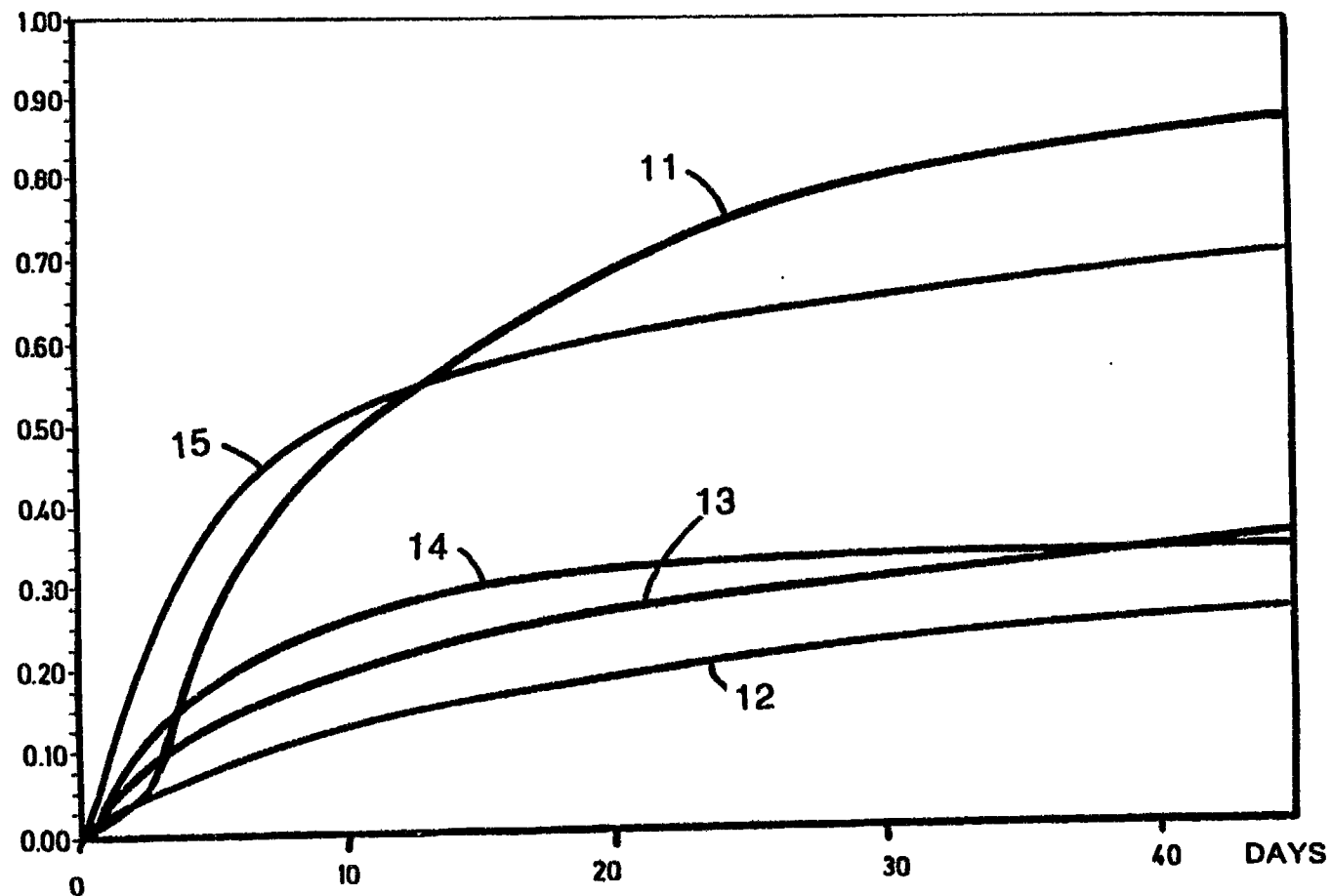


FIG. 7

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BIODEGRADABLE POLYMER MIXTURE

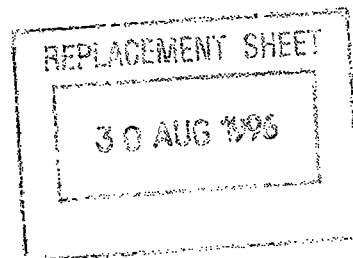
The invention presented here concerns a biologically degradable polymer mixture, consisting essentially of starch and at least one hydrophobic polymer, a method of producing a biologically degradable polymer mixture consisting essentially of starch and at least one hydrophobic polymer, as well as a single-layer or multi-layer sheet.

For controlling the problem of waste, plastics are more and more being taken into account as time passes, not least of all because their proportion in the treatment of waste is constantly increasing as a result of their increasing use as materials and/or semi-finished materials or raw materials. In contrast to other materials, such as, for instance, glass or metal, the recycling of plastics, although frequently attempted, is very problematical since it is practically impossible to return the very different types of plastics separately, which in itself would be necessary in order to be able to make again reasonable use of the plastics.

For this reason, it must be assumed that larger and larger amounts of plastic must be disposed of, so that the importance of so-called degradable plastics or polymers is increasing. In this connection, biologically degradable polymers are of particular interest which are degraded under the action of micro-organisms, bacteria, fungi, enzymes or the like, and as low-molecular products scarcely constitute a problem any longer.

The probably most widely used biopolymers are in most cases based on starch, in which connection, to be sure, starch is scarcely suitable as an industrially usable polymer. Polymer mixtures with starch are known, the starch or else other biopolymers being preferably used due to their biological degradability, due to their favorable price and due to the independence from petroleum products.

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BIODEGRADABLE POLYMER MIXTURE

Abstract :

A biologically degradable polymer mixture is proposed which consists essentially of starch and at least one hydrophobic polymer. The hydrophobic polymer in this connection is to be at least substantially biologically degradable and thermoplastically processable and the mixture with the starch is to include a polymer phase mediator or a macromolecular dispersing agent so that the starch is present in the mixture as disperse phase with the hydrophobic polymer as continuous phase, and the phase mediator or the dispersing agent is responsible for the molecular coupling of the two phases. As starch there is preferably used thermoplastic starch which has been prepared substantially with the exclusion of water by means of sorbitol or glycerol. The production of the biologically degradable polymer mixture is also carried out substantially with the exclusion of water.

Fig. 3

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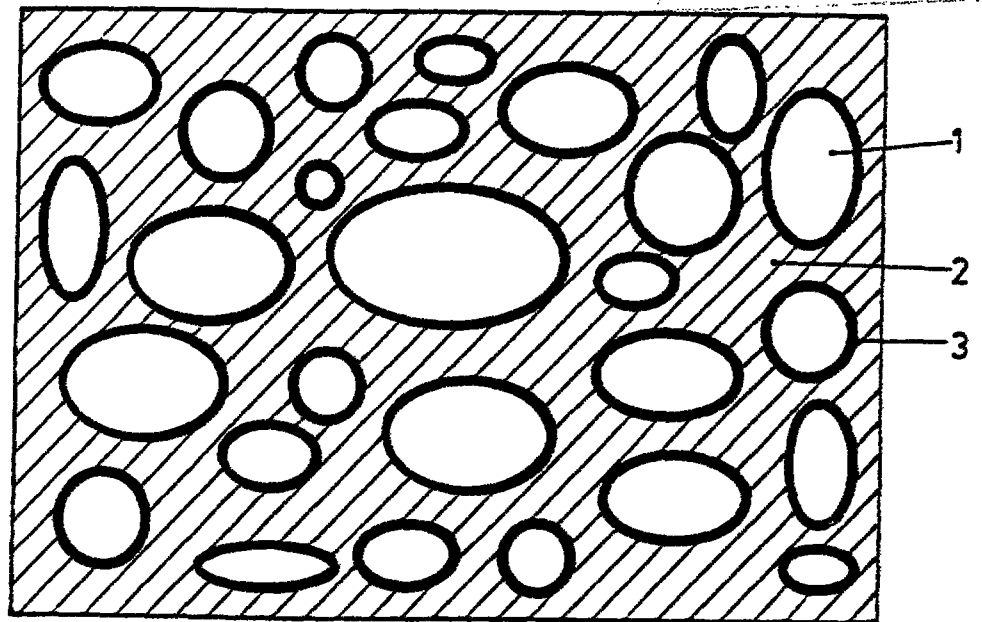


