(54) Title: A BIODEGRADABLE STARCH FILM

(57) Abstract: The present invention relates to a composition for making a biodegradable polymer comprising: a thermoplastic starch (TPS) that is grafted, or compounded for being grafted, to an aliphatic-aromatic copolyester, said aliphatic-aromatic copolyester being present in a continuous phase in amounts sufficient to disperse said TPS therein; a biodegradable polyester in the continuous phase; and a chain extender having epoxy functionality capable of reacting with the end groups of said TPS and biodegradable polyester to introduce chain extension therein and form a TPS-polyester co-polymer. The invention is also directed to a process of making the same composition and to a biodegradable film made in accordance with the process.
A Biodegradable Starch Film

Technical Field

This invention relates to a biodegradable starch composition and a process for manufacturing the same.

Background

Biodegradable plastic films are highly desirable due to their biodegradability. The use of biodegradable plastics is prominent in commercial applications such as packaging, e.g. crockery, cutlery, pots, bowls, straws. Furthermore, after their initial use, they can be easily recycled as organic waste as they decompose.

To further improve the biodegradability and to reduce the costs for producing such plastic films, conventional biodegradable polyesters such as polylactic acid (PLA), polycaprolactone (PCL) and poly (butylene succinate) (PBS) have been blended with thermoplastic starch (TPS) to produce a TPS-polyester blend. However, most of these polyesters are hydrophobic, whereas starch and/or TPS are contrastingly hydrophilic. Accordingly, the resulting TPS-polyester blends face problems of phase-separation and suffer from below par bonding strength.

To solve this problem, one known process describes the preparation a starch-polyester graft copolymer. In this known process, extrusion of starch and polyester are carried out in the presence of maleic anhydride (MAH) as a transesterification catalyst. However, this process contains certain drawbacks. For instance, the presence of acid and water promotes and induces undesirable reactions, particularly, the acid hydrolysis of ester bonds. Consequently, the stability of the resultant TPS-polyester composition is adversely affected which makes
it unsuitable for further processing, for example, in blown film applications. Additionally, plastic film produced from the above TPS-polyester composition also suffers from inferior mechanical qualities.

As most biodegradable polyesters are easily hydrolyzed when processed under high temperatures in the presence of water, TPS usually requires strict drying before being mixed with biodegradable polyesters. This requisite drying step further increases manufacturing costs and complicates the overall process.

Pertaining to blown film applications, it is noted that some biodegradable polyesters are not suitable for blown film applications. PLA is one such example. PLA has high tensile strength and excellent optical properties. However, PLA is rigid and brittle and its elongation values are very low. The tear resistance of PLA is also low, which creates technical difficulties in the film production. Attempts have been made to soften PLA by using plasticizers. In one known method, commercial plasticizers were used in order to lower the glass transition- temperature of PLA. In another known method, PLA was compounded with 20% PBS along with 15-30% acetyl tributyl citrate (ATBC) acting as a plasticizer, in the preparation of PLA film. However, the results of the produced film were modest in that high plasticizer content made the plastic film excessively soft and difficult to cut. Furthermore, plasticizers tended to evaporate / bleed-out from the plastic film after a short time period, thereby resulting in a shortened shelf-life of the film.

In another known process for preparing compatibilized PLA/starch blends, PLA is first grafted by maleic anhydride (MAH) and thereafter added into a mid-extruder to blend with TPS (starch/glycerol/water).
Although this particular process attempts to remove the water from TPS via a vacuum vent prior to blending, water that was chemically bound to the TPS still caused hydrolysis of the PLA-starch polymer and weakened its mechanical strength.

Furthermore, in conventional TPS-polyester blends, the polyester will typically form the major component of the blend, typically more than 60% to 70% by weight. This is to ensure that the TPS-polyester blend exhibits a reasonable level of mechanical strength. However, biodegradable polyesters can be costly and blends that require polyester as the major component may therefore be economically undesirable.

