

Biodegradable Mould Material

This invention concerns a biodegradable mould material or a polymer blend with enhanced resistance to water, a process for the production of a mould material or a polymer blend and a part of a mould or an extrudate consisting essentially of a mould material or a polymer blend.

At the current state of technology a number of mould materials are known which consist at least in part of starch or gelatine or of biopolymers and are therefore essentially biodegradable.

The increased application of biopolymers such as starch or gelatine in applications of plastics which are in themselves pure is attributable, on the one hand, to the desire to make increased use of renewable raw materials, instead of using a petrochemical or fossil basis for plastics, and, on the other hand, to the demand that plastic products produced from polymers should be biodegradable. For example, SP-A 0 118 240, EP-A 0 092 908, EP A-0 304 401 and EP-A 0 326 517 propose biopolymers or mould materials composed of destructured starch or gelatine and other hydrophilic biopolymers such as proteins, cellulose, etc., which are particularly suitable for injection moulding applications such as the production of capsules. The use of starch or gelatine alone or in the proposed mixtures is limited to only a few applications, as it presents problems because of the strongly hydrophilic properties of starch or gelatine and the tendency of these substances to swell, and also because of the relatively poorer mechanical properties resulting from the use of starch or gelatine or a mixture of the two. By cross-linking the starch polymers it is possible to reduce the swelling tendency, but this generally requires high cross-linkage densities. This calls for large quantities of cross-linking agents which are relatively costly and require special processes to obtain the appropriate cross-linking reactions.

For these reasons EP-A 402 826 proposes filled polymers or polymer blends produced by mixing crystal starch or its derivatives with ethylene copolymers. In WO 90-14388 it is proposed that, for the purpose of producing a polymer compound, natural starch should be mixed with polyethylene and that either ethylene acrylic acid copolymers or glycerine should be added. These polymer mixtures exhibit relatively poor mechanical properties even in the production of injected moulded shaped parts and are unsuitable, for example, for the production of sheets. It appears that the crystalline structure of the starch is retained in these blends, at least in part, and this apparently has a negative effect on their suitability as "engineering plastic". The proportion of ethylene acrylic acid copolymer also accounts for the fact that their biodegradability is very limited.

EP-A 0 327 505, EP-A 0 404 723, EP-A 0 407 350, EP-A 0 404 727 and EP-A 0 404 728 propose a number of polymer blends which, on the one hand, are based on destructured starch and furthermore on a wide variety of destructured starches and, on the other hand, also contain a wide variety of polymers or copolymers. Destructured starch is a modified form of starch obtained from crystal starch, which is processed with a moisture content of approximately 15-20%, i.e. the water content that is normal in crystal starch, using heat and mechanical input. Research, particularly in connection with WO 90-05161, has shown that destructured starch is of only limited use as an engineering plastic", as evidently crystalline structures are still present in this form of starch too. Moreover, the polymers proposed as additions to starch are biodegradable only to a very limited extent or over extremely long periods of time, so that they do not meet the biodegradability requirements.

It is also proposed in EP-A 0 400 531 and EP-A 0 400 532 that the starch should be destructured by means of a high-boiling plasticizing agent and a destructuring agent; the plasticizing agent may be glycerine and the

destructuring agent may be urea. To the starch which has been destructured by this method up to 15% of ethylene acrylic acid and/or polyvinyl alcohol copolymers are added. Use of the plasticizing agent and the destructuring agent does improve the destructuring effect in the crystal starch, but sheets, for example, produced in accordance with the quoted EP-A 0 400 531/2, is not of a quality which is adequate for it to be used as, for example, packing sheet with high mechanical requirements. Here again the proportion of ethylene acrylic acid and polyvinyl copolymers has the effect of substantially limiting biodegradability.

For this reason an attempt was made to take the thermoplastically processable starch proposed in WO 90-05161 as the basis. This starch is mostly free of crystalline structural components. Further details on the production and properties of thermoplastically processable starch will not be discussed here, but reference is made to WO 90-05161, the contents of which are hereby stated to form part of the present description.

Consequently, WO 91-16375 uses, as the starch basis for the production of a polymer blend, the abovementioned thermoplastically processable starch. In accordance with WO 91-16375 the thermoplastically processable starch (TPS) is, for the purpose of producing a blend, mixed with a polyolefin, such as polyethylene or polypropylene. The film produced from this blend exhibits good mechanical properties and good water resistance, but the biodegradability is still negatively affected by the proportion of polyolefin.

