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(54) Title: BIODEGRADABLE POLYMER COMPOSITION

(57) Abstract: The present invention relates to a method of preparing a biodegradable polymer composition, said method compris-
ing melt mixing a first polysaccharide, a first biodegradable polyester and a compatibiliser, wherein said compatibiliser has been
formed separately by reacting a second polysaccharide and a second biodegradable polyester in the presence of a transesterification
catalyst.

WO 2007/012142 A1

BIODEGRADABLE POLYMER COMPOSITION

FIELD OF THE INVENTION

5 The present invention relates generally to biodegradable polymer compositions. In particular, the invention relates to a method of preparing a biodegradable polymer composition, to the use of a compatibiliser in the manufacture of a biodegradable polymer composition, to a compatibiliser and to a method of preparing the compatibiliser.

10 BACKGROUND OF THE INVENTION

The disposal of consumer waste has become a significant problem in many industrialised countries. For example, there are relatively few sites that remain available for landfill in places such as Europe and Japan. A considerable volume of consumer waste is made up of
15 polymeric material, and there has been a concerted effort to introduce polymer recycling strategies to reduce such polymer waste going to landfill. However, unlike other materials such as glass, wood and metal, the recycling of polymers can be problematic. For example, polymer recycling techniques typically require the polymers to be sorted according to their chemical composition. However, due to the diverse array of different
20 commercial polymers it can be difficult to separate polymer materials from the waste stream in this manner. Furthermore, most polymer recycling techniques involve a melt processing stage which can reduce the physical and mechanical properties of the polymer. Recycled polymers therefore tend to have inferior properties and this can limit the range of applications in which they can be employed.

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Apart from problems associated with recycling waste polymer materials, the majority of polymers currently being used are derived from petroleum-based products, making their long-term manufacture unsustainable.

30 In response to these issues, there has been a marked increase in research directed toward developing biodegradable polymers that can at least in part be manufactured using renewable resources. Unlike conventional polymers, biodegradable polymers can be more readily degraded through the action of microorganisms to produce low molecular weight

products that present little, if any, environmental concern. Furthermore, through the action of biodegradation the volume occupied by such polymers in waste streams is significantly reduced.

- 5 Much of the research to-date in the field of biodegradable polymers has focussed on utilising naturally occurring bio-polymers such as polysaccharides. Perhaps the most widely studied polysaccharide in this regard is starch. Starch is a particularly suitable bio-polymer in that it is derived from renewable resources (i.e. plant products), readily available and relatively inexpensive. However, the physical and mechanical properties of
- 10 starch in its native form are relatively poor compared with those of conventional petroleum based (i.e. "synthetic") polymers.

A number of techniques have been developed to improve the physical and mechanical properties of native starch. One approach has involved converting native starch into a

15 thermoplastically processible starch (TPS). For example, PCT/WO90/05161 discloses a process for producing TPS which comprises melt mixing starch having a low water content with a plasticiser such as glycerol. Although the physical and mechanical properties of such TPS polymers are substantially better than native starch, these polymers typically have poor water resistance and can therefore only be used in limited applications.

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The water resistance of TPS polymers can be improved by blending these polymers with other thermoplastic polymers such as polyolefins, polyalcohols and ethylene-acrylic acid co-polymers. However, the biodegradability of these TPS polymer blends can be adversely affected due to the fact that polymers that are usually blended with the TPS are

25 relatively non-biodegradable. Furthermore, the physical and mechanical properties of such TPS polymer blends are often quite poor due to the immiscibility of the TPS with most other thermoplastic polymers employed in making the blends. In particular, polysaccharides such as starch and TPS are relatively hydrophilic, whereas most synthetic thermoplastic polymers are relatively hydrophobic. Accordingly, melt blending of starch

30 or TPS with other thermoplastic polymers typically results in the formation of a multi-phase morphology having a high interfacial tension which can negatively impact on the physical and mechanical properties of the resulting polymer blend.

Attempts have been made to improve the biodegradability and the physical and mechanical properties of TPS polymer blends. For example, US 5,844,023 discloses a biologically degradable polymer mixture comprising a biodegradable polyester, a TPS and a "polymer phase mediator". The polymer mixture is said to be readily biodegradable and the polymer phase mediator is said to promote coupling of hydrophobic polyester phase and hydrophilic TPS phase thereby improving the physical and mechanical properties of the polymer mixture. A biodegradable polymer composition disclosed in the US reference is formed through melt mixing a thermoplastic polyester with TPS. In this case, the polymer phase mediator is said to be formed *in situ* during this melt mixing process through transesterification between some of the polyester and some of the TPS. Formation of the phase mediator in this way is considered difficult to control, and the overall process is believed to provide a limited reduction in the interfacial tension between the immiscible polymer phases.

Despite representing an advance in the field of biodegradable polymers, the physical and mechanical properties of such polyester/TPS blends are still relatively poor compared with conventional petroleum based polymers due to only a marginal improvement in phase coupling of the immiscible phases. To compensate for this, such polyester/TPS blends are typically prepared with quite low levels of starch. However, lowering the starch content of the composition increases its cost and can reduce its biodegradability.

Accordingly, there remains a need to develop alternative biodegradable polymer compositions having good physical and mechanical properties.

SUMMARY OF THE INVENTION

The present invention provides a method of preparing a biodegradable polymer composition, said method comprising melt mixing a first polysaccharide, a first biodegradable polyester and a compatibiliser, wherein said compatibiliser has been formed separately by reacting a second polysaccharide and a second biodegradable polyester in the presence of a transesterification catalyst.

It has now been found that a polymer composition having excellent biodegradability and

physical and mechanical properties can be prepared using a compatibiliser that has been formed separately through the reaction of a polysaccharide and a biodegradable polyester in the presence of a transesterification catalyst.

- 5 Accordingly, the invention also provides the use of the compatibiliser in the manufacture of a biodegradable polymer composition, said compatibiliser being melt mixed with a polysaccharide and a biodegradable polyester.