International Patent Application publication No. WO 98/20073 discloses a method of making a polymeric composition containing starch. The method relates to plastic film blowing in which a blended composition of starch, polyester and an interfacial agent such as esters of polyols are extruded in an extruder and blown into plastic film. However, the films in this method are not mechanically strong and therefore are limited in the quantities of starch that may be used. In particular, the tensile and yield strength of such blends may be adversely impacted at a high loading of starch relative to polyester. Furthermore, blends produced from this known method may experience poor film processability due to a lack of stability in the blend composition. This lack of stability may be attributed to the tendency of starch to separate from the polyester phase. As starch is generally less expensive than polyester, the costs of producing plastic film of a reasonable mechanical-strength for applications such as plastic carrier bags, is high.
Accordingly, there is a need to provide a composition for producing a biodegradable film composition which overcomes, or at least ameliorates, the above technical problems. In particular, there is a need to provide a biodegradable composition that possesses high molecular weight and good resistance to hydrolysis. There is also a need to provide a biodegradable TPS-polyester composition in which starch forms a major component without compromising the mechanical strength and stability of a film produced from the composition. There is also a need to provide a process for producing the above biodegradable composition.

**Summary**

Accordingly in a first aspect, there is provided a composition for making a biodegradable polymer comprising: a thermoplastic starch (TPS) that is grafted, or capable of being grafted, to an aliphatic-aromatic copolyester, said aliphatic-aromatic co-polyester being present in a continuous phase in amounts sufficient to disperse said TPS therein; a biodegradable polyester in the continuous phase; and a chain extender having epoxy functionality capable of reacting with the end groups of said TPS and biodegradable polyester to introduce chain extension therein and form a TPS-polyester co-polymer.

Advantageously, the TPS may be capable of being grafted to a dispersing phase of an aliphatic-aromatic copolyester. This grafting by the copolyester increases the stability of the TPS by rendering the TPS substantially amorphous. Also advantageously, the use of the aliphatic-aromatic co-polyester for destructuring the starch negates the need to add water and/or excessive plasticizers. As a result, the TPS enjoys excellent processability and may be suitable for harsh downstream
processing, such as pelletization and extrusion. Furthermore, the aliphatic-aromatic co-polyester provides
the TPS with a generally hydrophobic environment, rendering the TPS less sensitive to moisture.

Advantageously, the resultant low water content of the TPS will improve the hydrolysis resistance of the TPS-polyester co-polymer formed. In one embodiment, the aliphatic-aromatic co-polyester is polybutylene adipate co-terephthalate (PBAT).

The composition may have a weight ratio of TPS to aliphatic-aromatic co-polyester of from about 1:1 to about 10:1. In one embodiment, the weight ratio of TPS to aliphatic-aromatic co-polyester is about 5:1. It is important to determine a suitable ratio of TPS to the aliphatic-aromatic co-polyester. Having too little co-polyester dispersed within the TPS will result in TPS that is hard to process and suffers from a tendency to retrograde during storage. Conversely, blending too much polyester with TPS will increase the production cost of the TPS significantly. The inventors have surprisingly found that having a TPS to co-polyester weight ratio of from about 1:1 to about 10:1 and preferably about 5:1, results in an optimal TPS having excellent processability whilst keeping the TPS cost effective to produce. This allows a high amount of TPS relative to biodegradable polyester to form a copolymer that has sufficient mechanical strength such that it can be used to blow a plastic polymer film that can be utilized in carry bags.

The chain extender may have epoxy functionality capable of reacting with the end groups of the TPS and biodegradable polyester. In one embodiment, the chain extender may comprise epoxy-functional (meth)acrylic monomers and at least one of non-functional (meth)acrylic and styrenic monomers. Preferably, each of the epoxy-
functional meth (acrylic) monomers comprises at least two epoxy groups. More preferably, each of the epoxy-functional meth (acrylic) monomers comprises at least three epoxy groups. The epoxy functional groups may be capable of forming bridging bonds between the reactive end groups of the TPS and polyester chains, to thereby extend the chain length and increase chain branching of the TPS-polyester copolymer. Advantageously, the chain extender increases the average molecular weight of the TPS-polyester copolymer and as such, reinforces the physical strength of the copolymer. More importantly, due to the increased chain length and branch density, the TPS-polyester copolymer also enjoys an increased resistance to hydrolysis. Such improved resistance to hydrolysis further improves the mechanical strength of a plastic film subsequently manufactured from the TPS-polyester copolymer.