FIG. 1

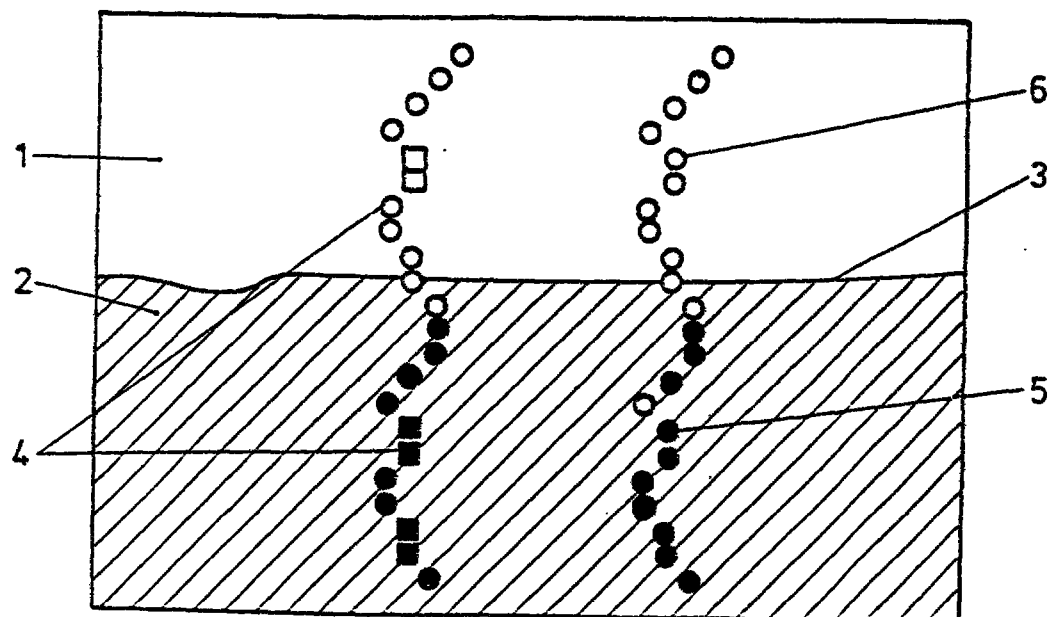


FIG. 2

Tension-Elongation Behaviour

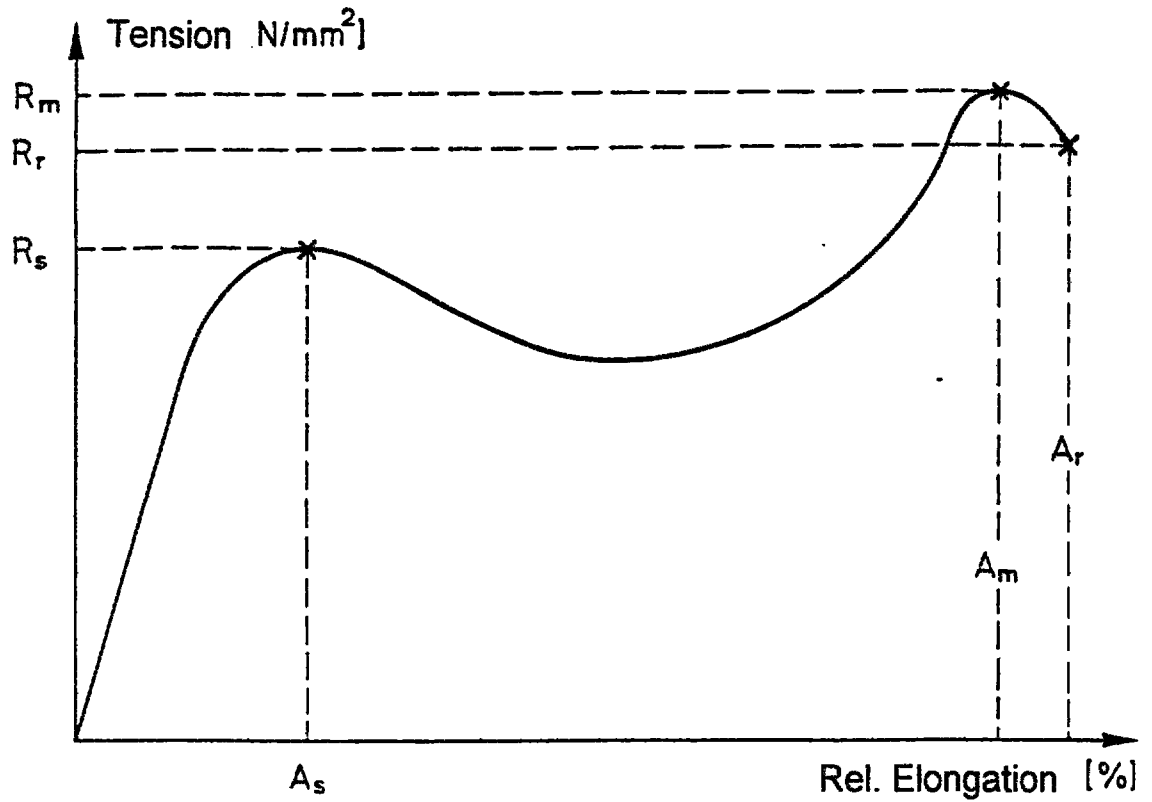


FIG.3

3/5

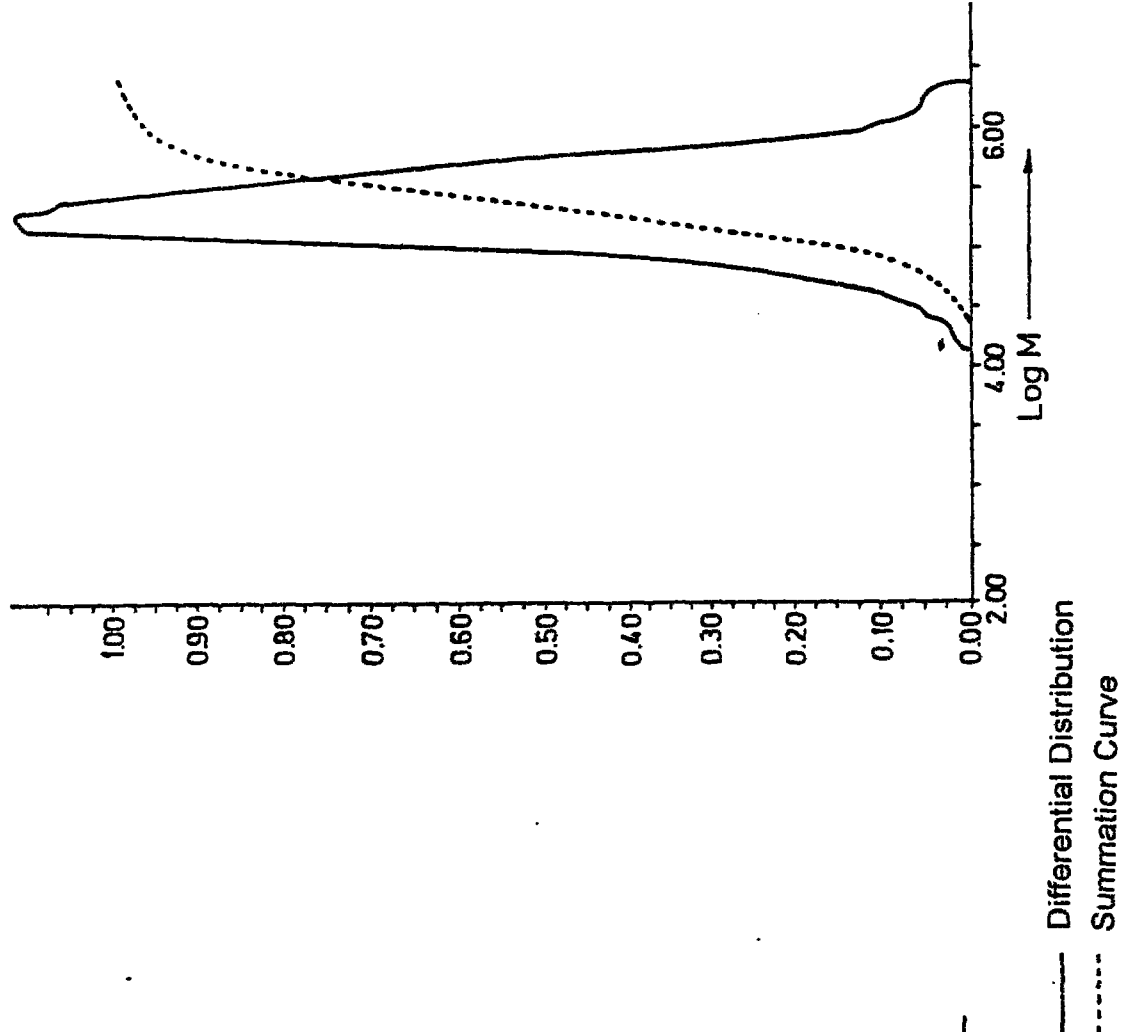


FIG. 5

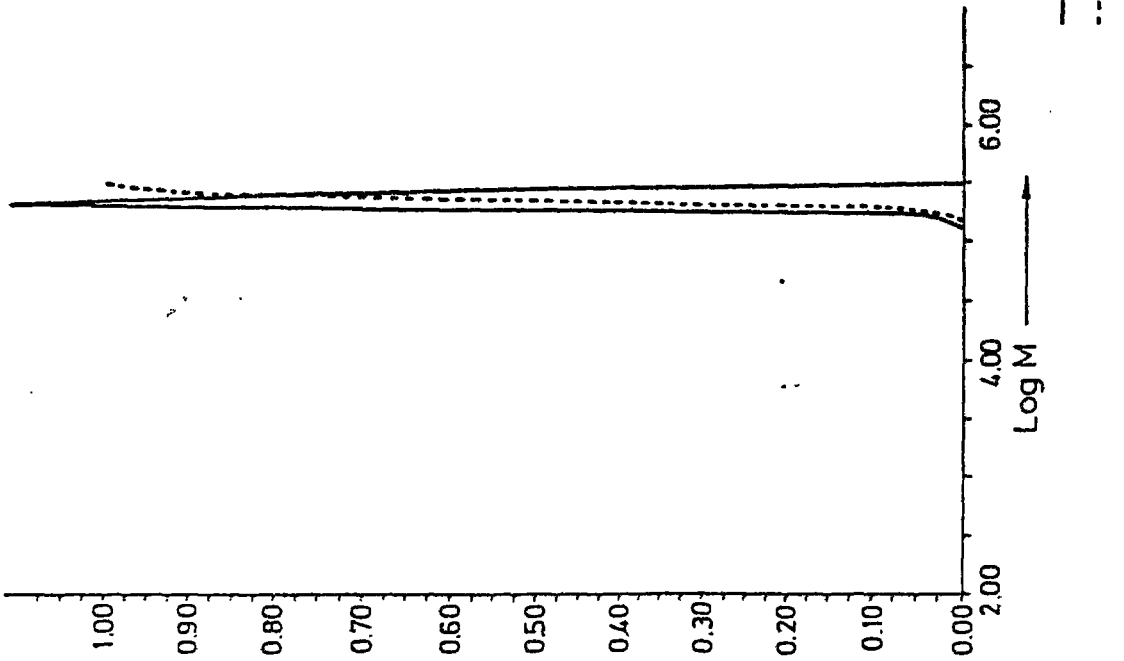


FIG. 4

BIOLOGICAL DEGRADATION OF A TPS/PCL BLEND
AS COMPARED WITH CELLULOSE

CONVERSION OF CARBON INTO CO₂ (%)

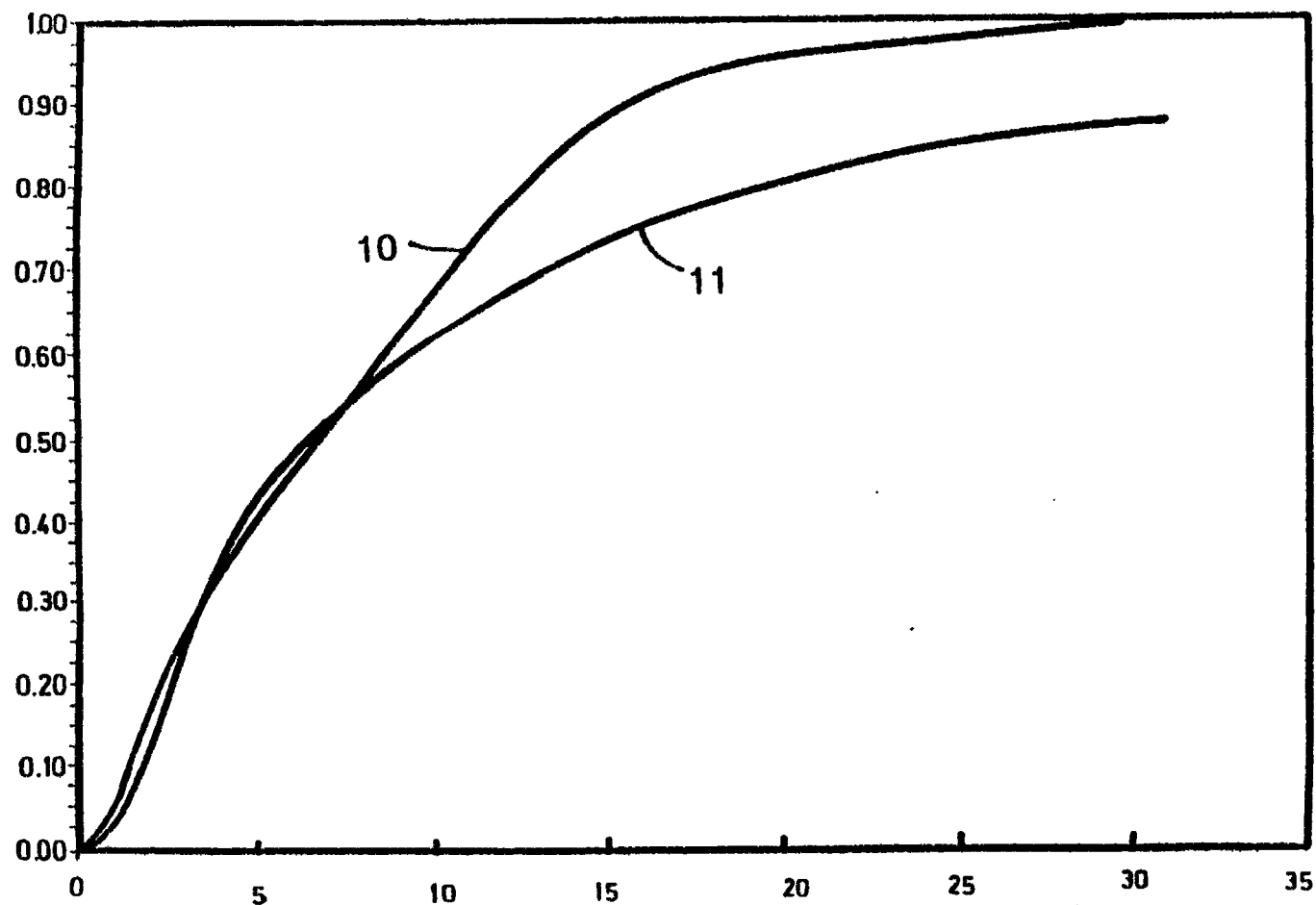
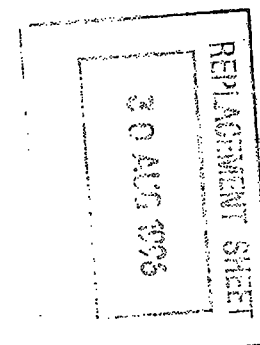


FIG. 6

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BIOLOGICAL DEGRADATION OF CELLULOSE AS COMPARED WITH
BIOLOGICALLY DEGRADABLE POLYMERS