One purpose of the present invention is therefore to propose a biodegradable mould material or a polymer blend with enhanced resistance to water. This material would be based, to a large extent, on renewable raw

materials, but nevertheless good mechanical properties when used in so-called plastics applications.

This purpose of the invention is achieved by means of a mould material or a polymer blend as described in Claim 1.

The mould material in accordance with the invention is characterized by the fact that it contains, in addition to the thermoplastically processable starch, which is itself hydrophilic, a cellulose derivative, preferably a cellulose ester, so that both components of the material are derived 100% from biological resources. The biodegradability is therefore essentially assured. However, the addition of the cellulose ester results in mechanical properties which are markedly superior to those of pure thermoplastically processable starch.

The mould material is characterized by the fact that the thermoplastically processable starch is encapsulated in a cellulose ester matrix, with the dispersed phase of the thermoplastically processable starch having a domain size, i.e. the size of the dispersed portions, of 0.5-10 μm (micro metres), but preferably $< 3 \mu\text{m}$.

Preferred compositions of the mould material or polymer blend in accordance with the invention are characterized in subclaims 2 through 8.

It is advantageous to use approximately 20-50% by volume of thermoplastically processable starch and approximately 30-60% by volume of cellulose ester, which may be cellulose acetate, cellulose propionate, cellulose butyrate or cellulose valerate, or a mixture thereof. Cellulose acetate may take the form of mono-, di- or tri-acetate, but, of course, other cellulose esters such as mixed esters can be used, and a mixture of several carbonic acids

may be used to produce them, including for example two or more of the following acids:

acetic acid, propionic acid, butyric acid, valeric acid, etc.

For the purpose of improving the phase mixing, the mould material or polymer blend may include a softener; the softener is added to adjust the viscosities of the two phases during the production of the mould material in such a manner that the proper morphology can be created. For softening a known softener of cellulose esters can be used, for example acetyl triethyl citrate or phthalic acid ester. However, all those substances are suitable for use as softeners which are defined in the abovementioned WO 90-05161 and WO 91-16375 as softeners or additives suitable for the production of thermoplastically processable starch.

As an alternative to adding a softener it is also advantageous to add a phasing agent to the mould material or the polymer blend; the agent makes it possible to improve the adhesion of the two phases through physical interaction and/or chemical reaction with the cellulose ester phase and the thermoplastically processable starch phase. One or more of the phasing agents proposed in the list in Claim 8 will be particularly suitable as phasing agents.

For the purpose of producing the mould materials or the polymer blend to which the invention refers, the invention proposes a process in which the thermoplastically processable starch, which is itself hydrophilic, is processed by the addition of a cellulose derivative, preferably a cellulose ester, to a material with a reduced sorption of water. As was mentioned above, this material can be obtained 100% from biological resources, so that the biodegradability is basically assured. Additional preferred execution variations of the process in accordance with the invention are characterized in subclaims 10 and 11.

The mould materials or polymer blends in accordance with the invention are basically suitable for all known so-called plastic applications, i.e. for the production of injection moulding parts and for the production of extrudates such as sheets and tubes.

The invention will now be explained in detail by means of examples and by reference to the attached diagrams, as follows:

Figure 1 shows a diagramme plotting the tensile stress of a polymer blend in accordance with the invention independence of the volume percentage of thermoplastically processable starch (TPS);

Figure 2 shows the energy at break in dependence of the volume percentage of TPS;

Figure 3 shows the effect of adding a softener or a phasing agent on the elongation at rupture of a polymer blend proposed in accordance with the invention;

Figure 4 shows the effect of a softener or phasing agent on the yield stress;

Figure 5 shows the effect of the softener or phasing agent on the tensile stress;

Figure 6 shows the effect of the softener or phasing agent on the energy at break;

Figures 7a and 7b show, by means of a view through a scanning electron microscope and in a diagramme, the effect of a softener on the

reciprocal ordering of the phases in a mould material in accordance with the invention;

Figures 8a and 8b show, also by means of a view through a scanning electron microscope and in a diagramme, the corresponding effect of a phasing agent on the reciprocal ordering of the phases, and

Figure 9 plots the water sorption of a polymer blend in accordance with the invention in dependence of the volume percentage of thermoplastically processable starch.

Examine 1: Mixtures of thermoplastically processable starch with cellulose acetobutyrate (CAB).

Starting materials: Granular substances composed essentially of water-free thermoplastically processable starch with 30% glycerine and cellulose acetobutyrate (Kodak Tenite Butyrate 525 granular material).