The presence of the chain extender may also allow the present composition to accommodate the use of TPS having high moisture content for bonding with the polyester, whilst minimizing the deleterious effects of hydrolysis. This therefore obviates the need for a pre-drying step often required to dehydrate the TPS prior to its addition to the composition. The chain extender may be selected from the group consisting of glycidyl acrylates, glycidyl methacrylates, glycidyl ethers, glycidyl esters and mixtures thereof. In one embodiment, the reactive stabilizer is glycidyl methacrylate. One exemplary chain extender that could be utilized is Joncryl AD™ chain extenders available from BASF Corporation of Florham Park, New Jersey, United States of America, as these chain extenders have high epoxy functionality.
Due to its epoxy functionality, the chain extender may further be capable of capping the reactive end groups of the TPS-polyester copolymer to thereby prevent further chemical reactions, substantially inhibiting the reactivity of the copolymer chains. The chain extender may be capable of repairing broken molecular chains in the TPS-polyester copolymer for maintaining its integrity. Advantageously, the TPS-polyester copolymer enjoys increased stability, reinforced mechanical strength and is highly resistant to chemical decomposition arising from its reactive end groups. The chain extender may be present in the composition in amounts ranging from 0.1% to 10% by weight. In one embodiment, the chain extender is present in the composition in amounts ranging from about 0.1% to 5% by weight.

The composition of the first aspect may contain a greater amount of TPS than polyester, from which a biodegradable polymer film having starch as a major component may be produced. Accordingly, the polyester and TPS may be mixed or blended in a weight ratio of from about 1:3 to about 1:4. In one embodiment, the ratio of the polyester to TPS is 1:1.5. Comparatively, presently known processes typically employ a polyester/TPS ratio of about 7:3, i.e. polyester is used as the major component. Advantageously, the present composition is able to produce biodegradable films having higher starch proportions than polyester proportions when compared to known TPS/polyester compositions. A large bulk of the cost in producing TPS-polyester films resides in the cost of the biodegradable polyester raw material. The present process is advantageously able to utilize less polyester whilst producing films of comparable, if not superior quality relative to the films produced by known
processes. As such, the present process advantageously results in significant cost savings.

The composition may further include a compatibilizer compound, to promote coupling reactions between the TPS and the polyester and improving the bonding strength of the TPS-polyester copolymer. The compatibilizer may also aid the grafting of the aliphatic-aromatic co-polyester to the TPS. The compatibilizer may be selected from the group consisting of anhydrides, carboxylic acids, alkyl carbamates, isocyanates, oxazoline and olefins. In one embodiment, the compatibilizer compound is maleic anhydride (MAH). Advantageously, MAH may serve as a bridging functional group between the TPS and biodegradable polyester, resulting in the formation of stable chemical bonds e.g. ester linkages, between the TPS and polyester chains, rendering the TPS-polyester co-polymer more resistant to phase separation.

The TPS may be processed from natural starch whereby the processed TPS exhibits thermoplastic properties. The TPS may be formed by adding a plasticizer to render the starch substantially thermoplastic. These plasticizers may be selected from the selected from alcohols, diols, triols, sugar alcohols, polyvinyl alcohol, hydroxy acids, salts of hydroxy acids, hydroxy acid oligomers, salts of hydroxy acid oligomers, low molecular weight polyesteramides, alkyl citrates and mixtures thereof. In one embodiment, the plasticizer may be selected from the group consisting of glycerol, sorbitol, acetyltributylcitric acid, triethyleneglycol diacetate and mixtures thereof. The weight ratio of starch to plasticizer may range from about 1:1 to 8:1. In one embodiment, the weight ratio of starch to plasticizer is 4:1. It is preferable to keep the starch to plasticizer ratio within the stipulated ratios. TPS having
plasticizer content that is too low (e.g. a starch to plasticizer ratio greater than 8:1) results in TPS that is not sufficiently amorphous and may consequently be unstable. On the other hand, having too high a plasticizer content may soften the TPS too much, causing the TPS to be difficult to cut at room temperatures.

The composition of the first aspect may also include a free radical initiator. Advantageously, the free radical initiator may promote grafting, cross-linking and coupling reactions between the TPS and polyester chains. The free radical initiator may serve to lower the activation energy ($E_A$) required for inter-/intra-molecular bonding to occur, thereby speeding up the rates of copolymer formation. In one embodiment, the free radical initiator may be an organic peroxide.