CONVERSION OF CARBON INTO CO₂

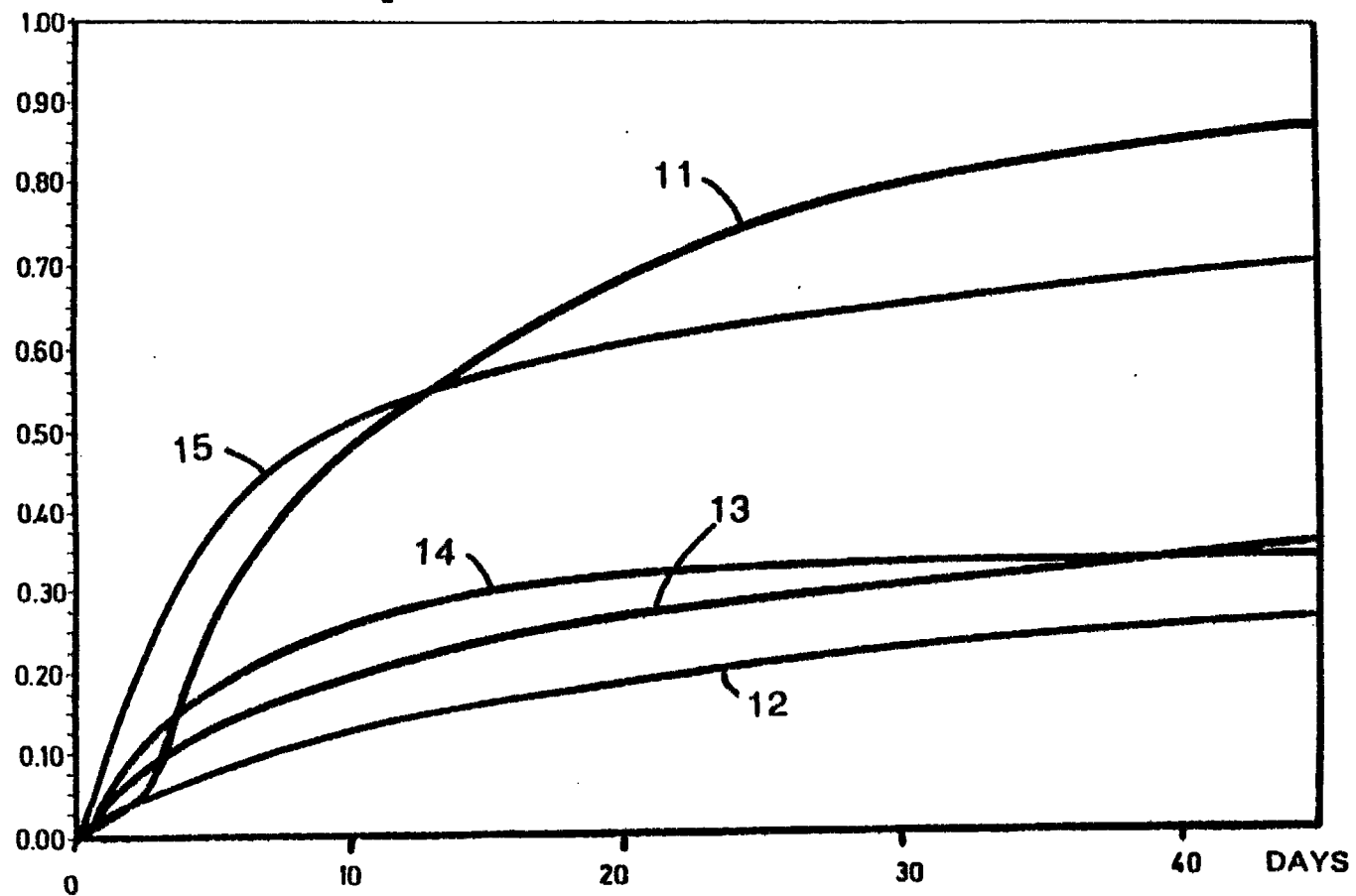
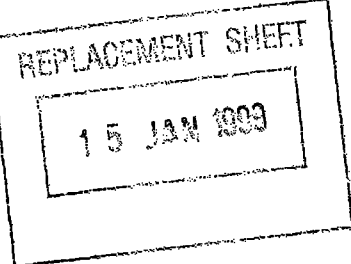


FIG. 7

5/5

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BIODEGRADABLE POLYMER MIXTURE

The present invention relates to a biologically decomposable polymer mixture, substantially consisting of starch and at least one hydrophobic biologically decomposable polymer, a method for the production of a biologically decomposable polymer mixture, substantially consisting of starch and at least one hydrophobic biologically decomposable polymer, and also a single- or multiple-sheet foil.

To overcome the problem of waste, the plastics are included the longer, the more, not least because their quota rises constantly as a consequence of the increasing use as materials or semi-tools or raw materials in the utilization of waste. In contrast to other materials, such as glass or metal for example, a recycling with plastics is very problematic, although it is repeatedly attempted, because it is almost impossible to return the most varied types of plastic separately, which per se would be necessary in order to be able to reasonably use plastics again.

For this reason, one must assume that increasingly large quantities of plastic are to be dealt with, for which reason the importance of so-called decomposable plastics or polymers is increasing. Here, the biologically decomposable polymers are of especial interest, which are decomposed under the action of microorganisms, bacteria, fungi, enzymes or the like and as low-molecular products are scarcely a concern any longer.

The biopolymers which are in fact the most widespread are in most cases composed on starch, with starch of course scarcely being suitable as a technically usable polymer. Polymer mixtures with starch are known, in which the starch or other biopolymers preferably are used owing to their biological decomposability, owing to their favourable price and owing to the independence of mineral oil products.

15 JAN 1993

In various patent documents, the use of biopolymers as technical plastic is described. In the EP-011 82 40, EP-28 24 51, EP-28 89 20, EP-30 44 01, EP-32 65 14, GB-22 14 919 and the EP-32 75 05 it is described how native starch, gelatins or other biopolymers are modified or destructured, in order to be able to be used as technical polymer. This occurs here through extrusion or kneading of the starch or of the biopolymer with the aid of the water held in the biopolymer or in the starch or through the addition of further water, in which, however, in fact the present, relative high water content is extremely undesirable for example in the extrusion of the thus destructured biopolymer.

Compared with this, in the WO-A-90/05161 it is proposed to convert native starch free of water and with the use of additives or softeners or swelling agents, such as glycerin for example, into a technically usable polymer, i.e. into so-called thermoplastically processable starch. The processability and the water resistance of this starch polymer is in fact substantially better than the starch polymers produced according to the manufacturing method described above, however the mechanical characteristics and in particular the water resistance, as before, are insufficient for many technical applications, such as in particular for the production of foils.

For this reason, in a number of patent documents it is proposed to mix the starch with further polymers, in order to thus achieve characteristics which permit a technical use. Thus in the CH-644 880, CH-644 881, DE-PS-24 62 802 and DE-24 55 732 it is proposed to surface-treat starch firstly with any additives and then to mix with thermoplastic polymers, such as polyethylene etc. In the DE-OS-40 38 732, a material is proposed based on starch with the addition of water and plasticizing agents and also an aqueous polymer dispersion formed from a thermoplastic polymer.

In contrast to the above-mentioned documents, in the patent documents such as

15 JAN 1999

EP-40 28 26, EP-40 47 23, EP-40 47 27, EP-40 27 28, EP-40 73 50, EP-40 97 88, EP-41 78 28, EP-0 32 802, US-39 52 347, US-50 95 054 and AT-365 619, instead of native starch, one proceeds from destructured starch, gelatinised starch or plasticized starch, which are mixed with thermoplastic plastics such as polyolefins, polyalcohols, ABS copolymers, ethylene acrylic acid copolymers, copolymers of vinyl pyrrolidines, copolymers with amino groups etc. In all the above-mentioned polymer mixtures, based on starch, the problem arises that the compatibility between starch and the further polymers is insufficient or the phase mixing of the individual polymers is poor. As is known, starch is extremely hydrophilic, whereas generally the polymers used for mixing are hydrophobic. Finally, the biological decomposability of all said polymer mixtures is still unsatisfactory, the decomposition time of the polymers which are used, these generally being synthetic polymers, being much too long, so that one can hardly speak in terms of biological decomposability.

To improve the mechanical characteristics, in a range of patent documents, such as the WO90/10671, the WO91/02023 and the WO91/02025 it is proposed to firstly destructure the starch at a high water content and then, with the production of the polymer mixture during the mixing process with an ethylene copolymer to reduce the water content to below 6 %. In the WO92/02363 it is additionally proposed to add to the polymer mixture a high-boiling plasticizing agent, whilst in the WO92/01743 of the same applicant, a boron compound is admixed to the polymer mixture. In the DE-39 39 721 it is further proposed to additionally add a cross-linking agent to a polyvinyl alcohol starch mixture, for the production of foils.

To increase the biological decomposability, in turn, the WO88/06609 proposes to add to a polymer mixture consisting of polyethylene and starch or modified starch, an iron compound and also a fatty acid. In the EP-282 368 in turn a biologically decomposable mixture is proposed, produced from polyurethane,

15 JAN 1999

PVC with softener, a carbohydrate such as starch, and also an aliphatic polyester, in which polyurethane, inter alia, based on polycaprolacton, is proposed. In all the above-mentioned documents in the prior art, it can clearly be seen that always some characteristics are improved by the selected solution, whereas others suffer therefrom. Thus, between the characteristics such as water resistance, biological decomposability, and also mechanical characteristics, a compromise always has to be made, in order to be able to improve some of these characteristics.

Thus, for example, it is found in the manufacture of foils from a polymer mixture, proposed according to a majority of the above-mentioned documents, that the non-starch component of polymer, present in the proposed mixtures, produced in itself alone as a foil, i.e. constructed with correspondingly substantially thinner wall thickness, has substantially better tearing strength than the thicker foils produced accordingly from the entire polymer mixture. The reason for this lies either in the high water uptake or else in the poor phase mixing between the various polymers.

According to the patent documents EP-40 05 31 and EP-40 05 32 it is proposed to treat the starch analogously to the WO90/05161 by means of a high-boiling softener such as glycerin, urea or sorbitol, in order to obtain thermoplastically processable starch, in order to then mix this with ethylene acrylic acid and/or polyvinyl alcohol copolymer. Foils produced from these starch/polymer mixtures in fact have a better tearing strength, but are still too sensitive to moisture.

The same applies to starch polymer mixtures, which are produced according to the WO90/14388, in which admixing is carried out to glycerin starch polyethylene and ethylene acrylic acid copolymer.

In the WO91/16375 in turn for the production of foils a polymer blend is

15 JAN 1999

proposed, which uses thermoplastically processable starch according to the WO90/05161, together with a polyolefin and also a phase- or adhesion agent, in order to improve the phase mixing between the starch and the polyolefin. Similarly, in the not previously published WO-A-92/020740 it is proposed to mix thermoplastically processable starch with at least one polyolefin and also at least one ethylene acrylate maleic acid anhydride copolymer, in which the esterification product between the starch and the added copolymer serves as phase agent between the starch phase and the polymer phase. The advantage of this polymer mixture lies in that owing to the good mixing of the starch phase with the further polymer phase, such as for example the hydrophobic polyolefin phase, in the production for example of foils, excellent mechanical characteristics can be achieved.

Of course, all these polymer mixtures also have the important disadvantage that their biological decomposability can in no way satisfy the requirements set today for such decomposability.

In connection with biologically decomposable polymers, therefore, for some time a direction is being followed which is freed of starch, in which for example aliphatic polyesters such as caprolacton- or polyhydroxy-butyrac acid/hydroxyvalerian acid copolymers (biopol) were developed, which can be decomposed biologically without problems. The problem of these products, however, lies in that they are very expensive to manufacture, for which reason a use as technical plastic material does not come into consideration.

In this connection, reference is to be made to an article in the journal Capital 6/92, page 208, "Wunderfolien reduzieren Plastikmüll", where such new developments are described. A further great advantage of these newly developed materials lies in that they are hydrophobic and are hence water-resistant, this being in contrast to starch, which is very hydrophilic. This difference, however,

also entails the fact that a "stretching" of the said expensive, biologically decomposable polymers with starch contains the problem that two non-miscible phases are present. This non-miscibility of starch with the said hydrophobic, biologically decomposable polymers leads in turn to the fact that mixed polymers, thus produced, yield poor mechanical characteristics, whereby the problem originally mentioned above is addressed, that compromises are to be made between water solubility, biological decomposability and the mechanical characteristics.

In the US-3 850 863 biologically decomposable thermoplastic oxyalkanoyl polymers are proposed, for example containing ϵ -caprolacton polymers, mixed with maize starch. In the international patent application WO 92/19680 in turn biologically decomposable polymer compositions are described, based on starch and a thermoplastic polymer. Inter alia, likewise, polycaprolacton is described as possible mixing component for the starch. The polymer mixtures thus described indeed generally fulfil the requirements of biological decomposability, however products produced therefrom in turn do not satisfy the requirements of the mechanical characteristics which are set, whereby the problem mentioned above also applies in relation to the two said materials which in themselves are biologically decomposable. In the EP 0 542 155, which was not yet published on the date of application of the present application, a biologically decomposable moulding material is described, having thermoplastically processable starch and also a cellulose derivative, such as cellulose ester for example. Here, inter alia, it is proposed for example to use epoxided soya oil as phase agent, in which by means of infrspectroscopy it was able to be proved that the epoxide groups partially react with the starch and/or with the glycerin.

The problem of the present invention now consists in proposing a solution for the problem stated above, in which a polymer mixture is created which has both good water resistance, is able to be decomposed biologically without difficulty

13 JAN 1990

and additionally produces good mechanical characteristics, so that a use as mass plastic comes into consideration. A further precondition for the suitability as mass plastic lies not least, however, also in that the price for the polymer mixture to be proposed according to the problem is at an acceptable level.

According to the invention, the previously proposed problem of a biologically decomposable polymer mixture is solved according to the wording of Claim 1.

A biologically decomposable polymer mixture is proposed, substantially consisting of starch and at least one hydrophobic, biologically decomposable polymer, obtained by mixing in the melt of starch or of thermolastic starch with a hydrophobic polymer, which is able to be processed thermoplastically and with a phase agent or a macromolecular dispersing agent, excepting epoxidized soya oil, or with a further polymer which is soluble in the hydrophobic polymer phase, with reactive groups with respect to starch, in which during mixing, the water content is reduced to below 1 % by weight in relation to the total weight of the mixture, in which in the mixture the starch is present as a disperse phase with the hydrophobic polymer as continuous phase and the phase agent or the dispersing agent is responsible for the molecular coupling of the two phases.

The proposed polymer mixture is therefore based on the same principle as set forth in the WO-A-92/020740 not previously published at the time of the application, in which surprisingly the phase agents proposed in the said international patent application are likewise suitable for bringing about the molecular coupling between the two phases.