The mixture of the two abovementioned materials was mixed for 10 minutes at 170° C in a Brabender kneader at 100 rpm and then pressed at 160° C to form 0.2 mm slab. The volume percentage of thermoplastically processable starch was 20-70%. Figures 1 and 2 respectively show, the tensile stress and the energy at break in dependence of the volume percentage of thermoplastically processable starch. The shape of the graph in both Figures 1 and 2 shows clearly that the mechanical properties of the mould material become markedly worse when the volume proportion of thermoplastically processable starch reaches 30-40%.

The mould material proposed in this example is suitable for injection moulding, but in no case should more than 40% of thermoplastically processable starch be used.

The mixtures produced from thermoplastically processable starch and cellulose acetobutyrate (CAB) in accordance with example 1 were also tested for moisture sorption, and samples produced from the equivalent blends were stored for 10 days at a relative humidity of 84% at 23° C. The results are shown in Figure 9, whereby the moisture intake appears as a function of the volume proportion of TPS in the sample. In this Figure, the absorption of water means the percentage by weight of the water in the wet sample. Figure 9 shows clearly that the moisture sorption of the blend produced in accordance with example 1 is clearly lower than the value which can be calculated on the assumption that the two components TPS and CAB display additive sorption. From this it is possible to infer an additional property of the blend produced in accordance with example 1, that is to say, the water sorption can be clearly reduced by the production of the blend.

Example 2: Mixture of thermoplastically processable starch with cellulose acetobutyrate and acetyl triethyl citrate as softeners.

Starting materials: Granular substances composed essentially of water-free thermoplastically processable starch with 30% glycerine, cellulose aceto-butyrate (CAB, Kodak Tenite Butyrate 525 granular material) and acetyl triethyl citrate (from Akzo).

Mixtures of the three abovementioned materials were mixed for 10 minutes at 170° C in a Brabender kneader at 100 rpm and then pressed at 160° C to form 0.2 mm slabs. The volume proportion of thermoplastically processable starch was 40%, the volume proportion of cellulose butyrate was 35-55% and the volume proportion of softeners was 5-25%. The mechanical values obtained are shown in Figures 3 through 6. Figure 7 shows a view through a scanning electron microscope of the samples with the best mechanical properties.

A comparison of the two Figures 1 and 5 shows that the addition of a small quantity of softeners, for example 5% by volume, results in an increase of approximately 30% in the tensile stress of the polymer blend. When 10% by volume of softener is added, the value of the tensile stress is identical with the value in Figure 1, i.e. when no softeners are added. The continued increase in the proportion of the volume represented by softeners has a negative effect on the tensile stress. On the other hand, comparison of Figures 2 and 6 gives a somewhat different picture, for in this case a proportion of 5% by volume of softener raises the energy at break of a polymer blend quite substantially in comparison with the value when no softener is used. Even a proportion of 25% by volume of softener still shows a energy at break which is clearly better than in the case where no softener is used.

Polymer blends, produced in accordance with this example, can attain an energy at break of up to 80%, so that these mould materials are suitable both for injection moulding and for sheet and film extrusion. The mixtures in this example therefore exhibit essentially better properties than the mixtures in example 1, at least where elongation at rupture is concerned.

Example 3: Thermoplastically processable starch, cellulose acetobutyrate (CAB) and epoxidized soybean oil as phasing agent.

Starting materials: Granular substances composed of thermoplastically processable starch with 30% glycerine, cellulose aceto-butyrate (Kodak Tenite Butyrate 525 granular material) and epoxidized soybean oil (ED 81 from Henkel Company).

Mixtures of the three named starting materials were mixed by blending for 10 minutes at 170° C in a Brabender kneader at 100 rpm and then

pressed at 160° C to form 0.2 mm slabs. The volume percentage of thermoplastically processable starch was 40%, the volume percentage of CAB was 35-55% and the volume percentage of epoxidized soybean oil was 5-25%. The mechanical data obtained are shown graphically in Figures 3 through 6. Figure 8 shows a view through a scanning electron microscope of the samples with the best mechanical properties.

Figures 3 through 6 make clear that the use of a phasing agent as "softener" makes possible, in part, a marked enhancement of the mechanical properties, as compared with the mixtures in which neither a phasing agent nor a softener, or only a pure softener, is used. In particular, Figure 3 shows clearly that with the mixtures produced in this Example it is possible to attain elongation at rupture of up to 100%.