The biodegradable polyester of the first aspect may be selected from a group of polyesters, including but not limited to, aliphatic polyesters, aliphatic copolyesters and aliphatic-aromatic copolyesters. Exemplary biodegradable polyesters may be selected from the group consisting of polylactic acid (PLA), polybutylene succinate (PBS), polybutylene adipate co-terephthalate (PBAT), poly(lactic-co-glycolic acid) (PLGA), polycaprolactone (PCL), polyglycolide (PGA). In one embodiment, the polyester is PBAT.

The TPS-polyester co-polymer may possess a high molecular weight from about 20,000 Daltons (Da) to about 500,000 Da. Advantageously, a high molecular weight confers upon the co-polymer desirable mechanical qualities and resistance to degradation.

In a second aspect, there is provided a process for producing a biodegradable film composition comprising: providing a thermoplastic starch (TPS) that is grafted, or capable of being grafted, to an aliphatic-aromatic co-
polyester; blending said TPS with a biodegradable polyester and a chain extender to form a TPS-polyester co-polymer; extruding the TPS-polyester co-polymer to produce said biodegradable film composition.

In the blending step, the TPS may be blended with the polyester and chain extender in a high speed mixer. A compatibilizer may be added to the high speed mixer during the blending step. The blended mixture may then be extruded with a twin screw extruder under temperatures ranging from 20°C to 200°C. The extruded material may be cooled using suitable cooling means and pelletized to thereby produce pellets comprising a biodegradable film composition. These pellets may optionally undergo drying using suitable drying means to remove surface moisture.

The process may further comprise the addition of plasticizers for rendering the TPS generally amorphous. The process may also comprise the addition of a free radical initiator to increase the rate of reaction.

The terms TPS, biodegradable polyester, aliphatic-aromatic co-polyester, chain extender, compatibilizer, plasticizer have the same meanings as described above.

In a third aspect, there is provided a biodegradable film made in a process as defined above.

**Definitions**

As used herein, the term "melt flow rate" (MFR) refers to a measure of the ease of flow of a material under a specified load. MFR is typically expressed in the units of weight per unit time, e.g. grams per 10 minutes.

As used herein, the term "thermoplastic starch" (TPS) refers to starch-based compositions made by mixing starch and with an appropriate plasticizer under conditions that yield a thermoplastic starch melt. It can be appreciated that other suitable additives known to
the skilled person for making TPS may be added, including additional plasticizers, inorganic fillers, organic fillers, biodegradable polymers, destructuring agents, stabilizers, antioxidants, flame retardants, dyes, cellulose esters, polyvinyl alcohol, polyvinyl acetate, polyacrylates, hydrophilic proteins, gelatin, zein, polysaccharides, fatty acid derivatives, lecithin, chitosan, shellac, and cross-linking agents and mixtures thereof. Particular additives may include calcium carbonate, talc, clay, silicon dioxide, titanium dioxide, urea, natural fibres and mixtures thereof.

As used herein, the term "chain extender" in the context of this specification refers to any compound having epoxy-functionality that is capable of reacting with the end groups of the TPS and biodegradable polyester to introduce chain extension therein and form the TPS-polyester copolymer.

As used herein, the term "low molecular weight" refers to a molecular weight of less than 5,000 Daltons (Da) and preferably less than 4,000 Da.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/-
3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Disclosure of Optional Embodiments

The starch used in producing the TPS of the present invention may be derived from natural sources. For example, the starch may be selected from the group consisting of corn, potato, wheat, rice, tapioca, sago and high amylase starch, which have natural water content of between 5-15%.

The biodegradable polyester may be present in the composition in an amount ranging from about 20% to about 40% by weight.

The TPS may be present in the composition in an amount ranging from about 50% to about 80% by weight.

The produced film composition preferably possesses high mechanical strength, in particular, characterized by
high yield strength and tensile strength. The yield
strength and tensile strength measurements are based on
an ASTM D-882 reference standard. The film may possess
yield strength of about at least 7 MPa to about 14 MPa in
the machine direction (MD). In one embodiment, the yield
strength (MD) is 13.5 MPa. The film may possess yield
strength of at least 3 MPa to about 6 MPa in the
transverse direction (TD). In one embodiment, the film
has a yield strength (TD) of about 4.3 MPa.