In addition, analogous to the WO-A-92/020740 preferably one proceeds from thermoplastically processable starch as is proposed for example in the WO90/05161 or the WO91/16375. In an analogous manner, therefore, it is proposed according to the invention to submit the starch as so-called

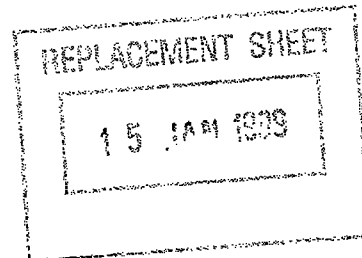
15 JAN 1939

thermoplastically processable starch (TPS), which is obtained ~~in that~~ native starch is mixed, substantially free of water, with at least one plasticizing- or swelling agent in the order to 15 to 40 % by weight in relation to the weight of the mixture, in which the plasticizing- or swelling agent which is used is suitable for at least swelling or dissolving the starch or derivatives thereof.

As suitable swelling- or plasticizing agents for the production of thermoplastically processable starch, in particular inter alia sorbitol, glycerin, hydroxy acids, such as for example lactic acid and salts thereof, and also polyvinyl alcohol are suitable. In addition, however, all swelling- or plasticizing agents are also suitable or else additives are mentioned, such as are used in the two above-mentioned international patent applications for the production of thermoplastically processable starch.

The essential advantage of the polymer mixture produced according to the invention compared with all the known polymer mixtures described in the prior art lies in that, based on starch, a thermoplastically processable technical "plastic" is present, which is, to the greatest extent, insensitive to water, because the hydrophobic polymer is present as a continuous phase or as a matrix in the mixture and on the other hand the polymer mixture is biologically decomposable without difficulty and within a reasonable time, because the hydrophobic polymer itself has good biological decomposability.

So that the hydrophilic starch phase and the hydrophobic polymer phase now have good miscibility or the starch is dispersible in the hydrophobic polymer without difficulty, the phase agent according to the invention or a macromolecular dispersing agent is provided, in which the phase agent on the one hand may be a block copolymer, which comprises at least two blocks, one block of which is at least soluble to the greatest extent in the hydrophobic polymer phase and the other block is at least soluble to the greatest extent in



the starch phase.

The phase agent, however, can also be formed by a reactive further polymer which is soluble to the greatest extent in the hydrophobic polymer phase and comprises reactive groups with respect to the starch, which groups react with at least a portion of the starch and thus forms the phase agent in the mixture, which is responsible for the above-mentioned molecular coupling of the two phases.

According to a further variant according to the invention, for the formation of the phase agent one can proceed from a hydrophobic polymer of the above-mentioned type, which polymer has ester groups incorporated in the molecule chain, which become reactive at increased temperature after their decomposition and react at least partially with at least a portion of the starch or the thermoplastically processable starch. The molecule chains of the hydrophobic polymer thus reacted with the starch or with the thermoplastically processable starch form the phase agent in the mixture, which is again responsible for the molecular coupling of the two phases.

In the polymer mixture produced according to the invention, it is now essential however that in every case the thermoplastically processable starch is present as a dispersed phase, for which reason the starch can only be present in the mixture up to a maximum quota, up to which quota the hydrophobic polymer is still present as a continuous phase which is cohesive to the greatest extent. As soon as the two phases for example are present in the same function in the mixture, i.e. both as continuous and as dispersed phase, then the water resistance of the polymer mixture is no longer guaranteed. In practice, it has been found that the thermoplastically processable starch can be present in the polymer mixture up to a quota of a maximum 70 % by weight in relation to the overall weight of the mixture, in which the starch is still present in a dispersed

15 JAN 1988

phase. If the starch quota is selected to be too small, then the problem arises again that the high cost of the hydrophobic biologically decomposable polymer becomes too important. Accordingly, the thermoplastically processable starch in the polymer mixture according to the invention is reasonably present with a quantity quota in the range between 30 to 70 % by weight, preferably 50 to 65 % by weight, in relation to the overall weight of the mixture.

In particular, the polymers listed below are suitable as hydrophobic, biologically decomposable thermoplastically processable polymers:

- cellulose derivatives with a degree of substitution ≤ 2 , such as cellulose ether, cellulose ester or -mixed ester;
- aliphatic polyesters such as caprolacton, polyhydroxy butyric acid, polyhydroxy butyric acid/hydroxy valerian acid copolymers and polylactic acid;
- hydrophobic proteins, such as zein; and/or
- polyvinyl alcohol, produced by non 100 % hydrolisation of polyvinyl acetate, preferably with a degree of hydrolisation of approximately 88 %.

As an example of a cellulose ether, cellulose diethyl ether (CdE) is mentioned, which is processable thermoplastically for example with diethyl tartarate as softener at approximately 190 °C and is biologically decomposable. The maximum water uptake at 20 °C in water only amounts to just 0.04 parts by weight.

As an example of cellulose ester, cellulose diacetate (CdA) is mentioned, or as mixed ester cellulose acetate butyrate, which are processable thermoplastically with softeners at 180 °C and are biologically decomposable. The maximum water

15 JAN 1959

uptake at 20 °C in water amounts to only just 0.05 parts by weight.

Both the above-mentioned examples for cellulose derivatives are offered on the market today at prices in the order of Sfr. 12.--/kg.

Caprolacton can be processed without a softener at 120 °C, is partially crystalline with a melting point between 60 and 80 °C and a glassy solidification at -50° C. The mechanical characteristics are comparable with those of low density polyethylene. The maximum water uptake at 20 °C is < 0.01 part by weight, in addition caprolacton is biologically decomposable. The prices move in the order of Fr. 10.-- to Fr. 12.--/kg.

Polyhydroxy butyric acid/hydroxy valerian acid copolymers are processable thermoplastically, have good mechanical characteristics and low water uptake of < 0.01 parts by weight and are additionally able to be decomposed well biologically. The relatively high price of Fr. 30.-- to Fr. 50.--/kg, however, limits the use of these polymers.

The same applies to polylactic acid which, although being able to be processed well thermoplastically, having good mechanical characteristics and being biologically decomposable, is scarcely used because its price is in the order of Fr. 1 000.-- to Fr. 3 000.--/kg.

Zein is proposed as hydrophobic protein, which is thermoplastically processable with 0.2 parts by weight of lauric acid or diaethyl tartrate at 130 °C. Zein is, in addition, biologically decomposable, and the costs are in the order of Fr. 20.-- to Fr. 30.--/kg. A disadvantage of zein lies in the relatively high water uptake, which lies distinctly above 0.1 parts by weight.

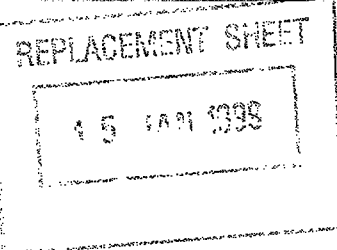
Finally, polyvinyl alcohol is to be mentioned, known under the trade name

Moviol, in which advantageously the polyvinyl acetate used for the production is 88 % hydrolysed.

As already mentioned above, it is possible to use two different groups of phase agents. Firstly, phase agents are proposed which are both compatible with respect to thermoplastically processable starch and at the same time with respect to the hydrophobic polymer. Owing to the different cohesion energy densities of starch and the hydrophobic polymer, only block copolymers come into consideration and namely those which consist of a block which is soluble in starch and of a block which is soluble in the hydrophobic polymer phase. Of course, it is essential here that the phase agent is likewise biologically decomposable and can be processed thermoplastically without difficulty. As an example of this, a polycaprolacton/polyvinyl alcohol copolymer is mentioned. In terms of parts, such a phase agent can be added up to 100 % in relation to the weight of the hydrophobic polymer, but preferably such a polymer is only used in the order of 5 to 50 % by weight for the production of the polymer mixture according to the invention.

The other group of phase agents comprises reaction products between a further biologically decomposable polymer with the starch, which has groups reactive with respect to the starch, and which is compatible with the hydrophobic polymer phase, in which these reactive groups may comprise for example epoxy groups or else acid anhydride groups. These reactive groups now react with a portion of the starch and thus form in the polymer mixture the phase agent which is responsible for the molecular coupling of the two phases.

Such a phase agent can be present in the polymer mixture in turn up to 100 % by weight in relation to the weight of the hydrophobic polymer, in which the polymer mixture preferably comprises a phase agent quota of 5 to 50 % by weight in relation to the weight of the hydrophobic polymer.



The further polymer used for the production of this type of phase agent can be a hydrophobic polymer here, taken from the list quoted above for hydrophobic polymers, which are used in the polymer mixture. Here, one of the listed polymers is provided with reactive groups such as for example with epoxide groups or with acid anhydride groups which then react strongly with the starch during the production of the polymer mixture. In principle, it would of course be conceivable that the hydrophobic polymer is entirely replaced by such a further polymer, whereby finally the polymer mixture would only consist of thermoplastically processable starch and the phase agent.

The introduction of the reactive groups takes place here in that the reactive groups are grafted on a hydrophobic polymer, such as for example a polymer according to the list quoted above, by means of vinyl polymerisation or condensation, in which this is achieved for the epoxide groups by means of a glycid ether and for acid anhydride groups for example with succinic acid anhydride. Of course, however, it is also possible to provide other reactive groups which can react with the starch molecules.

Compared with this, however, it is also possible to produce a polymer blend defined according to the invention, in the production of which the use of an externally added phase agent can be dispensed with; in which the phase agent is produced by itself during the manufacture of the polymer mixture. Here, it is proposed according to the invention that as hydrophobic polymer a polymer is used with ester groups incorporated in its molecule chains, which ester groups become reactive at increased temperature after decomposition and bring about both re-esterification of the hydrophobic polymer and also, partially occurring almost as a further polymer, react with a portion of the starch or the thermoplastically processable starch. The reaction products of the molecule chains thus reacting with the starch then form the phase agent which is again

15 JAN 1999

responsible for the molecular coupling of the two phases. Of course, it would be theoretically possible if all the molecule chains of the hydrophobic polymer would react with the starch, however generally one can assume that the re-esterification reaction is preferred to the esterification reaction with the starch, whereby only a portion of the hydrophobic polymer is converted to phase agent. Again in the finally produced polymer blend, the phase agent will be present in the order of approximately 5 to 50 % by weight, in relation to the overall weight of the hydrophobic polymer.

As an example of this, polycaprolacton is mentioned, which contains ester groups in the molecule chains, which ester groups for example at a temperature of approximately 190 °C can presumably undergo the above-mentioned re-esterification reaction with the starch.

Generalizing, it can be seen in particular from what has been stated above that in the polymer mixture according to the invention, the phase agent can be formed by starch or thermoplastically processable starch with grafted aliphatic polyester, for example obtained by conversion of polycaprolacton with the starch. Here, it has been found that the more starch is present with grafted polyester, the greater the water resistance of the polymer mixture can be increased.

The polymer mixtures proposed according to the invention can of course be mixed with any desired number of additives, supplements, fillers, pigments etc., as are generally known in polymers, such as in particular in thermoplastically processable plastics. Since their use is greatly dependent on usage and in addition such additives are very well known from practice, their use in connection with the polymer mixtures defined according to the invention is not entered into in further detail, with the exception of softeners. It is obvious that with the requirement for biological decomposability of the polymer mixtures, likewise of course the necessary note must be taken of this characteristic with

the use of such additives and supplements, otherwise of course the biological decomposability would suffer thereby.

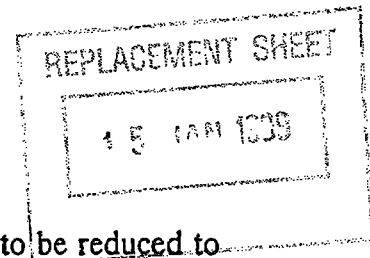
Worth mentioning as a supplement in particular is the admixing of a softener which is compatible with the hydrophobic polymer and preferably lowers its melting viscosity. On the one hand, the advantage of such a softener lies in that the hydrophobic biologically decomposable polymer is less brittle by the softener and in addition with the production of the polymer blend, the almost encapsulation of the thermoplastically processable starch is promoted by the hydrophobic phase through the reduction of the viscosity.

The method according to the wording of Claim 16 is particularly suitable for the production of the above-mentioned biologically decomposable polymer mixtures according to the invention.

Preferred variant embodiments of the method according to the invention are characterised in the dependent Claims 17 to 24.

For the production of the biologically decomposable polymer mixture according to the invention, either one can proceed from native starch or else from thermoplastically processable starch, as defined for example in the international patent application WO90/05161.