Without wishing to be limited by theory, the compatibiliser used in accordance with the
10 invention is believed to reduce the formation within the biodegradable polymer composition of multi-phase morphology having high interfacial energy. In particular, it is believed that forming the compatibiliser separately enables its production to be controlled and optimised to provide a highly efficient compatibiliser. Furthermore, by forming the compatibiliser separately it can be accurately introduced during the manufacture of the
15 biodegradable polymer composition to optimise compatibilisation between the first polysaccharide and the first biodegradable polyester. These features of the invention are believed to improve the physical and mechanical properties of the biodegradable polymer composition.

- 20 This is believed to be in contrast with a biodegradable polymer composition that is prepared by melt mixing a polysaccharide and a biodegradable polyester to form compatibiliser *in situ* (e.g. as in US 5,844,023). Using this methodology, it is believed only a relatively low degree of transesterification between the polysaccharide and polyester occurs, and therefore only a relatively small amount of useful compatibiliser is actually
25 formed. Accordingly, the efficiency of compatibiliser formed in this way to couple the immiscible polysaccharide and polyester phases is believed to be minimal at best.

Further aspects of the invention are described below.

30 DETAILED DESCRIPTION OF THE INVENTION

Those skilled in the art will appreciate that the term "biodegradable" does not have a universal definition. For avoidance of any doubt, the term "biodegradable" used herein in

association with the term "polymer", "polymer composition" or specific polymer materials such as a "polysaccharide" and "polyester", is intended to denote a material that meets the biodegradability criteria specified in EN 13432 or ASTM 6400. In other words, a polymer is considered to be biodegradable if, upon exposure to a composting environment, 90% of
5 it disintegrates into particles having an average size of less than 2mm within twelve weeks, and after six months at least 60wt.% of it, in the case of ASTM 6400, or at least 90% of it, in the case of EN 13432, has degraded into carbon dioxide and/or water. Preferably, biodegradable polymer compositions in accordance with the invention will meet the more stringent biodegradability criteria set forth in EN 13432.

10

The method of preparing the biodegradable polymer composition in accordance with the invention comprises melt mixing a first polysaccharide and a first biodegradable polyester in the presence of a compatibiliser. Melt mixing may be performed using techniques and equipment well known in the art. Preferably, melt mixing is achieved using continuous
15 extrusion equipment, such as twin screw extruders, single screw extruders, other multiple screw extruders or Farel continuous mixers. Melt mixing is conducted for sufficient time and at a suitable temperature to promote intimate mixing between the first polysaccharide, the first biodegradable polyester and the compatibiliser. Those skilled in the art will appreciate that melt mixing is generally performed within a suitable temperature range and
20 that this range will vary depending upon the nature of the polymer(s) being processed.

An advantage of preparing a biodegradable polymer composition in accordance with the invention is that melt mixing may be performed at a minimum melt processing temperature. This is in contrast with methods where compatibiliser is formed *in situ* by
25 melt mixing a polysaccharide (or TPS) *per se* with a biodegradable polyester to prepare a biodegradable polymer composition (e.g. as in US 5,844,023). Using this type of methodology, it will typically be necessary to employ temperatures above the minimum melt processing temperature to promote at least some transesterification between the polysaccharide (or TPS) and polyester and form the compatibiliser. A notable
30 disadvantage of performing the melt mixing process at a temperature above the minimum melt processing temperature is that the bulk polyester and polysaccharide (or TPS) can thermally degrade. This can have the effect of reducing the physical and mechanical properties of the resulting polymer composition.

Given that there is no need to form compatibiliser *in situ* during melt mixing of the first polyester and first polysaccharide in accordance with the invention, high melt processing temperatures can advantageously be avoided.

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As used herein, the expression "minimum melt processing temperature" of a polymer or polymer composition is considered to be the lowest temperature or temperature range at which that polymer or composition can be maintained to enable it to be effectively melt processed while minimising or avoiding degradation of the polymer or composition. The
10 minimum melt processing temperature will of course vary depending upon the materials being processed, and this can be readily determined by a person skilled in the art.

In some cases it may be desirable to vent or apply vacuum to the melt mixing process to allow volatile components such as water to be removed from the polymer melt.

15

The first polysaccharide used in accordance with the invention may be any polysaccharide that can be subjected to melt mixing. The polysaccharide preferably has a water content below about 1wt.%, more preferably below about 0.5wt.%. Suitable polysaccharides include, but are not limited to, starch, glycogen, chitosan and cellulose.

20

A preferred polysaccharide for use in accordance with the invention is starch. Starch is a particularly convenient polysaccharide in that it is relatively inexpensive, derived from a renewable resource and is readily available. Starch is found chiefly in seeds, fruits, tubers, roots and stem pith of plants, and is basically a polymer made up of repeating glucose
25 groups linked by glucosidic linkages in the 1-4 carbon positions. Starch consists of two types of alpha-D-glucose polymers: amylose, a substantially linear polymer with molecular weight of about 1×10^5 ; and amylopectin, a highly branched polymer with very high molecular weight of the order 1×10^7 . Each repeating glucose unit typically has three free hydroxyl groups, thereby providing the polymer with hydrophilic properties and reactive
30 functional groups. Most starches contain 20 to 30% amylose and 70 to 80% amylopectin. However, depending on the origin of the starch the ratio of amylose to amylopectin can vary significantly. For example, some corn hybrids provide starch with 100% amylopectin (waxy corn starch), or progressively higher amylose content ranging from 50 to 95%.

Starch usually has a water content of about 15wt.%. However, the starch can be dried to reduce its water content to below 1%.

Starch typically exists in small granules having a crystallinity ranging from about 15 to 5 45%. The size of the granules may vary depending upon the origin of the starch. For example, corn starch typically has a particle size diameter ranging from about 5 to 40µm, whereas potato starch typically has a particle size diameter ranging from about 50 to 100µm. In this "native" form, starch can be difficult to melt process. To improve the melt processability of starch, the starch may be destructured or converted to a TPS by means 10 well known in the art. Thus, TPS may be used as the first polysaccharide in accordance with the invention. For example, native starch may be melt processed with one or more plasticisers such as water, glycerine, di – or ethyleneglycol, trimethylene glycol, sorbitol or other low molecular weight polyether compounds.