The film composition may possess tensile strength
(MD) from at least 7 MPa to about 16 MPa and tensile
strength (TD) from at least about 5 MPa to about 11 MPa.
In one embodiment, the film may have a tensile strength
(MD) of about 15.5 MPa and a tensile strength (TD) of
about 8.4 MPa. Particularly, the mechanical strength of
the film composition does not deteriorate after a period
of storage of from 3 months to 6 months. The film
composition may also possess tensile elongation ranging
from about 150% to about 800%. The resulting mixture may
be extruded in a twin-screw extruder at temperatures of
ranging from about 20°C to about 200°C. The extrusion
profile may be divided into from at least 6 zones to 13
zones. In one embodiment, the extrusion is divided into
13 zones, having a temperature profile (°C) as follows:

The compatibilizer may be added in relatively small
amounts, typically from about 0.1% to 30% by weight based
on the total weight of the composition. Exemplary
compatibilizers include, but are not limited to, MAH and
d poly (ethylene-co-acrylic acid) (EAA).

The composition may further comprise a free radical-
initiator. One exemplary form of a free radical initiator
is organic peroxide. Any form of known peroxides may be
used, including but not limited to the following.
peroxides, diaroyl peroxide, dialkanoyl peroxide, tert-butyl peroxy benzonate, di-tert-butyl peroxide, dibenzoyl peroxide, tert-Butyl peroxyacetate, dicumyl peroxide, tert-Butylperoxy 2-ethylhexyl carbonate.

**Description of figures**

Fig. I A is a graph showing the rheological curves of compositions prepared with TPS complex and chain extenders and compositions prepared without TPS complex and without chain extenders at 180°C.

Fig. I B is a graph showing the rheological curves of compositions prepared with TPS complex and chain extenders and compositions prepared without TPS complex but with chain extenders at 180°C.

Figure 2 A is a picture showing the results of a first set of Molau tests according to a comparative example.

Figure 2 B is a picture showing the results a first set of Molau tests according to a comparative example.

Figure 2 C is a picture showing the results a first set of Molau tests according to a disclosed example.

Figure 3 A is a picture showing the results of a second set of Molau tests according to a comparative example.

Figure 3 B is a picture showing the results of a second set of Molau tests according to a comparative example.

Figure 3 C is a picture showing the results of a second set of Molau tests according to a disclosed example.

**Examples**

Non-limiting examples of the invention will be further described in greater detail by reference to
specific Examples and comparative examples, which should not be construed as in any way limiting the scope of the invention.

Methods:

Film properties

The mechanical properties are characterized by a tensile test. Mechanical properties are measured both in the machine direction (MD) and the transverse direction (TD). The following parameters are tested:

(i) Yield Strength and Tensile strength (measured according to ASTM D-882); and

(ii) Percentage of Elongation (measured according to ASTM D-882).

Each of yield strength, tensile strength and percentage elongation are measured at least 5 times for each tested film. An average value is tabulated.

Storage stability test

The film sample was put into the thermo-hygrostat laboratory at 25°C and 100% relative humidity (RH). The tensile test was carried out once every three months, and calculated for the change ratio to initial yield strength, tensile strength and percentage of elongation.

Film processability

Film processability is characterized by the following evaluation criterion as set out under Table 1:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Evaluation Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Bubble is stable and a blown film of a predetermined blow up ratio can be readily obtained.</td>
</tr>
<tr>
<td>Δ</td>
<td>Bubble is slightly unstable, and requires adjustments to obtain a film having a predetermined blow up ratio.</td>
</tr>
</tbody>
</table>
Table 1:

Materials

The main biodegradable polyesters used in the present experiments are listed on Table 2.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Type</th>
<th>Trade name</th>
<th>MP (°C)</th>
<th>MFR* (g/10min)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Aliphatic-aromatic</td>
<td>Ecoflex® F</td>
<td>110</td>
<td>2.7 4.9</td>
<td>BASF, Taiwan</td>
</tr>
<tr>
<td></td>
<td>copolyester</td>
<td>BX 7011</td>
<td>130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Aliphatic polymer</td>
<td>Natureworks</td>
<td>150</td>
<td>10 25</td>
<td>Natureworks LLC, USA</td>
</tr>
<tr>
<td></td>
<td>copolyester</td>
<td>3051D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Aliphatic copolyester</td>
<td>Bionolle</td>
<td>115</td>
<td>1.3</td>
<td>Showa High Polymer Co., Ltd, Japan</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1001</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 *MFR measurement carried out at 190°C and load of 2.16kg