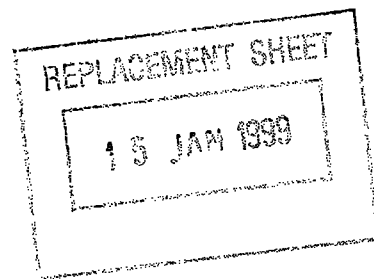
In the case where one proceeds from native starch, this must firstly be decomposed with the aid of at least one plasticizing- or swelling agent, in which for this decomposing the native starch should have a water content of $< 10\%$, better $< 6\%$ by weight. Of course, a certain water content in the order of up to 6% by weight can be entirely advantageous for the decomposition of native starch, for example with glycerin or sorbitol. Then, the thus produced mixture is melted for the formation of the thermoplastically processable starch, and is



mechanically mixed, in which however the water content is now to be reduced to below 1 % by weight, preferably < 0.5 % by weight in relation to the overall weight of the mixture, and then the mixing is continued until a homogeneous mass is reached.

The thermoplastically processable starch is now mixed together with at least one biologically decomposable hydrophobic polymer, which is thermoplastically processable, and with a phase agent or with a dispersing agent or with a further polymer soluble in the hydrophobic polymer phase, with groups reactive with respect to starch in the melt, in which before or during the mixing of the said components the water content is reduced to below 1.0 % by weight, better < 0.5 % by weight, in relation to the overall weight of the mixture, in order to thus obtain the biologically decomposable polymer mixture defined according to the invention, in which in the case of the use of a further polymer, the phase agent in the polymer mixture is formed by the reaction of this further polymer with a portion of the thermoplastically processable starch.

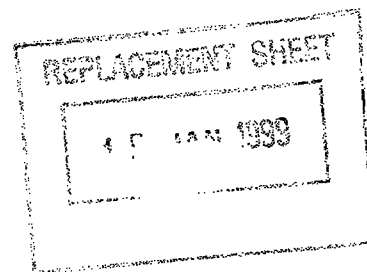
The fact that the polymer blend production takes place substantially with the exclusion of water is important, because otherwise the dispersing of the starch in the hydrophobic polymer does not come about correctly with the action of the phase agent. Thus, for example, the acid anhydride groups in the presence of water do not react with the starch to form the phase agent, but rather they hydrolyse. Hence, however, the formation of the phase agent is prevented, whereby, as mentioned, a problem-free dispersing is made impossible. The presence of a dispersion in the polymer blend which is problem-free to the greatest extent is, however, a precondition for the good mechanical characteristics of the mixture which are required according to the invention. In addition, the danger of the formation of bubbles exists in the processing of the polymer mixture. A subsequent drying of the polymer blend after its production is not suitable for subsequently improving an incorrectly produced polymer



mixture as a result of humidity.

For the production of the polymer mixture according to the invention, up to 70 % by weight, in relation to the overall weight of the mixture, of thermoplastically processable starch can be used, in order to ensure that, as required above, the hydrophobic polymer is still present to the greatest extent as a continuous phase. The remaining components in the polymer mixture according to the invention are taken up on the one hand by the hydrophobic polymer and on the other hand by the phase agent which, in relation to the weight of the hydrophobic polymer phase, can be 2 to 100 % by weight, preferably 5 to 50 % by weight. Accordingly, in the production of the polymer mixture either 2 to 100 % by weight, in relation to the weight of the hydrophobic polymer phase, of a phase agent are added or else the same percentages by weight of a further polymer which comprises the reactive groups, in order to form the phase agent in the polymer mixture through reaction with parts of the starch.

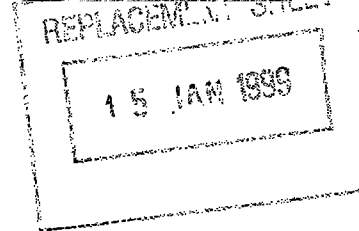
Whereas for the production of the thermoplastically processable starch, the starch is mixed with the swelling- or plasticizing agent in a temperature range in the order of 150 to 190 ° C, the mixing of the thermoplastically processable starch with the hydrophobic polymer and the phase agent or with the further polymer takes place in a temperature range in the order to 150 to 230 °C. The mixing temperature which is to be selected is determined here substantially by the processing temperature of the selected hydrophobic polymer, for which reason for example with the use of cellulose derivatives, rather a temperature in the order of 190 to 220 ° C is used, whereas with the use of polycaprolacton, the production of the polymer mixture according to the invention preferably takes place in a range of approximately 150 °C to 190 ° C. With respect to the hydrophobic polymers to be used, reference is to be made to the list set out in connection with the characterising of the polymer mixtures according to the



invention, relating to suitable hydrophobic polymers.

Likewise, as already stated in the characterising of the various polymer mixtures according to the invention, basically polymer mixtures can be produced with two different types of phase agents. According to a first variant, the thermoplastically processable starch is mixed with preferably 5 to 50 % by weight, in relation to the weight of the hydrophobic polymer, of a block copolymer as phase agent, which phase agent at least consists of a block soluble in the starch phase and of a block soluble in the hydrophobic polymer phase, such as for example a polycaprolacton/polyvinyl alcohol copolymer, in which finally, together with the phase agent, the at least one hydrophobic polymer, such as polycaprolacton for example, is admixed. Of course, phase agents other than the one mentioned above can be used, such as for example partially hydrolised polyvinyl acetate or a polyvinyl acetate/polyvinyl pyrrolidyn block copolymer, it is essential here that the phase agent which is used contains in each case at least one block which in each case is soluble in one of the two phases.

In the other case, either firstly the reactive groups are grafted on a hydrophobic polymer, suitable for the production of the polymer mixture according to the invention, by means of vinyl polymerisation or condensation through conversion with a glycidyl ether or at least one aliphatic di- or polycarboxylic acid anhydride, such as for example succinic acid anhydride, in which the further polymer which is thus formed together with the hydrophobic polymer and thermoplastically processable starch are mixed intensively in the melt with a water content of < 0.5 , preferably < 0.1 %. Or else, a hydrophobic polymer is used, with ester groups incorporated in its molecule chains, which ester groups become reactive at increased temperature after decomposition and lead both to a re-esterification of the hydrophobic polymer and also, intermediately occurring as further polymer, partially react with a portion of the starch or the thermoplastically processable starch for the formation of the phase agent.



Accordingly, a hydrophobic polymer with ester groups incorporated in its molecule chains is likewise intensively mixed with the thermoplastically processable starch in the melt and with the above-mentioned low water content. This mixing takes place for example in a plastic-processing device or machine, such as a kneader or extruder, in which with this mixing process the reactive groups of the said further polymer or the decomposing incorporated ester groups react with a portion of the starch or of the thermoplastically processable starch for the production of the phase agent. It is essential here that in the use of a further polymer with the reactive groups, a polymer is concerned which is soluble to the greatest extent in the hydrophobic polymer phase or is well miscible therewith. With the use of a polymer with ester groups incorporated in its molecule chain, this occurs automatically.

For the production of a further polymer, for example one can proceed from ethyl cellulose, which is mixed with oleic acid or generally with an unsaturated fatty acid or a corresponding triglyceride. By means of radical reaction of the vinyl groups, the maleic acid anhydride groups are grafted to the ethyl cellulose, which groups, as mentioned above, are capable of reacting with the starch in order to thus form the phase agent.

As an example of a hydrophobic polymer with ester groups incorporated in its molecule chains, polycaprolacton is mentioned, the ester groups of which from a certain temperature permit re-esterification reactions with the starch.

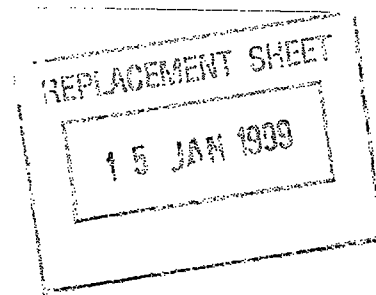
According to a further variant embodiment of the invention, it is possible to produce a polymer mixture according to the invention by the mixing of thermoplastically processable starch with a hydrophobic polymer, which consists almost exclusively of macromolecules, which have groups which are reactive with respect to the starch. In this case, the hydrophobic polymer and the phase agent in the polymer mixture according to the invention are identical to the greatest

15 JAN 1958

extent. Of course, also in this case the hydrophobic polymer or the phase agent in the polymer mixture must naturally have a quota such that, as required according to the invention, the starch is still present as a dispersed phase with the hydrophobic polymer or the phase agent as continuous phase, in which through the bonds between the hydrophobic polymer and a portion of the starch molecules, the molecular coupling of the two phases exists.

To return to the above-mentioned example of the ethyl cellulose converted by means of oleic acid, accordingly for the production of the polymer blend exclusively ethyl cellulose is used, which comprises suspended maleic acid anhydride groups. Depending on the selected processing temperature, mixing relationship and processing duration, accordingly more or less phase agent is formed, in which, as mentioned, in every case it is to be noted that the starch is still present as a dispersed phase. Under the consideration that the hydrophobic polymer and the further polymer are identical to the greatest possible extent, of course also the instance can be included where, as mentioned, the hydrophobic polymer contains ester groups incorporated in its molecule chains.

According to a further variant of the method according to the invention, it has proved to be advantageous when the hydrophobic polymer before mixing with the starch or with the thermoplastically processable starch is mixed with a softener. Here, it is advantageous if the selected softener is at least to the greatest extent compatible only with the hydrophobic polymer, i.e. is only soluble in the hydrophobic phase. In addition, it has proved to be advantageous if the selected softener lowers the melting viscosity of the hydrophobic polymer. The idea is suggested that the formation of a dispersion with the starch as dispersed phase and with the hydrophobic polymer as continuous phase is additionally promoted when the hydrophobic polymer is mixed with a softener which lowers its melt viscosity. Generally, as is known, the phase with the lower viscosity in a dispersion forms the continuous phase.



Also in connection with the method defined according to the invention, the representation of polymers which are filled, coloured, reinforced etc., is dispensed with, because the representation of such a polymer mixture in the plastic-processing industry is very well known.

The biologically decomposable polymer mixtures previously defined according to the invention are suitable both for injection moulding- and also for extrusion applications, in which reference is made at this point specifically to the production of single- or multiple-layered foils. Here, at least one layer of such a foil consists of a polymer mixture according to one of Claims 1 to 15. Therefore a single-layer foil is conceivable, produced entirely from a polymer mixture according to the invention, or else for example a triple-layer foil comprising a central middle layer, produced for example exclusively from thermoplastically processable starch, whereas the two outer layers overlapping the starch layer can be produced from a polymer mixture, as defined according to the invention. Thereby, a foil can be produced which is water resistant to the greatest extent, which in total consists of 80 % by weight or even more of thermoplastically processable starch and which as a whole corresponds to the requirements set with regard to biological decomposability.

The invention is now explained in further detail hereinbelow partially with reference to the enclosed figures and with the aid of theoretical considerations and practical examples.

The enclosed figures show here:

Fig. 1 diagrammatically illustrated, the morphology of a polymer mixture according to the invention;

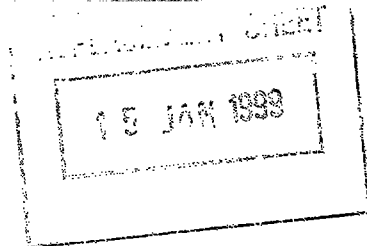


Fig. 2 diagrammatically illustrated, the mechanism of the phase agency in a polymer mixture according to the invention;

Fig. 3 diagrammatically illustrated, a representative stress/strain diagram for determining the mechanical characteristics of test bodies produced by means of polymer mixture according to the invention;

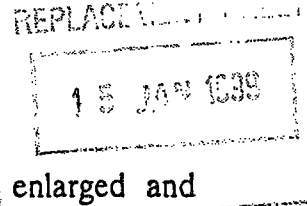
Fig. 4 and 5 molecular weight distributions of polycaprolacton - non-pretreated and pretreated by re-esterification;

Fig. 6 the biological decomposability of a polymer mixture according to the invention compared with cellulose; and

Fig. 7 the biological decomposability of cellulose compared with various, so-called biologically decomposable polymers.

Firstly, with reference to Figures 1 and 2, once again the basic problem or the setting of the task of the present invention is to be dealt with, which has led to the representation of the polymer mixtures defined according to the invention.

The incompatibility of the thermoplastically processable starch with hydrophobic polymers can be used, as illustrated diagrammatically in Fig. 1, in order to disperse it in a matrix of a hydrophobic material. With this structure, it is to be expected that the swelling of the thermoplastically processable starch can be effectively restricted with storing under water or the water vapour absorption. The diagrammatic representation of the morphology of a polymer mixture according to the invention shows on the one hand the thermoplastically processable starch 1 as disperse phase and the hydrophobic polymer 2 as continuous phase.



The boundary surface 3 occurring here is illustrated greatly enlarged and diagrammatically in Fig. 2. The disperse distribution of the thermoplastically processable starch 1 in the hydrophobic polymer 2 is made possible with the action of the phase agent 4, which phase agent 4 comprises a segment 6 which is miscible with the thermoplastically processable starch 1, and also a segment 5 miscible with the hydrophobic polymer 2. The phase with the lower viscosity generally forms here the continuous phase, for which reason it is advisable if necessary to add to the hydrophobic polymer a viscosity-reducing additive, such as for example a softener. Here, it is advantageous if this softener is only compatible with the hydrophobic phase, in order to thus bring about the lowering of viscosity to specific objectives in the hydrophobic phase.