15 Water is an excellent plasticiser for the manufacture of TPS. However, due to its relatively low boiling point, the presence of water above about 1wt.% in TPS can cause an undesirable degree of volatilisation of water during melt mixing. Furthermore, the presence of too much water during the preparation of the compatibiliser or biodegradable polymer composition can cause an undesirable degree of hydrolysis of the polyester.

20 Preferred plasticisers for the manufacture of TPS include glycerol and sorbitol. These, and other suitable plasticisers are typically used in an amount ranging from about 5wt.% to about 50wt.%, preferably in an amount ranging from about 10wt.% to about 40wt.%, more preferably in an amount ranging from about 15wt.% to about 30wt.%, relative to the total 25 mass of native starch.

Chemically modified starch may also be used as the first polysaccharide in accordance with the invention. Chemically modified starch includes, but is not limited to, oxidised starch, etherificated starch, esterified starch, cross-linked starch or a combination of such 30 chemical modifications (e.g., etherificated and esterified starch). Typically, modified starch is prepared by reacting the hydroxyl groups of the polymer with one or more reagents. The degree of reaction, often referred to the degree of substitution (DS), can significantly alter the physicochemical properties of the modified starch compared with the

corresponding native starch. The DS for a native starch is designated as 0, and can range up to 3 for a fully substituted modified starch. Where the substituent groups have hydrophobic character, a DS approaching 3 can afford a modified starch that is relatively hydrophobic in character. Such modified starches can be more readily melt blended with
5 the first biodegradable polyester, relative to native starch.

A chemically modified starch may also be converted to TPS by melt mixing it with plasticiser as hereinbefore described. In this case, the aforementioned amounts of plasticiser used will be relative to the total mass of the chemically modified starch.

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Starches that are chemically modified are preferably etherificated or esterified. Suitable etherificated starches include, but are not limited to, those which are substituted with ethyl and/or propyl groups. Suitable esterified starches include, but are not limited to, those that are substituted with acetyl, propanoyl and/or butanoyl groups.

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Etherificated starches may be prepared using techniques well known in the art, such as reacting starch with an appropriate alkylene oxide. Esterified starches may also be prepared using techniques well known in the art, such as reacting starch with appropriate anhydride, carboxylic acid or acid chloride reagents.

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When starch is used as the first polysaccharide, it may be in its native form, in the form of a TPS, a chemically modified starch, or a combination such starches may be used. In all cases, it is preferable that the water content of the starch is less than about 1wt.%, preferably less than about 0.5wt.%.

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It will of course also be possible to form a TPS during the melt mixing process used to prepare the biodegradable polymer composition. For example, the method of producing the biodegradable polymer composition may comprise melt mixing native and/or chemically modified starch, plasticiser, biodegradable polyester and the compatibiliser. In
30 this case, the amount of plasticiser employed is as hereinbefore described, relative to the total mass of starch.

Preferred types of starch materials include, but are not limited to, corn starch, potato

starch, wheat starch, soybean starch, tapioca starch, high-amylose starch or combinations thereof.

When preparing the biodegradable polymer composition, it has been found that relatively
5 high levels of the first polysaccharide can be melt mixed with the first biodegradable polyester while still maintaining excellent physical and mechanical properties of the resulting polymer composition. This effect is believed to stem from the compatibiliser being formed separately and in advance of preparing the biodegradable polymer composition, which in turn provides for a more effective compatibiliser and enables the
10 compatibiliser to be used in an amount which optimises compatibilisation between the first polysaccharide and the first biodegradable polyester.

The first biodegradable polyester used in accordance with the invention may be any biodegradable polyester that can be subjected to melt mixing. Examples of suitable
15 biodegradable polyesters include, but are not limited to, polycaprolactone (PCL) as sold by Union Carbide under the trade name ToneTM (i.e. Tone P-300, P-700, P-767 and P-787 having a weight average molecular weight of about 10,000, 40,000, 43,000 and 80,000, respectively), or those sold by Solvay under the trade name CAPA 6800 and CAPA FB100 having a molecular weight of 80,000 and 100,000 Daltons, respectively; polylactic acid
20 (PLA) as sold under the trade name NatureworksTM PLA by Cargill; polyhydroxy butyrate (PHB) as sold under the trade name BiocycleTM or BiomerTM by Biomer, Germany; polyethylene succinate (PES) and polybutylene succinate (PBS) as sold under the trade name BionolleTM by Showa Hi Polymer Company (i.e. BionolleTM 1001 (PBS) and BionelleTM 6000 (PES)); and polybutylene adipate (PBA) as sold under the trade name
25 SkygreenTM SG100 from SK Chemicals Korea; poly(butylene adipate/terephthalate) (PBAT) aliphatic/aromatic copolyesters such as EcoflexTM by BASF, or EnPOLTM G8060 and EnPOLTM 8000 by Ire Chemical Ltd of Seoul; poly(hydroxybutyrate valerate) (PHBV) by Metabolix Inc. USA; cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) supplied by Eastman Chemicals; or combinations thereof.

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As previously mentioned, the hydrophilic nature of the first polysaccharide and the hydrophobic nature of the first biodegradable polyester renders these polymers substantially immiscible in the molten state. Such immiscibility can inhibit intimate

- mixing of the polymers and reduce the physical and mechanical properties of the resultant polymer blend. The addition of a suitable compatibiliser to such an immiscible polymer blend can modify the interfacial character of the multiphase system and stabilise its morphology. This in turn facilitates intimate mixing of the polymers and improves the physical and mechanical properties of the resultant polymer blend. To impart such an effect, the compatibiliser will typically have a molecular structure which comprises a section(s) or region(s) that is miscible with the first polysaccharide and a section(s) or region(s) that is miscible with the first biodegradable polyester (i.e. comprise both hydrophilic and hydrophobic sections or regions). Accordingly, the compatibiliser can be seen to comprise molecules having an ability to bridge the hydrophilic and hydrophobic phases of the immiscible blend and thereby facilitate coupling of the phases. In other words, the compatibiliser may be seen to function as an emulsifier to decrease the interfacial tension between and promote the coupling of the immiscible phases.
- 15 In the method of preparing the biodegradable polymer composition, the compatibiliser is formed separately. By being "formed separately" is meant that the compatibiliser is prepared in advance and is subsequently melt mixed with the first biodegradable polyester and the first polysaccharide. The compatibiliser can therefore be prepared and conveniently stored for future use. Alternatively, the compatibiliser may be prepared and then immediately combined with the first biodegradable polyester and the first polysaccharide in the melt mixing process to form the polymer composition.