Because of the good mechanical properties, and particularly because of the excellent elongation at rupture, the mould materials proposed in this Example are suitable not only for injection moulding but also for sheets and for extrusion in general. In contrast to the mixtures in Examples 1 and 2, there are noticeable improvements in the mechanical properties. Moreover, it can be demonstrated by infrared spectroscopy that there is a partial reaction of the epoxide groups with the starch and/or the glycerine.

Furthermore, a comparison of Figures 7a, b and 8a, b shows that the reciprocal distribution of the phases of the thermoplastically processable starch and the cellulose ester is considerably more uniform when the phasing agent is used (Figure 8) than it is when use is made of a pure softener, as shown in Figure 7. This more uniform reciprocal distribution is probably also the reason why the mechanical properties are considerably better when a phasing agent is used than when use is made of a pure softener. Figures 7a and 8a respectively

show views through a scanning electron microscope and Figures 7b and 8b show graphic conversion of the electron microscope views.

Example 4 : thermoplastically processable starch/cellulose aceto-butyrate (cAB) / epoxidized soybean oil as phasing agent and partially acetylated starch as additional phasing agent.

Starting materials: Granular substances composed essentially of water-free thermoplastically processable starch with 30% glycerine, cellulose aceto-butyrate (Kodak Tenite Butyrate 525 granular material), epoxidized soybean oil (ED 81 from the Henkel Company) and partially acetylated starch, produced by the Mehlreter method (Lit), produced in acetane hydride with a degree of substitution (DS) of 0.83, 1.2, 1.94 and 2.0.

Mixtures of the four abovenamed materials were mixed by blending for 10 minutes at 170° C in a Brabender kneader at 100 rpm and then pressed at 160° C to form 0.2 mm slabs. The proportion of thermoplastically processable starch was between 34 and 38%, the volume percentage of the cellulose ester (CAB) was 39-43%, the volume percentage of the epoxidized soybean oil was 15% and the volume percentage of the acetylated starch was 4-12%. The precise compositions can be found in the following Table 1. This Table also shows the relevant mechanical data.

The degree of substitution (DS) listed in the following Table 1 indicates how many hydroxyl groups in the anhydrous glucose unit of the starch are esterified. For example, DS 3 means that all three hydroxyl groups are esterified, that is to say, this is the maximum degree of substitution.

The advantage of on addition of partially acetylated starch is, on the one hand, that the percentage of starch can be increased, so that, on the

other hand, the percentage of cellulose acetate is reduced, and the phase adhesion between the two phases - thermoplastically processable starch and cellulose ester - can be improved; one consequence is that crazing no longer occurs in sheets produced from a polymer blend of this kind. In addition, the increased proportion of starch markedly improves biodegradability, but there is some loss of strength when the proportion of partially acetylated starch is high.

The examples described above, showing a mould material or polymer blend in accordance with the invention, are intended to make the invention more easily understandable and can of course be altered or modified at choice, in any number of ways. For example, any currently known and technically usable cellulose esters can be used as cellulose derivatives, and any substances used as softeners or plasticizing agents either for cellulose esters or for starch are suitable for use as softeners. Moreover, the list of phasing agents can be extended at will, the essential requirement being that the phasing agent makes it possible to improve the adhesion of the two phases.

a)

Degree of Substitution DS = 0.83

CAB Vol%	TPS Vol%	Acet. Starch Vol%	Yield Stress N/mm ²	Rupture %	Tensile Stress N/mm ₂	Rupture Elongatio n %	Rupture Energy J/mm ²
43	38	4	7.3	6.2	10.4	67.0	550000
41	36	8	7.5	6.6	10.6	70.5	590000

Degree of Substitution DS = 1.2

CAB Vol%	TPS Vol%	Acet. Starch Vol%	Yield Stress N/mm ²	Rupture %	Tensile Stress N/mm ₂	Rupture Elongatio n %	Rupture Energy J/mm ²
43	38	4	7.5	5.90	10.3	66	530000
41	36	8	7.9	6.81	9.3	48	460000
39	34	12	7.9	-	8.0	43	300000

Degree of Substitution DS = 1.94

CAB Vol%	TPS Vol%	Acet. Starch Vol%	Yield Stress N/mm ²	Rupture %	Tensile Stress N/mm ₂	Rupture Elongatio n %	Rupture Energy J/mm ²
43	38	4	7.7	7.36	11.6	82.2	720000
41	36	8	7.5	5.22	11.6	80.0	700000
39	34	12	6.5	7.36	9.5	71.0	540000

Degree of Substitution DS = 2.0

CAB Vol%	TPS Vol%	Acet. Starch Vol%	Yield Stress N/mm ²	Rupture %	Tensile Stress N/mm ₂	Rupture Elongatio n %	Rupture Energy J/mm ²
43	38	4	7.5	6.04	9.6	56	450000
41	36	8	7.8	6.07	8.6	41	310000
39	34	12	7.8	7.46	9.8	63	520000



Claims

1. Biodegradable mould material or polymer blend with a high resistance to water, containing at least thermoplastically processable starch and one cellulose derivative.