The exact particle size of the individual phases, as illustrated in Fig. 1, is determined by the rheological behaviour of the individual phases, the type of the mixing process and by the boundary surface energy. Owing to the thermodynamically dependent incompatibility of the thermoplastically processable starch with the hydrophobic polymer only a small mixing of the two polymers takes place at the phase boundary, which generally leads to an impairment of the mechanical characteristics of a mixture of the two substances. For this reason, it is necessary that a sufficient mechanical coupling of the two phases is achieved or a low boundary surface energy, which can be achieved through the use of the block copolymer or phase agent illustrated diagrammatically in Fig. 2. This phase agent penetrates the phase boundary 3. Generally, these phase agents consist of two blocks, which are respectively sufficiently compatible with one of the two polymers.

With the aid of the following examples, the representation of polymer mixtures defined according to the invention will now be explained in further detail, in which the basic theoretical considerations cited above are taken into account, in order to obtain the good characteristics, required according to the problem, of a

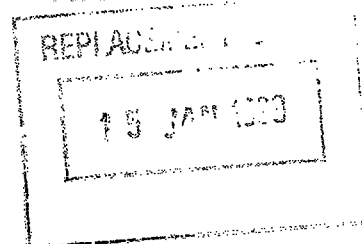
thermoplastically processable, biologically decomposable polymer mixture.

1. Polymer mixture of cellulose acetate butyrate and thermoplastically processable starch

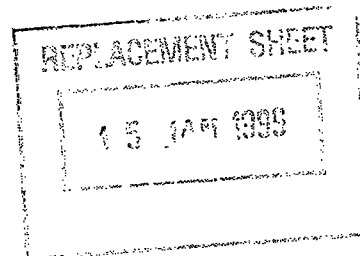
As cellulose ester, cellulose acetate/butyrate (ZAB) was mixed together with thermoplastically processable starch (TBS) in a brabander kneader at 160 °C under various mixing conditions. Here as TPS a starch was used which was converted with 30 % by weight glycerin and namely according to the processing conditions as disclosed for example in the WO90/05161 or in the WO91/16375. As cellulose acetate butyrate mixed ester, tenite butyrate 525 of the firm Eastman Kodak was used.

Firstly the two polymers were mixed without any additives in the range of 30 parts by volume ZAB to 80 parts by volume ZAB and the remainder TPS and with the aid of pressing plates produced therefrom the swelling in water was examined and tensile tests were carried out with the aid of test bodies. It has been found here that from approximately 55 percent by volume ZAB, the swelling was still low and in addition the test bodies have undergone an increase in weight which leads one to conclude that the TPS phase was no longer able to be extracted from the test bodies.

The values determined in the tensile tests for expansion on fracture and energy of fracture can be seen from the following Table 1.1. Here, it can be seen that as a function of the volume quota of the ZAB, the energy of fracture and the elongation on fracture runs through a minimum at approximately 50 to 60 volume quota ZAB, in which the energy of fracture at 80 volume parts increases by approximately twenty times. It can be concluded from this that in this range the transition of TPS to ZAB is present as a continuous phase. With the simple mixing of TPS and ZAB, therefore only a drastic impairment of the mechanical



characteristics is achieved; without doubt, this lies in the insufficient dispersing of the TPS phase in the ZAB matrix and a very small mechanical coupling of the phases.

Table 1.1

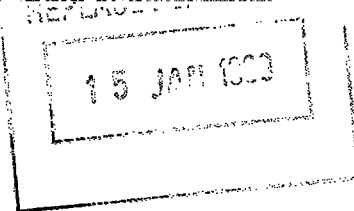
Volume quota ZAB (%V/V _{tot})	Elongation on fracture (%)	Energy of fracture (kJ/mm ²)
30 %	10 %	10
40 %	10 %	37
50 %	8%	35
60 %	4%	28
70 %	6%	66
80 %	37%	800

Energy of fracture and elongation on fracture of TPS/ZAB blends as a function of the ZAB volume quota; produced at 160 °C kneading temperature, tensile tests carried out on 0.3 mm pressing plates.

As with incompatible polymer mixtures the continuous phase is formed from the component with the lower viscosity, as in our case of hydrophobic polymer or the ZAB, a softener was now added to the mixture, which softener is only compatible with the ZAB phase and hence reduces its viscosity selectively. In this way, a better dispersing of the TPS phase is to be achieved. As softener, owing to its biological decomposability acetyl-triethyl-citrate (ATZ) was used. Mixtures were produced with a TPS volume quota of 40 % with variation of the volume ratio ATZ/ZAB, and the mechanical characteristics which were achieved are represented in the following Table 1.2:

Table 1.2

Vol. quot.ATZ (%V/V _{tot})	Vol.quot.ZAB (%V/V _{tot})	Elong. fract. (%)	Energy on fract. (kJ/mm ²)
8.3 %	91.7 %	40 %	670



20 %	80 %	50 %	620
25 %	75 %	61 %	450
33 %	67 %	61 %	270
42 %	58 %	70 %	160

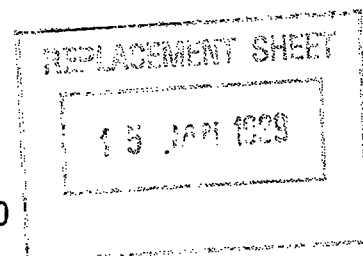
Energy of fracture and elongation on fracture of TPS/ZAB/ATZ blends as a function of the volume quota of ATZ in the ATZ/ZAB/phase. Mixtures produced at 160 °C kneading temperature, tensile tests carried out on 0.3 mm pressing plates.

With 8.3 ATZ in the ZAB phase, an increase in the energy of fracture by twenty times with respect to a sample without ATZ quota but with otherwise the same TPS quota (40 % by volume) is already achieved, in which the material can be elongated up to 70 %. With the aid of a screen electron microscopy recording of the polymer mixtures with an ATZ quota of 25 % by volume in the ZAB phase, it was able to be proven that the desired morphology was achieved and ZAB forms the continuous phase. Of course, it could be seen from the recording of the polymer mixture that the size of the TPS microphases is still considerable and the dispersing which is achieved is unsatisfactory. This can also be seen from Table 1.2, where under a volume quota of 75 % ZAB the mechanical characteristics are unsatisfactory.

A further improvement to the mechanical characteristics was now able to be achieved in that a phase agent (PA) was incorporated into the polymer mixture. The measured mechanical characteristics for samples with 40 parts by weight TPS are represented in the Table 1.3.

Table 1.3

Vol. quot. (PA)	vol.quot.ZAB	Elong. on fract/	Energy of fract.
(%V/V _{tot})	(%V/V _{tot})	(%)	(kJ/mm ²)



8.3%	91.7%	20%	600
20%	80%	53%	620
25%	75%	92%	880
33%	67%	93%	790
42%	58%	94%	600

Energy of fracture and elongation on fracture of a blend of (1) 40%V/V_{tot} TPS, (2) 60%V/V_{tot} ZAB/PA, the volume quotas in the table relate to the ZAB/PA phase, energy of fracture and elongation were determined on 0.3 mm pressing plates, blend at 160°C produced in the brabender kneader.

In the manufacture of polymer mixtures of cellulose acetate butyrate mixed ester and thermoplastically processable starch, it was therefore able to be shown that with the selection of a suitable phase agent, blends with good mechanical characteristics were obtained, in which the required morphology, i.e. an encapsulation of the TPS phase into the ZAB matrix was achieved. Shaped parts of this material remain stable when stored under water and only have a very small swelling. Here, a morphology was obtained which is distinguished by an extent of the TPS microphases below 2 to 3 µm. It is therefore to be assumed, as mentioned above, that the phase agent not only influences the viscosity of the ZAB phase, but also brings about a certain reduction of the boundary surface energy between the two phases. A chemical reaction with the starch is therefore to be assumed. At the phase boundary therefore a chemical modification of the starch takes place, whereby a certain compatibility with the ZAB phase has been brought about.

2. Polymer blend produced from thermoplastically processable starch and polycaprolacton

Polycaprolacton (PCL) has proved to be suitable for the production of polymer

15 JAN 1969

blends with thermoplastic starch (TPS). Polycaprolacton is a homopolymer of E-caprolacton and according to the statements of the manufacturer (Union Carbide) it is fully decomposable biologically, is non-poisonous and is suitable for the production of foils and as polymer additive.

For the production of various polymer blends, three different TPS types were used, and namely designated hereinafter as glycerin TPS, standing for a thermoplastically processable starch, containing 30 % by weight glycerin; as TPS-LSM 1 for a thermoplastically processable starch, containing 15 % by weight glycerin and 15 % by weight sorbitol; and also as TPS-LSM2 for a thermoplastically processable starch, containing 30 % by weight sorbitol.

All three TPS types were extruded in a ratio of 1 : 1 together with caprolacton, in which for the tests which were carried out, the two types PCL 787 and PCL 767E of Union Carbide were used.

In order to find conditions which are as free of water as possible in the extrusion, the thermoplastically processable starch was degassed atmospherically before the addition of the polycaprolacton, whereby the water content came to lie distinctly below 0.5 % by weight. The extrusion was carried out on a Theysohn twin screw extruder, in which for every mixture samples were produced with various temperature profiles. By average, the following temperature profile for instance was selected in the extruder:

80 to 160° / 160 to 170° / 180 to 190° / 150 to 180° / 130 to 140° / 130°/100 to 140°.

The throughput of the various polymer mixtures was varied between 20 kg/h to 40 kg/h. The rotation rate in the extruder was selected in a range between 170 and 300 revolutions/min. The introduced energy therefore produced a value of

approximately 270 to 440W/kg polymer mixture. The measured water content amounted to 0.26 to 0.6 % by weight H_2O .

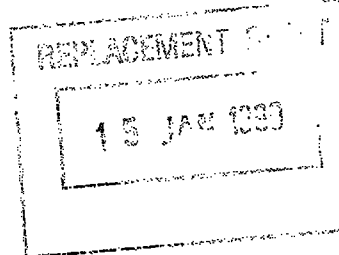
From the polymer mixtures produced with the three TPS types and the two PCL types, foils were then blown, in which owing to the low melting point of the PCL (approximately 60° C) the take-up rollers were to be cooled or even better the foils were to be produced by pulling up. With the foils thus produced, tensile tests were carried out in order to measure, inter alia, tearing strength and energy of fracture. Here, the foils were both tested at room temperature conditioned after 24 hours and also after 24 hours water storage.

In order to better interpret the measurement values of the tensile tests set out hereinbelow in Table 2.1, reference is first made to Fig. 3 in which a stress/strain diagram is illustrated diagrammatically. The characters used in the said Fig. 3 are defined in the following list:

- Rs stretching-strain limit
- As relative elongation at the stretching/strain limit
- Rm maximum tension
- Am relative elongation at maximum tension
- Rr tearing tension
- Ar relative elongation on fracture

In addition, in the following Table 2.1

- d thickness of the foil
- b width of the foil for all assessed foils = 15.0 mm
- SO cross-section of the foil (reference quantity for the tension)
- W energy of fracture (proportional to the area under the curve according to Fig. 3)
- N identification of the measured foil sample



Here:

N = 1 Foil, produced from glycerin-TPS and PCL, in which the measured values represented in Table 2.1 each represent a mean value, averaged over the values measured from various samples, on the one hand produced with the two PCL types 787 and 767 E and also with the various above-mentioned extrusion conditions.

N = 2 Samples of glycerin TPS and PCL, after 24 hours water storage.

N = 3 Samples of TPS, LSM 1 and PCL, conditioned 24 hours at room temperature,

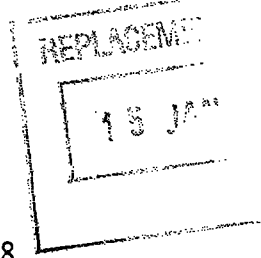
N = 4 Samples of TPS, LSM 1/PCL after 24 hours in water storage,

N = 5 TPS, LSM 2 and PCL, conditioned 24 hours at room temperature, and

N = 6 TPS, LSM 2 and PCL after 24 hours water storage.

Table 2.1

N	Rs	As	Rm	Am	Rr	Ar	d	SO	W	E-Mod.
	N/mm ²	%	N/mm ²	%	N/mm ²	%	μm	mm ²	J/m ²	N/mm ²
1	10.4	25.5	25.7	781	25.7	782	47.0	0.72	5.30	220
2	13.5	5.8	14.1	5.0	14.0	6.0	45.0	0.68	0.11	630
3	15.4	7.9	19.2	607	19.2	607	22.3	0.35	4.35	693
4	18.6	10.2	20.1	290	17.9	317	19.9	0.32	3.17	359
5	19.0	10.3	21.7	615	20.7	685	92.2	1.38	6.52	717



6 12.7 13.0 22.4 675 18.0 785 90.7 1.21 7.08 468

As can be seen from Table 2.1, the glycerin blend in the dry state shows a tearing strength of approximately 25N/mm^2 and an energy of fracture of approximately 5J/m^2 . After 24 hours water bath, the tearing strength falls, however, to approximately 14N/mm^2 and the energy of fracture even falls distinctly to below 1J/m^2 . This massive drop of the mechanical values can possibly be derived from a washing out of glycerin.