Formation of the biodegradable polymer composition is therefore not reliant on compatibiliser being formed *in situ* during melt mixing of the first biodegradable polyester with the first polysaccharide. Having said this, it will of course be possible for compatibiliser to be formed *in situ* during the melt mixing process. However, as indicated, it is believed that only a relatively small amount of compatibiliser is likely to be formed *in situ*.

- 30 When preparing the biodegradable polymer composition in accordance with the invention, the first polysaccharide will generally be used in an amount ranging from about 5wt.% to about 90wt.%, preferably in an amount ranging from about 20wt.% to about 70wt.%, more preferably in an amount ranging from about 30wt.% to about 60wt.%, the first

biodegradable polyester will generally be used in an amount ranging from about 5wt.% to about 90wt.%, preferably in an amount ranging from about 20wt.% to about 80wt.%, more preferably in an amount ranging from about 30wt.% to about 60wt.%, and the compatibiliser will generally be used in an amount ranging from about 5wt.% to about 60wt.%, preferably in an amount ranging from about 5wt.% to about 50wt.%, more preferably in an amount ranging from about 8wt.% to about 20wt.%, relative to the total mass of the first biodegradable polyester, the first polysaccharide and the compatibiliser, and such that the total mass of these three components represents at least 65wt.%, preferably at least 70wt.%, more preferably at least 75wt.%, most preferably at least 80wt.% of the total mass of the biodegradable polymer composition. Where the total mass of the biodegradable polymer composition is not made up entirely of the first biodegradable polyester, the first polysaccharide and the compatibiliser, the remainder of the composition will include one or more additives such as plasticiser hereinbefore described and other additives described in more detail below.

15

The compatibiliser used in accordance with the invention is prepared by reacting a second polysaccharide and a second biodegradable polyester in the presence of a transesterification catalyst. The second polysaccharide and the second biodegradable polyester may be selected independently as described above in respect of the first polysaccharide and first biodegradable polyester, respectively. The second polysaccharide and second biodegradable polyester may each be the same as or different from the first polysaccharide and first biodegradable polyester, respectively. Unless otherwise stated, for convenience, the first and second polysaccharides and the first and second biodegradable polyesters will hereinafter simply be referred to as the "polysaccharide" and the "biodegradable polyester", respectively.

25

When preparing the compatibiliser, the reaction between the polysaccharide and the biodegradable polyester is believed to proceed by a transesterification mechanism. The reaction is preferably conducted using a melt mixing process. Melt mixing may be performed using equipment and techniques hereinbefore described. The transesterification reaction is preferably conducted at temperatures ranging from about 180°C to about 250°C, preferably from about 200°C to about 220°C. When the reaction performed by a melt mixing process and conducted using a continuous screw extruder, the rotational speed

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of the screw will generally range from about 50 to about 200 rpm and the residence time of the reaction mixture will range from about 5 to about 20 minutes.

A transesterification catalyst is used in accordance with the invention and is believed to promote the reaction between the polysaccharide and the biodegradable polyester. Suitable transesterification catalysts include, but are not limited to, alkali metal hydroxides such as sodium and/or potassium hydroxide. The type of catalysts employed preferably have low ecotoxicity. Atimony based catalysts will therefore not generally be used.

- 10 Where the polysaccharide used to form the compatibiliser is native starch, transesterification between the starch and the biodegradable polyester can be further enhanced by introducing during the reaction plasticiser such as glycerine and/or sorbitol. In this case, plasticiser will generally be used in amounts hereinbefore described. Preferably, this will result in an amount of plasticiser ranging from about 10wt.% to about 15 20wt.%, relative to the total mass of the compatibiliser.

- Transesterification between the starch and the biodegradable polyester can also be further enhanced through using chemically modified starch. In this case, it is preferable to use esterified starch as hereinbefore described having a DS ranging from about 0.1 to about 1, 20 more preferably ranging from about 0.5 to about 1. It may also be preferable to introduce with the modified starch during melt mixing a plasticiser as hereinbefore described.

- As part of the method of forming the compatibiliser, it may also be desirable to use a relatively low weight average molecular weight biodegradable polyester (i.e., ranging from 25 about 30,000 to about 40,000) in order to further enhance transesterification with the polysaccharide. In this case, it is preferred that the first biodegradable polyester has a weight average molecular weight ranging from about 80,000 to about 100,000.

- When preparing the compatibiliser, it is particularly preferred that the polysaccharide is an 30 esterified starch having a degree of substitution ranging from about 0.1 to about 1, the biodegradable polyester has a molecular weight ranging from about 30,000 to about 40,000, and if used, the plasticiser is glycerol and/or sorbitol.

The polysaccharide used in forming the compatibiliser preferably has a water content below about 1wt.%, more preferably below about 0.5wt.%.

When preparing the biodegradable polymer composition in accordance with the invention,
5 there is no particular limitation on the amount of polysaccharide and biodegradable polyester that may be used to prepare the compatibiliser. However, in the case where only a relatively low proportion of polysaccharide is used in preparing the biodegradable polymer composition, the compatibiliser will generally be prepared using a relatively high proportion of polysaccharide in order to maximise the total amount of polysaccharide that
10 is ultimately included in the biodegradable polymer composition.

Thus, when preparing the biodegradable polymer composition in accordance with the invention, the compatibiliser used will generally be prepared by reacting, preferably by melt mixing, about 20wt.% to about 75wt.%, preferably about 30wt.% to about 65wt.%,
15 more preferably about 30wt.% to about 60wt.% of the polysaccharide, and about 20wt.% to about 75wt.%, preferably about 30wt.% to about 65wt.%, more preferably about 30wt.% to about 60wt.% of the biodegradable polyester in the presence of about 0.1wt.% to about 1wt.%, preferably about 0.1wt.% to about 0.5wt.%, more preferably about 0.15wt.% to about 0.5wt.% of the transesterification catalyst, relative to the total mass of the
20 polysaccharide, the biodegradable polyester and the transesterification catalyst, and such that the total mass of these three components represents at least 65wt.%, preferably at least 70wt.%, more preferably at least 75wt.%, most preferably at least 80wt.%, of the total mass of the compatibiliser. Where the total mass of the compatibiliser is not made up entirely of the biodegradable polyester, the polysaccharide and the transesterification
25 catalyst, the remainder of the compatibiliser will include one or more additives such as plasticiser hereinbefore described and other additives described in more detail below.