Other materials include:

i) Polymer chain extender D, ADR4385/ADR4368c supplied by BASF;

ii) Compatibilizer E, maleic anhydride (MAH), supplied by Megachem Singapore Pte Ltd;

iii) Glycerine, supplied by Avantchem Co., Ltd;

iv) Sorbitol, purchased from Kimic Chemitech Singapore Pte Ltd.

v) Urea, purchased from Alfa Aesar;

vi) Perbutyl Z (T-Butyl Peroxy Benzoate), 98%, supplied by Megachem Singapore Pte Ltd.
vii) Talc powder, supplied by Longsheng Risheng Talc Powder Co., Ltd, China;
viii) Calcium stearate (CaSt), supplied by Megachem Singapore Pte Ltd;
ix) Acetyl tributyl citrate (ATBC), purchased from Jiang Su Lemon Chem. & Tech. Co., Ltd, China;
x) Corn starch, Supplied by Shandong Zhucheng Xingmao Corn Developing Co., Ltd, China;

Example 1

Example 1-A - Preparation of the TPS complex

20.0kg corn starch, 8.0kg glycerine, 3.0kg polyester A, 400g urea, 1.0kg talc powder, 200g calcium stearate are mixed in a high speed mixer (SHR-200A, Zhangjiagang Fanfeng Machinery Co. Ltd). The blend is then prepared using a 50mm co-rotating twin screw extruder (manufactured by Nanjing Jieya Extrusion Equipment Co., Ltd, China), having a barrel length to diameter ratio of 52:1 and is divided into 13 zones.

Extrusion is then carried out according to following temperature profile (°C): 60-90-110-130-140-150-155-150-140-135-120; the screw speed is set at 150 rpm. And the extruded polymer strands are cooled using airflow on a conveyor belt, and pelletized in line. The extruded polymer strands are easily pelletized into particles at room temperature, without the need for the provision of a moisture- or temperature-controlled environment.

Example 1-B - Preparation of biodegradable film composition

4.0kg of the TPS complex prepared in Example 1-A is mixed with 6.0kg of polyester A (which is pre-blended with 100g ADR4385, 100g ADR4368c, 200g maleic anhydride and 50g Perbutyl Z) in a high speed mixer. The blend is
subsequently prepared using a 36mm co-rotating twin screw extruder (Nanjing Jieya Extrusion Equipment Co., Ltd), having a barrel length to diameter ratio of 40:1 and is divided into 6 zones. A typical extrusion has the following temperature profile (°C): 60-90-130-150-130-120, and the screw speed is set at 120 rpm. And the extruded copolymer strands are cooled using a water bath, and thereafter pelletized in line. The pellets were dried in a vacuum oven at 70°C for 5 hours, to remove the surface moisture.

**Example 1-C - Film blowing**

The biodegradable film composition prepared by Example 1-B is blown into film using a blow film machine. An exemplary blow film machine is the MF-400 Blow Film Machine, manufactured by Zhangjiagang Shen Xin Plastic and Rubber Equipment Co. The blow film machine consists of a single extruder and a film tower. The pellets (of Example 1-B) are compacted and heated into molten polymer and extruded through the single extruder according to the following temperature profile (°C): 100-150-150-160-160. The extruded polymer is then inflated in the film tower to form a thin film bubble. The bubble film is thereafter cooled and undergoes solidification. The bubble film is received by a set of rollers which keeps the bubble and collects it into thin film layers.

**Example 2**

**Example 2-A - Preparation of TPS complex**

50.0kg corn starch, 20.0kg glycerine, 7.5 kg polyester A, 1.0kg urea, 3.0 kg talc powder, are mixed in a high speed mixer. The final blend is then prepared using a 50mm co-rotating twin screw extruder (Nanjing Jieya Extrusion Equipment Co., Ltd), having a barrel...
length to diameter ratio of 52:1 and is divided into 13 zones. A typical extrusion the following temperature profile(°C): 60-90-110-130-150-155-150-150-140-135-120; the screw speed is set at 150 rpm. The extruded polymer strands are thereafter cooled to 30°C using air-flow on a conveyor belt, and pelletized in line.