Compared with this, the foil, produced from TPS LSM 1 and PCL in dry state has a tearing strength of approximately 19N/mm^2 and an energy of fracture of around 4J/m^2 . Also in the "softened" state the corresponding measured values only deviate to an insignificant extent from those mentioned, only the energy of fracture falls to approximately 3J/m^2 .

The sorbitol foil tears at approximately 21N/mm^2 with an energy of fracture of approximately 6.5N/mm^2 . These values fortunately also do not alter after 24 hours water bath, i.e. rather, they increase further.

By way of comparison, it is also mentioned that foils, produced from pure polycaprolacton, have a tearing strength of approximately 18 to 20N/mm^2 and have an energy of fracture in the order of 7 to 9J/m^2 .

The polymer mixtures produced with thermoplastic starch and polycaprolacton in the ratio $1 : 1$ on a twin shaft extruder are suitable both for injection moulding, fishtail extrusion and also for the blowing of foils. In particular, the polymer mixtures produced with the sorbitol starch show excellent mechanical

15 JAN 1999

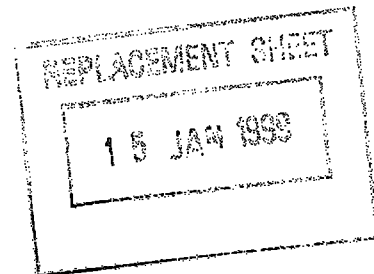
characteristics, for which reason, on the basis of the above-mentioned theoretical considerations concerning polymer mixtures, containing two different phases, it must be assumed that a mechanical coupling of the two phases occurs at the boundary surfaces.

It was therefore to be assumed that the ester groups incorporated in the molecule chains in the polycaprolacton undergo esterification reactions with the thermoplastic starch, whereby the thus reacting molecule chains with the starch again form the phase agent mentioned according to the invention. This assumption was strengthened by the circumstance that in the polycaprolacton from a certain temperature re-esterification reactions occur, which was able to be proved with the aid of molecular weight distributions. With the aid of molecular weight distributions in Fig. 4 and 5 this circumstance is to be explained in further detail.

In Fig. 4 a differential molecular weight distribution of poly epsilon caprolacton P787 of Union Carbide Corporation is illustrated, which is not pre-treated. The determined mean molecular weight here amounts to 215 500, the minimum measured molecular weight 212 400 and the maximum determined molecular weight 218 600.

The polycaprolacton used for determining the curve in Fig. 4 was then heated to 190°C and then cooled. The molecular weight distribution was measured again, which is now illustrated in Fig. 5. Already with the aid of the representation in Fig. 5 it can be clearly seen that the molecular weight distribution is substantially broader, whereby it already becomes clear that an internal rearrangement of the molecule chains has taken place. Owing to the ester groups occurring in the molecule chain, a re-esterification reaction has taken place.

The values determined with the aid of the distribution of Fig. 5 produced the



following pattern:

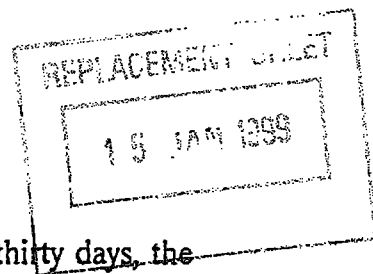
Weight average of the molecular weight:	280 000
maximum molecular weight:	538 400 and
minimum molecular weight:	146 300.

As the internal re-esterification of the molecule chains in the polycaprolacton is in competition with corresponding esterification reactions with the starch, it is clear that therefore in the processing of the polycaprolacton with the thermoplastic starch, a portion of the polycaprolacton reacts with the starch, whereby, as required according to the invention, the phase agent is formed, which is responsible for the molecular coupling of the two phases. The presence of reaction products between polycaprolacton molecule chains with the TPS, was finally able to be proven with the aid of a heat flow diagram, whereby the above-mentioned assumption was finally able to be proven.

3. Measurement of the biological decomposability or compostability of a polymer mixture according to the invention produced by way of example

The polymer mixture used in Example 2, consisting of a 1 : 1 mixture between polycaprolacton and thermoplastically processable starch, in which the latter has been destructured with 30 % sorbitol, was subjected to a composting test or the determining of the biological decomposability. Comparably therewith, likewise the biological decomposability of cellulose was measured.

The corresponding results of the decomposability are represented in Fig. 6, in which the continuing decomposition was measured as a function of the percentual conversion of carbon in CO₂. The diagram of Fig. 6 therefore shows on the one hand the composting of the caprolacton/TPC mixture, which is represented by a curve, designated by 10. Compared with this, the decomposability of cellulose is represented by the curve, designated by 11.



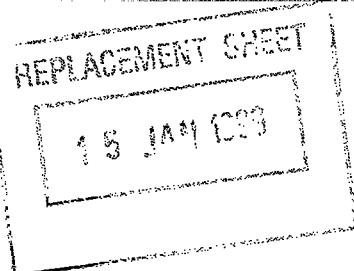
Whereas the PCL/TPS mixture is already fully decomposed after thirty days, the decomposition of cellulose is not yet completed after thirty days. The measurement of the decomposability took place through the Organic Waste Systems Inc, in Ghent, Belgium and as measurement method the American Standard AFTM D 5338 was used.

In order to further document the excellent decomposability of the polymer mixture produced according to the invention, in Fig. 7 the biological decomposability of cellulose is represented compared with various so-called biologically decomposable polymers which are commercially available. Here, in turn, the curve 11 designates the decomposition of cellulose, whilst the curve 12 refers to a first pattern and namely a material of the firm Novamont with the name "Chart BI". This material is a mixture of approximately 50 % thermoplastically processable starch with an ethylene vinyl acetate copolymer with a hydrolysis content of approximately 75% and a quota of polyethylene as copolymer. The thermoplastically processable starch contains inter alia urea, sorbitol and glycerin as plasticizing agent.

The curves 13 and 14 refer to pattern 2 and 3, comprising materials of the name "Mater BI" of the firm Novamont, in which these materials in turn contain 50 % thermoplastically processable starch, approximately 40 % polyvinyl acetate (at approx. 85 % hydrolysed to polyvinyl alcohol) and approximately 10 % polyethylene as copolymer.

Finally, curve 15 refers to a fourth pattern of the firm Novon, in which a foamed material is concerned, consisting of approximately 80 % starch and approximately 20 % polyvinyl acetate, in which the latter is hydrolysed to approximately 85. % to polyvinyl alcohol.

The patterns 1 to 4 all comprise materials which are offered on the market as



so-called biologically decomposable polymers. As can be clearly seen from Fig. 7, however, the biological decomposability is partly substantially poorer than that of cellulose, its decomposability itself in turn, as illustrated in Fig. 6, is poorer than the biological decomposability of a polymer mixture produced according to the invention.

Also the curves according to Fig. 7 were carried out by the OWS Institute in Ghent, Belgium and namely in accordance with the AFTM D5338 standard.

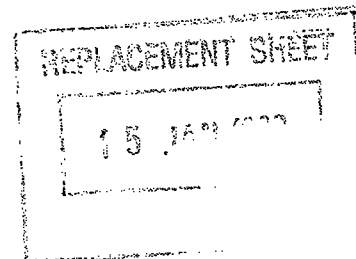
The fact that the excellent biological decomposability of the PCL/TPS polymer mixture produced according to the invention is not achieved at the expense of the mechanical characteristics is documented with the aid of the values in the following Table 3.1, in which table the mechanical characteristics of a PCL/TPS mixture are set out in comparison with the characteristics of the samples 1 and 2 according to Fig. 7. Here, of the three materials, the tensile stress on fracture, the elongation on fracture and the energy density on fracture are represented both of "dry" materials and also of materials which have been stored in water for forty hours.

Here, sample 6 designates the TPS/PCL polymer mixture produced according to the invention, the biological decomposability of which is represented in Fig. 6 with the aid of curve 10.

Table 3.1

Alteration of the mechanical strength of blast-extruded foils, "dry" and after storage in water

	Tensile stress on fracture (MPa)	Elongation on fracture (%)	Energy density as a result of fracture (MJ/m ³)
Sample 1	31	174	4.9

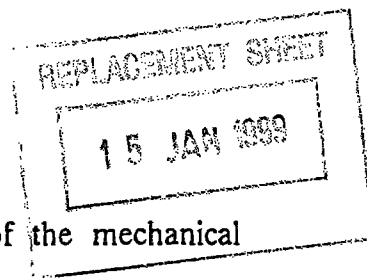


Sample 1 after 40 hrs storage			
in water	27	255	6.2
Sample 2	16	176	2.3
Sample 2 after 40 hrs storage			
in water	48	6	0.2
Sample 6	21	650	6.5
Sample 6 after 40 hrs storage			
in water	19	850	8.0

It can clearly be seen from Table 3.1 that sample 2 is hydrolysed relatively intensively on storage in water or that the material has a relatively poor water resistance. Compared with this, samples 1 and 6, i.e. in particular the polymer mixture produced according to the invention, have an excellent water resistance. Also the mechanical characteristics in themselves are identical to the greatest extent, in which those of sample 6 are rather better classified than those of sample 1.

In addition also a test of sample 4 is included in the series of tests, however a storage in water was not possible, because the Novon material already fully dissolved after a few minutes. A measurement of the mechanical characteristics was accordingly not possible.

As a conclusion from the measurements according to Example 3 it can clearly be seen that the biological decomposability of the polymer mixture produced according to the invention is excellent and substantially better than the corresponding decomposability of so-called biologically decomposable polymers available commercially today. In addition, it was able to be proven that the



excellent composability was not achieved at the expense of the mechanical characteristics and the water resistance.

In the previously described examples, the concern of course is only with a small selection of possibilities for the representation of a polymer blend according to the invention. Basically, of course, it is possible to mix any hydrophobic polymer which is thermoplastically processable and biologically decomposable to the greatest extent, with thermoplastic starch, in which, however, it is essential that to achieve sufficient mechanical characteristics of the polymer mixture thus produced, a phase agent must be present in order to reduce the boundary surface energy at the phase boundary. In addition, it is essential that the hydrophobic polymer forms a matrix in the mixture, in which the starch is included, encapsulated.

In addition, it has been found that it is essential to the invention that the production of the polymer blend takes place to the greatest extent with the exclusion of water, so as not to disturb or prevent the mode of operation or the formation of the phase agent.

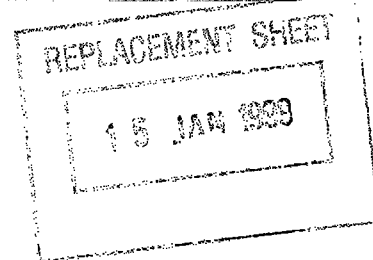
As a supplement, a list is to be set out hereinbelow of possible biologically decomposable polymers currently available commercially:

Zein (Zein F 4000) of the firm Benzian AG, CH-6002 Lucerne,

Ethyl cellulose (ethyl cellulose N 50) of the firm Aqualon East BV, NL-2288 ER Rijswijk,

Poly-E-caprolacton of the firm TONE-Polymers (Union Carbide Corporation),

Poly-L-lactid of the firm PURAC biochem, NL-4200 AA Gorinchem,



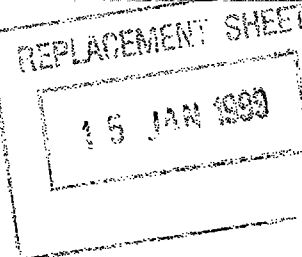
Cellulose diacetate (with unknown softener) (BIOCETA) of the form TUBIZE PLASTICS, B-1480 Tubize.

The list quoted only represents a few examples of biologically decomposable polymers and is, of course, incomplete. Of course, all e.g. synthetically produced hydrophobic polymers are also suitable for the production of a polymer mixture according to the invention, provided that they are biologically decomposable: As an example of this, polyhydroxybutyric acid is mentioned.

Finally, it is also to be added that a number of the possible biologically decomposable polymers are advantageously used with a softener for the production of a polymer blend according to the invention, because on the one hand these polymers are very brittle without a softener and in addition the use of a softener has proved to be advantageous, not least in order to reduce the melting viscosity. Thus it is almost impossible, for example, to process zein without a softener, because this material is very brittle. With the use of softeners, it is of course advantageous if this itself is likewise biologically decomposable. In addition, it is to be noted that, if the softener is hydrophilic, the additional quantity does not exceed a certain value, otherwise the water resistance of the entire polymer mixture is substantially impaired.