2. Mould material or polymer blend, preferably in accordance with Claim 1, containing a portion of 10-80 % by volume of thermoplastically processable starch and a remaining portion consisting at least partially of cellulose ester.

3. Mould material or polymer blend, preferably in accordance with one of the Claims 1 or 2, containing a portion of 20-50 % by volume, preferably approximately 40 % by volume of thermoplastically processable starch.

4. Mould material or polymer blend, preferably in accordance with one of the Claims 1 through 3, characterized by the fact that cellulose acetate, cellulose propionate, and/or cellulose butyrate, or a mixture thereof, is used as cellulose ester.

5. Mould material or polymer blend, preferably in accordance with one of the Claims 1 through 4, characterized by the fact that a mixed ester is used as cellulose ester; with an acid mixture containing at least two of the carbonic acids listed below serving as esterifying component in the production of the mixed ester:

- acetic acid
- propionic acid
- butyric acid
- valeric acid



6. Mould material or polymer blend, preferably in accordance with one of the Claims 1 through 5, characterized by the fact that the mixture contains 5-25 % by volume of a softener, such as for example acetyl triethyl citrate or phthalic acid ester.

7. Mould material or polymer blend, preferably in accordance with one of the Claims 1 through 6, characterized by the fact that the mixture contains 5-25 % by volume of a phasing agent, which by physical interaction and/or chemical reaction with the cellulose ester phase and the phase of the thermoplastically processable starch makes it possible to improve the adhesion of both phases.

8. Mould material or polymer, preferably in accordance with Claim 7, characterised by the fact that the phasing agent contains at least one substance from the list of materials given below:

- block copolymers, consisting of at least two blocks A and B, of which at least one can be mixed at least partially with the terephthalic acid and of which at least one can be mixed at least partially with the cellulose ester phase, such as for example partially hydrolyzed polyvinyl acetate or polyvinyl acetate-polyvinyl pyrrolidine block copolymer;
- reactive copolymers, carrying reactive groups and therefore being able to form a covalent bond with the starch and/or the cellulose ester phase, such as for example polyvinyl acetate, which is copolymerized with small quantities of maleic anhydride, or polyvinyl acetate, which is copolymerized with small quantities of acrylic acid glycidic esters;



- low-molecular phasing agents which can be mixed, at least in part, with the cellulose ester phase and/or the terephthalic acid phase and which can also react with one of the two phases, such as for example epoxidized soybean oil; and/or
 - starch derivatives, which are wholly or partially compatible with the corresponding cellulose esters, such as for example starch acetate or starch graft copolymers, in which a polymer compatible with the corresponding cellulose ester is bonded with the starch by a covalent bond, such as for example starch vinyl acetate graft; whereby conversely and in the same manner, the cellulose ester molecule can be reinforced with a polymer that is compatible with the starch, such as for example polyvinyl pyrrolidine.
9. Process for the production of a mould material or a polymer blend in accordance with one of the Claims 1 through 8, characterized by the fact that 10-80 % by volume, preferably 20-50 % by volume of essentially water-free thermoplastically processable starch is mixed at raised temperatures, preferably approximately 160° C to 200° C in the melt, with a cellulose derivative, such as preferably a cellulose ester, .
10. Process, preferably in accordance with Claim 9, characterized by the fact that 20-50 % by volume of thermoplastically processable starch, 30-60 % by volume of a cellulose ester, such as for example cellulose acetate, cellulose propionate and/or cellulose butyrate are closely mixed or kneaded with 5-25% by volume of a softener or a phasing agent at a temperature of approximately 160° C to 200° C and by the fact that the material, which is at least almost homogeneous, is then extruded or processed by injection moulding techniques.



11. Process, preferably in accordance with one of the Claims 10 or 11, characterized by the fact that a softener and/or a phasing agent is admixed, as defined in one of the Claims 7 through 9, to the mixture during the production of the mould material or polymer blend.
12. Mould material or extrudate, consisting essentially of a mould material or a polymer blend in accordance with one of the Claims 1 through 8.