The transesterification catalyst will generally be used in an amount ranging from about 0.1wt.% to about 1wt.%, preferably in an amount ranging from about 0.2wt.% to about
30 0.5wt.%, relative to the total mass of the compatibiliser. The catalyst may be used in the form of a solution, for example in the form of an aqueous solution.

By preparing the compatibiliser separately as herein described, it is believed that a more

effective compatibiliser can be produced compared with that which may be formed *in situ* during conventional methods of forming biodegradable polymer compositions. In particular, by dedicating the reaction process to forming the compatibiliser, the conditions of, and the reagents used in, the reaction can be tailored to forming the compatibiliser without concern for any other processing issues (eg. thermal degradation of at least the polyester). Furthermore, by isolating the compatibiliser rather than forming it *in situ*, it can be introduced into the melt mixing process for preparing the polymer composition at levels that optimise compatibilisation of the polysaccharide and the biodegradable polyester.

It will be appreciated that the efficiency of a given compatibiliser will vary depending upon the nature of the polysaccharide and biodegradable polyester used to form it, the form of the compatibiliser on a molecular level (e.g. the degree of transesterification that has taken place between the biodegradable polyester and the polysaccharide), and also upon the nature of the polysaccharide and biodegradable polyester used in preparing the polymer composition. In preparing biodegradable polymer compositions in accordance with the invention, it is preferred that the type and amount of compatibiliser used provides for optimum compatibilisation between the polysaccharide and the biodegradable polyester. Such optimum compatibilisation can be readily determined experimentally by imaging the polymer composition and/or by measuring the physical and mechanical properties of the polymer composition. For example, the composition may be cryogenically frozen, fractured then view under a scanning electron microscope to evaluate the level of adhesion between the dispersed phase and the continuous phase.

Those skilled in the art will appreciate that by forming the compatibiliser separately in the manner herein described, the composition of the compatibiliser is likely to be different from that which may be formed *in situ* during preparation of the biodegradable polymer. Without wishing to be limited by theory, it is believed that the compatibiliser prepared in accordance with the invention comprises polysaccharide having a relatively high DS with biodegradable polyester (i.e. the polysaccharide and biodegradable polyester have undergone a relatively high degree of transesterification). Accordingly, the compatibiliser may be described as comprising a polysaccharide, a biodegradable polyester and/or the reaction product derived from the polysaccharide undergoing transesterification with the

biodegradable polyester.

The invention also provides a compatibiliser suitable for use in preparing a biodegradable polymer composition, said compatibiliser comprising the reaction product, preferably
5 derived through the melt mixing, of 20wt.% to less than 45wt.%, preferably 20wt.% to 40wt.% of polysaccharide, 20wt.% to 75wt.%, preferably 30wt.% to 65wt.%, more preferably 30wt.% to 60wt.% of biodegradable polyester, and 0.1wt.% to 1wt.%, preferably 0.1wt.% to 0.5wt.%, more preferably 0.15wt.% to 0.5wt.% of transesterification catalyst, relative to the total mass of the polysaccharide, the biodegradable polyester and
10 the transesterification catalyst, and such that the total mass of the reaction product from these three components represents at least 60wt.%, preferably at least 65wt.%, more preferably at least 70wt.%, most preferably at least 75wt.% of the total mass of the compatibiliser. Where the total mass of the compatibiliser is not made up entirely of the polysaccharide, the biodegradable polyester and the catalyst, the remainder of the
15 compatibiliser will include one or more additives such as plasticiser hereinbefore described and other additives described in more detail below.

The invention also provides a method of preparing a compatibiliser suitable for use in the manufacture of a biodegradable polymer composition, said method comprising reacting,
20 preferably by melt mixing, 20wt.% to less than 45wt.% , preferably 20wt.% to 40wt.% of polysaccharide, 20wt.% to 75wt.%, preferably 30wt.% to 65wt.%, more preferably 30wt.% to 60wt.% of biodegradable polyester, and 0.1wt.% to 1wt.%, preferably 0.1wt.% to 0.5wt.%, more preferably 0.15wt.% to 0.5wt.% of transesterification catalyst, relative to the total mass of the polysaccharide, the biodegradable polyester and the transesterification
25 catalyst, and such that the total mass of the reaction product from these three components represents at least 60wt.%, preferably at least 65wt.%, more preferably at least 70wt.%, most preferably at least 75wt.% of the total mass of the compatibiliser. Where the total mass of the compatibiliser is not made up entirely of the polysaccharide, the biodegradable polyester and the catalyst, the remainder of the compatibiliser will include one or more
30 additives such as plasticiser hereinbefore described and other additives described in more detail below.

The compatibiliser may be provided in any suitable form that can be subsequently melt

mixed with the biodegradable polyester and the polysaccharide to form the biodegradable polymer composition in accordance with the invention. Generally the compatibiliser will be provided in the form of pellets.

- 5 The biodegradable polymer composition, compatibiliser and methods for the preparation thereof in accordance with the invention may comprise or comprise a step of introducing, respectively, one or more additives provided that such additives do not adversely impact on the biodegradability of the polymer composition. Such additives may include fillers such as calcium carbonate, silicone dioxide, talc, clays such as montmorillonite, titanium
- 10 dioxide and natural fibres such as wood powder, paper pulp and/or other cellulosic materials; pigments; anti-static agents; stabilisers; blowing agents; processing aids such as lubricants; fluidity enhancers; anti-retrogradation additives; plasticisers as hereinbefore described, and antiblocking agents such as silicon dioxide.
- 15 Common lubricants include, but are not limited to, calcium stearate, steric acid, magnesium stearate, sodium stearate, oxidised polyethylene, oleamide, stearamide and erucamide. A lubricant will generally be used in an amount to provide for an amount ranging from about 0.2wt.% to 0.7wt.% in the biodegradable polymer composition.
- 20 Common fluidity enhancers include, but are not limited to, monoglycerides, glucose fat diethylene glycol dinitrate and products sold under the trade name Siben-60 or Siben-80. A fluidity enhancer will generally be used in an amount to provide for an amount ranging from about 1wt.% to about 2wt.% in the biodegradable polymer composition.
- 25 A common anti-retrogradation additive includes, but is not limited to, a distilled monoglyceride. Anti-retrogradation additives will generally be used in an amount to provide for an amount ranging from about 0.5wt.% to about 1wt.% in the biodegradable polymer composition. An additive such as distilled monoglyceride is also believed to assist with the dispersability and stabilisation of the polysaccharide.
- 30 An antiblocking agent such as silicon dioxide may be used in an amount to provide for an amount ranging from about 0.25wt.% to 0.5wt.% in the biodegradable polymer composition.