As suitable softeners for the various biologically decomposable hydrophobic polymers, the following substances inter alia have presented themselves:

- for zein
 - palmitic acid
 - glycerin monostearate
 - sorbitol
 - triacetin
 - carvon
 - 1,2-dodecandiol



lauric acid
ethyl laevulinate
dibutyl tartrate
sebacinic acid
diethyl tartrate
butyl lactate
polyethylene glycol
E-caprolactam
laevulinic acid
E-caprolacton
glycerin
triethylene glycol

- for ethyl cellulose

triacetin
castor oil
tributylcitrate
acetyltributylcitrate
bis(2-ethylhexyl)phthalate
bis(2-ethylhexyl)sebacate
dibutyladipat
palmitic acid
lauryl alcohol
diethyl tartrate
triglyceride

- for cellulose acetate

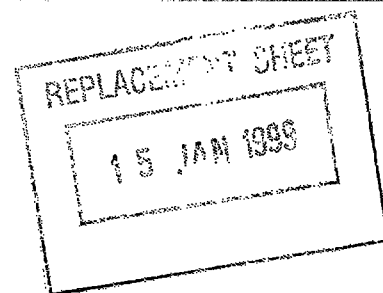
butyrate

acetyl-tri-ethylcitrate
triglyceride
oleic acid derivatives



The aliphatic polyesters are generally processed without softeners.

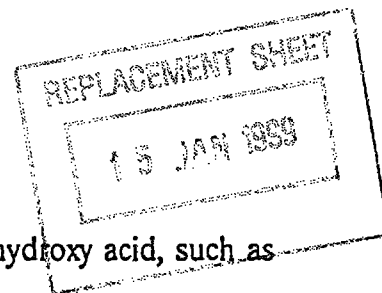
The list of suitable softeners cited above is to indicate a range of possible examples, by means of which substances biologically decomposable hydrophobic polymers can be softened. Of course, the softeners quoted for a polymer are partly suitable also for other biologically decomposable hydrophobic polymers such as, for example, a range of softeners suitable for ethyl cellulose are likewise suitable for the softening of cellulose acetate butyrate mixed esters.



Claims

1. A biologically decomposable polymer mixture, substantially consisting of thermoplastic starch, containing a plasticizing- or swelling agent in the order of 15 - 40 % by weight, in relation to the starch/plasticizing- or swelling agent mixture, and at least one biologically decomposable hydrophobic polymer, obtained by mixing in the melt of starch or of thermoplastic starch with a biologically decomposable hydrophobic polymer, which is able to be processed thermoplastically and with a phase agent excepting epoxidized soya oil, or with a macromolecular dispersing agent or a further polymer which is soluble in the hydrophobic polymer phase, with reactive groups with respect to starch, in which during mixing, the water content is reduced to below 1 % by weight in relation to the total weight of the mixture, and in which in the mixture the starch is present as a disperse phase with the hydrophobic polymer as continuous phase and the phase agent or the dispersing agent is responsible for the molecular coupling of the two phases or in which the reactive groups of the further polymer react with at least one part of the starch or of the thermoplastically processable starch and thus form in the mixture the phase agent which is responsible for the molecular coupling of the two phases.
2. A biologically decomposable polymer mixture according to Claim 1, characterised in that the starch is present as so-called thermoplastically processable starch (TPS), obtained by substantially water-free mixing of native starch with at least one plasticizing- or swelling agent in the order to 15-40 % by weight, preferably 20-36 % by weight, in relation to the mixture, with native starch or a derivative thereof, which plasticizing- or swelling agent is suited to at least swelling or dissolving the starch or the derivative.
3. A polymer mixture according to Claim 2, characterised in that the thermoplastically processable starch contains as swelling- or plasticizing agent at





least one of the following substances : sorbitol, glycerin, a hydroxy acid, such as lactic acid and or its salt, and/or polyvinyl alcohol.

4. A polymer mixture according to one of Claims 1 to 3, characterised in that the phase agent is a block copolymer, at least comprising two blocks, in which one block in the hydrophobic polymer phase is at least largely soluble and the other block at least largely soluble in the starch phase.

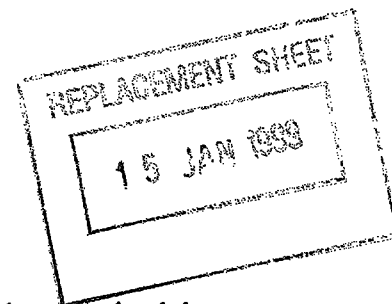
5. A polymer mixture according to one of Claims 1 to 3, obtained by substantially water-free mixing of starch or thermoplastically processable starch with a hydrophobic polymer of the said type, comprising ester groups incorporated in the molecule chain which become reactive at increased temperature after disintegration and react at least partially with at least a part of the starch or the thermoplastically processable starch, which molecule chains of the hydrophobic polymer, reacted with starch or with thermoplastically processable starch, thus form in the mixture the phase agent, which is responsible for the molecular coupling of the two phases.

6. A polymer mixture according to one of Claims 1 to 6, characterised in that the phase agent is formed by starch or thermoplastically processable starch with grafted aliphatic polyester.

7. A polymer mixture according to one of Claims 1 to 7, characterised in that the proportion of starch or thermoplastically processable starch amounts to up to 70 % by weight, in relation to the total weight of the mixture.

8. A polymer mixture according to one of Claims 1 to 8, characterised in that the proportion of starch or thermoplastically processable starch amounts to 30 to 70, preferably 50 to 65 % by weight, in relation to the total weight of the mixture.





9. A polymer mixture according to one of Claims 1 to 8, characterised in that the proportion of phase agent amounts to from 2 to 100 % by weight, in relation to the weight of the hydrophobic polymer, preferably 5 to 50 % by weight.

10. A polymer mixture according to one of Claims 1 to 10, characterised in that as hydrophobic polymer at least one of the following polymers is present in the mixture:

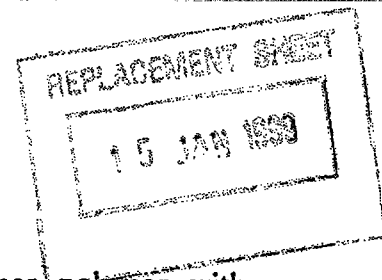
- a cellulose derivative with a degree of substitution ≤ 2 , such as a cellulose ether, a cellulose ester or a cellulose acetate butyrate mixed ester;
- an aliphatic polyester, such as polycaprolactone, polyhydroxy butyric acid/hydroxy valerian acid copolymer and/or polylactic acid;
- a hydrophobic protein, such as zein, and/or
- polyvinyl alcohol, not 100% hydrolised.

11. A polymer mixture according to one of Claims 1 to 10, characterised in that the mixture contains at least thermoplastic starch and also polycaprolacton, polyhydroxy butyric acid and/or polylactic acid.

12. A polymer mixture according to one of Claims 1 to 4 or 8 to 11, characterised in that as phase agent a polycaprolacton/polyvinyl alcohol copolymer is provided.

13. A polymer mixture according to one of Claims 1 to 3 or 5 to 11, characterised in that the mixture contains as phase agent a reaction product of





starch or thermoplastically processable starch and a further polymer with epoxide-, ester- or acid anhydride groups reactive with respect to starch.

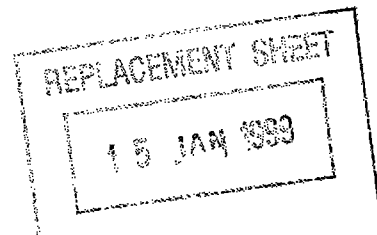
14. A polymer mixture according to Claim 13, characterised in that the further polymer for the formation of the reaction product with reactive groups with respect to starch consists substantially of a polymer according to Claim 11, on which the reactive epoxide-, ester- or acid anhydride groups are grafted by vinyl polymerisation or by condensation.

15. A polymer mixture according to one of Claims 1 to 14, characterised in that the hydrophobic phase or the hydrophobic polymer comprises a softener which is preferably only compatible with the hydrophobic phase and selectively reduces its melting viscosity.

16. A method for the manufacture of a biologically decomposable polymer mixture, substantially consisting of starch and at least of one biologically decomposable hydrophobic polymer, characterised in that starch together with at least one biologically decomposable hydrophobic polymer and a phase agent or macromolecular dispersing agent, excepting epoxided soya oil, or a further polymer soluble in the hydrophobic polymer phase with groups, reactive with respect to starch, is mixed in the melt, in which before or during mixing, the water content is reduced to < 1.0 % by weight, in relation to the weight of the mixture, and in which if necessary the further polymer forms the phase agent through reaction with the starch.

17. A method according to Claim 16, characterised in that native starch or derivatives thereof are decomposed with at least one plasticising- or swelling agent and for the formation of thermoplastically processable starch is brought into melt, in which the water content before or during mixing is reduced to < 1 % by weight, preferably 0.5 % by weight and subsequently up to 70 % by weight





of this thermoplastically processable starch are mixed with the hydrophobic polymer and 2 to 100 % by weight, preferably 5 to 50 % by weight, in relation to the weight of the hydrophobic polymer, of a phase agent and/or a further polymer.

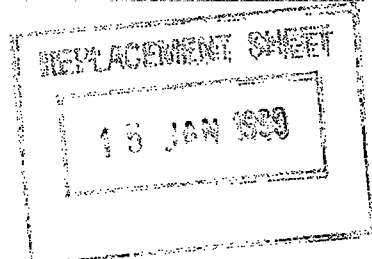
18. A method according to one of Claims 16 or 17, characterised in that the mixing of starch or of thermoplastically processable starch with the hydrophobic polymer and the phase agent or the further polymer takes place in a temperature range of 150 to 230° C and as hydrophobic polymer at least one of the following materials is used:

- a cellulose derivative with degree of substitution ≤ 2 , such as cellulose ether, cellulose ester or a cellulose acetate butyrate mixed ester;
- an aliphatic polyester, such as polycaprolacton, polyhydroxy-butyric acid, a polyhydroxy butyric acid/hydroxy valerian acid copolymer and/or polylactic acid;
- a hydrophobic protein, such as zein, and/or
- polyvinyl alcohol, not hydrolised 100%.

19. A method according to one of Claims 16 to 18, characterised in that the starch or the thermoplastically processable starch is mixed with 5 to 50 % by weight, in relation to the weight of the hydrophobic polymer, of a block copolymer as phase agent, at least consisting of a block soluble in the starch phase and a block soluble in the hydrophobic polymer phase, such as for example polycaprolacton/polyvinyl alcohol copolymer, and the at least one hydrophobic polymer.

20. A method according to one of Claims 16 to 18, characterised in that the



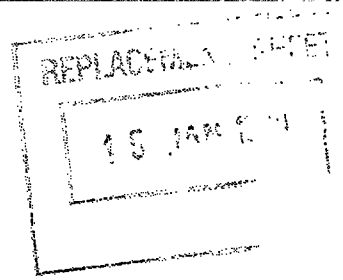


reactive groups are grafted on the hydrophobic polymer by means of vinyl polymerisation or condensation through conversion with a glycidic ether or at least one aliphatic di- or polycarboxylic acid anhydride, such as for example succinic acid anhydride, in order to produce the further polymer, and then the thus produced further polymer and the hydrophobic polymer are mixed intensively in the melt with the starch or the thermoplastically processable starch at a water content of < 0.5 % by weight, preferably < 0.1 %, such as for example in a plastic-processing device or machine, such as kneader or an extruder.

21. A method according to one of Claims 16 to 18, characterised in that as hydrophobic polymer a polymer is used with ester groups incorporated in its molecule chains, which ester groups become reactive at increased temperature after decomposition and bring about both ester interchange of the hydrophobic polymer and also intermediately occurring as further polymer, partially react with a portion of the starch or the thermoplastically processable starch for the formation of the phase agent, in which the hydrophobic polymer, containing the incorporated ester groups, such as for example polycaprolacton, is mixed intensively with the starch at a water content of < 0.5 % by weight, preferably < 0.1 % by weight in the melt, such as for example in a plastic-processing device or machine, such as a kneader or an extruder.

22. A method according to one of Claims 16 to 21, characterised in that native starch or derivatives thereof with a water content of a maximum 6 % by weight, preferably 1 to 4 % by weight, with 25 to 35 % by weight, in relation to the weight of the mixture, of a plasticising- or swelling agent, such as sorbitol or glycerin, is decomposed and then under reduction of the water content to < 0.5 % by weight and brought to a temperature of approximately 170 to 190°C, is mixed for the production of thermoplastically processable starch, after which there are added to the thermoplastically processable starch melt approximately





30 to 45 % by weight of the hydrophobic polymer and 5 to 15 % by weight of the phase agent or 5 to 20 % by weight of the further polymer, in relation to the total weight of the mixture including the starch, and are mixed in melt in a temperature range of approximately 150 to 230 ° C at a humidity content of < 0.5 % by weight, preferably < 0.1 % by weight.

23. A method according to one of Claims 16 to 18 or 20 to 22, characterised in that the hydrophobic polymer and the further polymer are largely identical.

24. A method according to one of Claims 16 to 23, characterised in that the hydrophobic polymer, before mixing with the starch or with the thermoplastically processable starch, is mixed with a softener, in which the softener preferably is only compatible with the hydrophobic phase or is miscible therein, and reduces the melting viscosity of the hydrophobic polymer.

25. A single- or multiple-sheet foil, characterised by at least one layer, consisting of a polymer mixture according to one of Claims 1 to 15.