Example 2-B - Preparation of TPS-polyester blend

4.0kg of polyester A, 150g of ADR4385, 150g of ADR4368C, 200g maleic anhydride, 50g Perbutyl Z are preblended in a high speed mixer (SHR-200A, Zhangjiagang Fanfeng Machinery Co. Ltd). The preblend is then mixed with 6kg of the TPS complex (prepared in Example 2-A) in a high speed mixer. Thereafter, the blend was prepared using a 36mm co-rotating twin screw extruder (Nanjing Jieya Extrusion Equipment Co., Ltd), having a barrel length to diameter ratio of 40:1 and is divided into 6 zones. Extrusion is carried out according to the following temperature profile(°C): 60-80-135-170-170-165. The screw speed is set at 120 rpm. And the extruded copolymer strands are cooled to 30°C using a water bath, and pelletized in line. The pellets are then dried in a vacuum oven at 70°C for 5 hours, to remove surface moisture.

Example 2-C - Film blowing

The pellets (of Example 2-B) are compacted and heated into molten polymer and extruded through a single extruder according to the following temperature profile (°C): 100-150-150-160-160. The extruded polymer is then inflated in the film tower to form a thin film-bubble. The bubble film is thereafter cooled and undergoes solidification. The bubble film is received by
a set of rollers which keeps the bubble and collects it into thin film layers.

**Example 3**

3.0kg polyester A, 150g ADR4385, 150g ADR4368c, 300g maleic anhydride, 100g Perbutyl Z are pre-blended in a high speed mixer (SHR-25A manufactured by Zhangjiagang Xinrong Machinery Co., Ltd). The preblend is mixed with 7.0kg of TPS complex (prepared in Example 2-A), in a high speed mixer. Thereafter, the TPS-polyester blend is prepared using a 36mm co-rotating twin screw extruder, having a barrel length to diameter ratio of 40:1 and is divided into 6 zones. A typical extrusion has the following temperature profile(°C): 60-80-135-170-170-165; the screw speed is set at 120 rpm. And the extruded copolymer strands is cooled to 30°C using a water bath, and pelletized in line. The pellets are dried in a vacuum oven at 70°C for 5 hours, to remove the surface moisture.

**Film blowing**

A single extruder and -film tower are used to produce blown film as described above. Film blowing is carried out according to the following temperature profile (°C): 100-150-150-160-160.

**Comparative Example 4**

6.0kg of TPS complex (prepared in Example 2-A) and 4.0kg of polyester A are mixed in a high speed mixer. The blend is then prepared using a 36mm co-rotating twin screw extruder (as above), having a barrel length to diameter ratio of 40:1 and divided into 6 zones. Extrusion is carried out according to the following temperature profile (°C): 60-90-130-150-130-120; the screw speed is set at 120 rpm. The extruded polymer strands is
cooled to 30°C using a water bath, and pelletized in line. The pellets were dried in a vacuum oven at 70°C for 5 hours, to remove the surface moisture.

**Film blowing**

The biodegradable film composition was blown into film using a blow film machine according to the protocol described above. Film blowing is carried out according to the following temperature profile (°C): 100-140-140-150-150.

**Comparative Example 5**

4.0kg of polyester A, 200g maleic anhydride, 50g Perbutyl Z are preblended in a high speed mixer (SHR-200A, Zhangjiagang Fanfeng Machinery Co. Ltd). The preblend is then mixed with 6kg of the TPS complex (prepared in Example 2-A) in a high speed mixer. Thereafter, the blend was prepared using a 36mm co-rotating twin screw extruder (Nanjing Jieya Extrusion Equipment Co., Ltd), having a barrel length to diameter ratio of 40:1 and is divided into 6 zones. Extrusion is carried out according to the following temperature profile (°C): 60-80-135-170-170-165. The screw speed is set at 120 rpm. And the extruded polymer strands are cooled to 30°C using a water bath, and pelletized in line. The pellets are then dried in a vacuum oven at 70°C for 5 hours, to remove surface moisture.

**Film blowing**

The biodegradable film composition was blown into film using a blow film machine according to the protocol described above. Film blowing is carried out according to the following temperature profile (°C): 100-140-140-150-150.
Comparative Example 6

7.0kg of TPS complex (prepared in Example 2-A), 3.0kg polyester A, are mixed in the high speed mixer, then the blend is prepared using a 36mm co-rotating twin screw extruder, having a barrel length to diameter ratio of 40:1 and is divided into 6 zones. The extrusion has the following temperature profile (°C): 60-90-130-150-130-120; the screw speed is set at 120 rpm. And the extruded polymer strands is cooled to 30°C using a water bath, and pelletized in line. The pellets were dried in a vacuum oven at 70°C for 5 hours, to remove the surface moisture.