To minimise an undesirable degree of hydrolysis occurring during melt mixing, the first biodegradable polyester, the first polysaccharide, the compatibiliser and any other additives used in preparing the polymer composition will preferably each have a water
5 content of less than about 2wt.%, more preferably of less than about 1wt.%, most preferably of less than about 0.6wt.%.

In a preferred embodiment of the invention, the method of preparing the biodegradable polymer composition comprises melt mixing about 5wt.% to about 85wt.% of a first
10 polysaccharide, about 5wt.% to about 85wt.% of a first biodegradable polyester in the presence of about 5wt.% to about 60wt.% of a compatibiliser and about 10wt.% to about 20wt.% of plasticiser, relative to the total mass of the first polysaccharide, the first biodegradable polyester, the compatibiliser and the plasticiser, and such that the total mass
15 of these four components represents at least 95wt.% of the total mass of the biodegradable polymer composition, wherein said compatibiliser has been formed separately by reacting, preferably by melt mixing, about 20wt.% to about 75wt.% of a second polysaccharide, about 20wt.% to about 75wt.% of a second biodegradable polyester in the presence of about 0.1wt.% to about 1wt.% of a transesterification catalyst and about 5wt.% to about 50wt.% of plasticiser, relative to the total mass of the second polysaccharide, the second
20 biodegradable polyester, the transesterification catalyst and the plasticiser, and such that the total mass of these four components represents at least 95wt.% of the total of the compatibiliser. Where composition or compatibiliser is not made up entirely of the relevant components referred to above, the remainder of the composition or compatibiliser will include one or more additives hereinbefore described.

25

The biodegradable polymer composition prepared in accordance with the invention has excellent physical and mechanical properties and is readily biodegradable. The composition can be conveniently processed using conventional polymer converting techniques such as extrusion, injection moulding, and thermoforming. The composition is
30 particularly suited for manufacturing film and sheet that may be converted into packaging materials. In this case, PCL, PBAT, PHBV, PES and PBS are preferably used as the biodegradable polyester. The composition may also be used in the manufacture of food utensils such as cups, plates, cutlery and trays. In this case, the biodegradable polyester

used in preferably PLA and CAB.

The invention also provides a sheet or film formed from the biodegradable polymer composition prepared in accordance with the invention.

5

The biodegradable polymer composition may be provided in any suitable form that can be processed into a desired product such as sheet or film. Generally, the composition will be provided in the form of pellets.

- 10 Embodiments of the invention are further described with reference to the following non-limiting examples.

EXAMPLE 1: *Preparation of Compatibiliser from Starch and PCL (ST-PCL)*

- 15 50kg of acetate butyrate starch (Degree of Substitution at 0.5) having a water content of less than 1%, 10kg of sorbitol, 10kg of glycerine, 0.2kg sodium hydroxide and 50kg PCL (Tone P-700) were melt mixed in a ZSK-58 Twin Screw Extruder (L/D=48). The temperature profile of the extruder was set at 60°C/ 180°C/ 220°C/ 220°C/ 180°C/ 160°C. The rotation speed of the screw was set at 100rpm. After the reactive extrusion process,
20 the melt was extruded as a strand, air cooled and cut into pellets. The resulting compatibiliser was referred to as ST-PCL.

EXAMPLE 2: *Preparation of Compatibiliser from Starch and PBS (ST-PBS)*

- 25 50kg of acetate butyrate esterificated starch (Degree of Substitution at 0.5) having a water content of less than 1%, 10kg of sorbitol, 10kg of glycerine, 0.2kg sodium hydroxide and 50kg PBS were melt mixed in a ZSK-58 Twin Screw Extruder. The temperature profile of the extruder was set at 90°C/ 180°C/ 220°C/ 220°C/ 200°C/ 170°C. The rotation speed of the screw was set at 100rpm. After the reactive extrusion process, the melt was extruded
30 as a strand, air cooled and cut into pellets. The resulting compatibiliser was referred to as ST-PBS.

COMPARATIVE EXAMPLE 1 AND EXAMPLES 3 AND 4: *Preparation of a Biodegradable Polymer*

The polymer was prepared using a ZSK-58 Twin Screw Extruder (L/D=48). The polymer produced was injected into strips for ASTM D638 mechanical strength testing. A film blower with a diameter of 60mm was also used to blow film for mechanical performance testing. The film blower extruder had a L/D=30. The temperature profile of the extruder was set at 90°C/ 110°C/ 130°C/ 150°C/ 130°C. Vacuum was applied to remove water. The extrudate was water cooled and pelletised to form the biodegradable polymer in accordance with the invention. Composition details and test results are shown below in Table 1.

Table 1: Composition details and test results for Comparative Example 1 and Examples 3 and 4

<i>Ingredient</i>	<i>Comparative Example 1</i>	<i>Example 3</i>	<i>Example 4</i>
Corn starch	40kg	36kg	32kg
Sorbitol	10kg	9kg	8kg
Glycerine	10kg	9kg	8kg
PCL (P-787)	40kg	36kg	32kg
ST-PCL	---	10kg	20kg
Glucose stearate	1.0kg	1.0kg	1.0kg
Stearamide	0.5kg	0.5kg	0.5kg
Calcium stearate	0.2kg	0.2kg	0.2kg
<i>Polymer performance</i>	<i>Comparative Example 1</i>	<i>Example 3</i>	<i>Example 4</i>
Tensile strength	16 MPa	22 MPa	24 MPa
% Elongation	150%	240%	400%
Surface Smoothness	Relative Rough	Smooth	Very smooth

EXAMPLE 5: *Preparation of a Biodegradable Polymer*

32kg of corn starch, 8kg of glycerine, 8kg of sorbitol, 32kg of PBS, 20kg of ST-PBS, 1kg of glucose stearate, 0.5kg of stearamide, 0.2kg of calcium stearate were melt mixed using a ZSK-58 Twin Screw Extruder with a rotational speed of 300rpm. The temperature profile of the extruder was set at 90°C/ 160°C/ 185°C/ 185°C/ 180°C/ 160°C. Vacuum was

applied to remove water. The extrudate was water cooled and cut into pellets. The polymer was then blown into a film, with the temperature profile at 90°C/ 140°C/ 160°C/ 160°C/ 155°C. The film surface was smooth. The longitudinal strength of the film was 21MPa and the elongation ratio was 420%.

5

EXAMPLE 6: *Preparation of a Biodegradable Polymer*

36kg corn starch, 4kg glycerine, 4kg sorbitol, 36kg PLA, 20kg ST-PBS, 1kg glucose stearate, 0.5kg stearamide, 0.2kg calcium stearate were melt mixed using a ZSK-58 Twin
10 Screw Extruder with a rotational speed of 300rpm. The temperature profile of the extruder was set at 90°C/ 160°C/ 200°C/ 200°C/ 180°C/ 160°C. Vacuum was applied to remove water. The extrudate was water cooled and cut into pellets. The polymer was then blown into a film, with the temperature profile set at 95°C/ 160°C/ 190°C/ 200°C/ 180°C/ 165°C. The film surface was smooth. The longitudinal strength of the film was 31MPa and the
15 elongation ratio was 60%.

Biodegradable polymer compositions prepared in Examples 3 to 6 were tested in accordance ISO 16929 for their biodegradability and found to meet the criteria specified therein. Details on certain test parameters in this regard are outlined below.

20

EN 13432 is a performance standard entitled "Packaging: Requirements for packaging recoverable through composting and biodegradation; Test scheme and evaluation criteria for the final acceptance of packaging"

25 EN 13432 is underpinned by the following test methods: ISO 16929 (12 week disintegration test in compost), ISO 14855 (in vessel composting test for CO₂ evolution), heavy metals, compost quality, volatile solids and the OECD 208 A germination test.

The European Norm EN 13432 and the American Society for Testing and Materials
30 (ASTM International) D6400-99 standards all define biodegradability in respect of a time period of 6 months. In the case of EN 13432 a material is deemed biodegradable if it will break down to the extent of at least 90% to H₂O and CO₂ and biomass within a period of 6

months. While for the ASTM D-6400 it is necessary for the material to break down to the extent of at least 60%.

Both standards state that in order for a product to be compostable the following criteria
5 need to be met:

- 1) Disintegration, the ability to fragment into non-distinguishable pieces after screening and safely support bio-assimilation and microbial growth;
 - 2) Inherent Biodegradation, conversion of carbon to carbon dioxide to the level of 60%, over a period of 180 days (as specified ASTM D6400-99) and 90% in 180 days for the
10 European standard (EN 13432);
 - 3) Safety, that there is no evidence of any eco-toxicity in finished compost and soils and it can support plant growth; and
 - 4) Toxicity, that heavy metal concentrations are less than 50% recommended values.
- 15 Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.
- 20 The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

CLAIMS:

1. A method of preparing a biodegradable polymer composition, said method comprising melt mixing a first polysaccharide, a first biodegradable polyester and a
5 compatibiliser, wherein said compatibiliser has been formed separately by reacting a second polysaccharide and a second biodegradable polyester in the presence of a transesterification catalyst.
2. The method according to claim 1, wherein the first polysaccharide is used in an
10 amount ranging from about 5wt.% to about 90wt.%, the first biodegradable polyester is used in an amount ranging from about 5wt.% to about 90wt.%, and the compatibiliser is used in an amount ranging from about 5wt.% to about 60wt.%, relative to the total mass of the first polysaccharide, the first biodegradable polyester and the compatibiliser, and such
15 that the total mass of these three components represents at least 65wt.% of the total mass of the biodegradable polymer composition.
3. The method according to claim 2, wherein the compatibiliser is prepared by reacting about 20wt.% to about 75wt.% of the second polysaccharide and about 20wt.% to
20 about 75wt.% of the second biodegradable polyester in the presence of about 0.1wt.% to about 1wt.% of the transesterification catalyst, relative to the total mass of the second polysaccharide, the second biodegradable polyester and the transesterification catalyst, and such that the total mass of these three components represents at least 65wt.% of the total mass of the compatibiliser.
- 25 4. The method according to claim 1, wherein the first and second polysaccharides are independently selected from starch, glycogen, chitosan and cellulose.
5. The method according to claim 4, wherein the first and second polysaccharides are both starch and independently selected from native starch, thermoplastically processable
30 starch (TPS) and chemically modified starch.
6. The method according to claim 1, wherein the first and second biodegradable polyesters are independently selected from polycaprolactone, polylactic acid, polyhydroxy

butyrate, polyethylene succinate, polybutylene adipate terephthate, poly hydroxy butyrate valerate, polybutylene succinate, polybutylene adipate, cellulose acetate butyrate, and cellulose acetate propionate.

5 7. The method according to claim 1, wherein the transesterification catalyst is an alkali metal hydroxide.

8. The method according to claim 1, wherein plasticiser is also melt mixed with the first polysaccharide, the first biodegradable polyester and the compatibiliser, and wherein
10 the compatibiliser is formed by reacting the second polysaccharide and the second biodegradable polyester in the presence of the transesterification catalyst and plasticiser.

9. The method according to claim 1, wherein the biodegradable polymer composition prepared meets biodegradability criteria set forth in EN 13432.

15

10. The method according to claim 1, wherein said compatibiliser has been formed separately by melt mixing the second polysaccharide and the second biodegradable polyester in the presence of the transesterification catalyst.

20 11. A compatibiliser suitable for use in preparing a biodegradable polymer composition, said compatibiliser comprising the reaction product of 20wt.% to less than 40wt.% of polysaccharide, 20wt.% to 75wt.% of biodegradable polyester, and 0.1wt.% to 1wt.% of transesterification catalyst, relative to the total mass of the polysaccharide, the biodegradable polyester and the transesterification catalyst, and such that the total mass of
25 the reaction product from these three components represents at least 60wt.% of the total mass of the compatibiliser.

12. The compatibiliser according to claim 11, wherein the reaction product is that derived from melt mixing the polysaccharide and the biodegradable polyester in the
30 presence of the transesterification catalyst.

13. A method of preparing a compatibiliser suitable for use in the manufacture of a biodegradable polymer composition, said method comprising reacting 20wt.% to less than

45wt.% of polysaccharide, 20wt.% to 75wt.% of biodegradable polyester and 0.1wt.% to 1wt.% transesterification catalyst, relative to the total mass of the polysaccharide, the biodegradable polyester and the transesterification catalyst, and such that the total mass of the reaction product from these three components represents at least 60wt.% of the total
5 mass of the compatibiliser.

14. The method according to claim 13, wherein the reaction product is that derived from melt mixing the polysaccharide and the biodegradable polyester in the presence of the transesterification catalyst.

10

15. A biodegradable polymer composition prepared in accordance with the method of claim 1.

16. The biodegradable polymer composition in accordance with claim 15, wherein said
15 composition meets biodegradability criteria set forth in EN 13432.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2006/001077

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C08L 3/02 (2006.01)

C08L 3/04 (2006.01)

C08L 67/00 (2006.01)

C08G 81/00 (2006.01)

C08L 3/06 (2006.01)

C08L 67/04 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Derwent: DWPI, JAPIO; C08L 3/02, C08L 3/04, C08L 3/06, C08L 67/00, C08L 67/04, C08G 81/00; STN: CaPlus;

Key words: polyester, starch, polysaccharide, biodegradable, compatibil+, transesterif+, polycaprolactone, polylactic+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
D, X	US 5844023 A (TOMKA) 1 December 1998 abstract; col. 4, lines 32-48; col. 5, lines 13-41; col. 5, line 65 – col. 6, line 6; col. 7, lines 13-59; col. 8, lines 1-11; col. 9, lines 26-42; claims	1-16
X	PHILIPPE DUBOIS et al. " Biodegradable compositions by reactive processing of aliphatic polyester/polysaccharide blends ", Macromol. Symp. (2003), 198, 233-243 whole document, particularly pages 238-242	1-16
X	PHILIPPE DUBOIS et al. " Aliphatic polyester-based biodegradable materials: new amphiphilic graft copolymers ", Polymer Degradation and Stability (2001), 73(3), 561-566 whole document	1-16

☒ Further documents are listed in the continuation of Box C☒ See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

15 August 2006

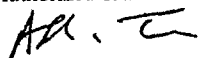
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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	R.P. SINGH et al. " Biodegradation of poly(ϵ -caprolactone)/starch blends and composites in composting and culture environments: the effect of compatibilization on the inherent biodegradability of the host polymer ", Carbohydrate Research (2003), 338(17), 1759-1769 whole document, particularly paragraphs 2.2.3 & 3.3 at pages 1761 & 1765	1-16
X	Chemical Abstract Online Accession Number 2000:233474 (DN 132:348462), " Synthesis and characterisation of HEMA-PCL macromer grafted onto starch ", Polymer (Korea) (2000), 24(2), 141-148 abstract	1-10, 15, 16
X	Chemical Abstract Online Accession Number 2005:1015807 (DN 143: 287269), " Biodegradable aliphatic polyester/starch composite ", Faming Zhuanli Shenging Gongkai Shuomingshu, 9 pp ; and CN 1450120A (SICHUAN UNIVERSITY) 22 October 2003 abstract	1-10, 15, 16
X	US 6117925A (TOMKA) 12 September 2000 abstract; col. 4, lines 4-29; col. 6, lines 1-40; claims	11-14
X	US 6525145 B (GEVAERT et al.) 25 February 2003 abstract; col. 3, line 29 – col. 5, line 20; claims 1, 6	11-14
X	US 5616671 A (NARAYAN et al.) 1 April 1997 col. 2, line 65 – col. 3, line 2; col. 3, lines 18-26; col. 5, lines 4-8; col. 7, lines 8-57; examples 1-3	11-14
A	US 6235815 B (LOERCKS et al.) 22 May 2001 col. 2, lines 37-48; col. 4, lines 5-8; col. 8, lines 4-19, 40-46; col. 9, lines 24-30; Tables 1-4	1-16
A	US 6231970 B (ANDERSEN et al.) 15 May 2001 col. 18, lines 57-62; col. 24, lines 24-39; examples 1-19; claims 17, 28, 42-56, 92, 93	1-16
A	US 6506824 B (BASTIOLI et al.) 14 January 2003 abstract; col. 3, line 7; claims 1, 2, 11, 12	1-16
A	US 5500465 A (KRISHNAN et al.) 19 March 1996 col. 4, lines 6-33; col. 5, lines 21-41; col. 7, lines 7-23; claims	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2006/001077

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
US	5844023	BR	9304477	CN	1088226
		EP	0596437	HK	1014016
		US	6214907	DE	4237535
US	6117925	AU	33562/97	BR	9711036
		CN	1227568	EP	0917540
		WO	9806755	CA	2263122
US	6525145	AU	55453/01	US	2002161136
US	5616671	US	5540929	US	5578691
US	6235815	AU	30445/97	AU	75443/98
		CA	2258843	CN	1222171
		DE	19624641	EP	0906367
		EP	0991713	KR	2000016673
		PL	337455	US	6472497
		WO	9748764	WO	9858798
US	6231970	AU	15857/01	BR	0016960
		CN	1451027	EP	1265957
US	6506824	AU	40917/96	CA	2166921
		CZ	9600077	EP	0722980
		HU	9600062	IL	116698
		IT	MI950023	JP	8231762
		NZ	280798	PL	312236
		ZA	9600184	SK	3596
US	5500465	CA	2183772	EP	0749460
<p>Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.</p> <p>END OF ANNEX</p>					