Film blowing

The biodegradable film composition was blown into film in accordance with the above described protocol. Film blowing is carried out according to the following temperature profile (°C): 100-140-140-150-150.

Example 7

2.0kg of polyester B is pre-blended with 100g ADR4385, 100g ADR4368c, 200g maleic anhydride, 50g Perbutyl Z. The preblend is mixed in a high speed mixer with 6.0kg of TPS complex prepared in Example 2A and 2.0kg of polyester A. The resulting blend is prepared using a 36mm co-rotating twin screw extruder, having a barrel length to diameter ratio of 40:1 and is divided into 6 zones. Extrusion was carried out according to the following temperature profile (°C): 60-130-150-170-150-130, and the screw speed is set at 120 rpm. The extruded stranded is cooled to 30°C using a water bath, and pelletized in line. The pellets are then dried in a
vacuum oven at 70°C for 5 hours, to remove the surface moisture.

**Film blowing**

The biodegradable film composition is blown into film in accordance with the above described protocol. Film blowing is carried out according to the following temperature profile (°C): 100-140-140-150-150.

**Example 8**

1.5kg of polyester B is pre-blended with 150g ADR4385, 150g ADR4368c, 300g maleic anhydride, 100g Perbutyl Z, and 700g ATBC. The preblend is then mixed in a super high speed mixer with 7.0kg TPS (prepared in Example 2A) and 1.5kg of polyester A. The resultant blend is prepared using a 36mm co-rotating twin screw extruder, having a barrel length to diameter of about 40:1 and is divided into 6 zones. Extrusion is carried out according to the following temperature profile (°C): 60-130-150-170-150-130, and the screw speed is set at 120 rpm. And the extruded strands was cooled to 30°C using a water bath, and pelletized in line. The pellets are dried in a vacuum oven at 70°C for 5 hours, to remove the surface moisture.

**Film blowing**

The biodegradable film composition is blown into film in accordance with the above described protocol. Film blowing is carried out according to the following temperature profile (°C): 100-160-160-160.

**Example 9**

6.0kg polyester C is pre-blended with 100g ADR4385, 100g ADR4368C, 200g maleic anhydride, 50g Perbutyl Z. The preblend is mixed with 4.0kg TPS complex prepared in
Example 2A in a high speed mixer. Thereafter, the blend is prepared using a 36mm co-rotating twin screw extruder, having a barrel length to diameter ratio of 40:1 and is divided into 6 zones. Extrusion is carried out according to the following temperature profile (°C): 60-130-150-170-150-130, and the screw speed is set at 120 rpm. The extruded copolymer strands was cooled to 30°C using a water bath, and pelletized in line. The pellets were dried in a vacuum oven at 70°C for 5 hours, to remove the surface moisture.

**Film blowing**

The biodegradable film composition is blown into film in accordance with the above described protocol. Film blowing is carried out according to the following temperature profile (°C):100-150-150-160-160.

Table 3 below summarizes the diagnostic tests carried out film samples produced in accordance with the above nine Examples.
<table>
<thead>
<tr>
<th>Examples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>4 (Comp.)</th>
<th>5 (Comp.)</th>
<th>6 (Comp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS complex</td>
<td>4kg</td>
<td>6kg</td>
<td>7kg</td>
<td>6kg</td>
<td>7kg</td>
<td>4kg</td>
<td>6kg</td>
<td>6kg</td>
<td>7kg</td>
</tr>
<tr>
<td>Polyester blends</td>
<td>Polyester A</td>
<td>6kg</td>
<td>4kg</td>
<td>3kg</td>
<td>2kg</td>
<td>1.5kg</td>
<td>0</td>
<td>4kg</td>
<td>4kg</td>
</tr>
<tr>
<td>Polyester B</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2kg</td>
<td>1.5kg</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polyester C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6kg</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Reagent D (ADR)</td>
<td>200g</td>
<td>300g</td>
<td>300g</td>
<td>200g</td>
<td>300g</td>
<td>200g</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Reagent E (Compatibilizer)</td>
<td>200g</td>
<td>200g</td>
<td>300g</td>
<td>300g</td>
<td>300g</td>
<td>200g</td>
<td>0</td>
<td>200g</td>
<td>0</td>
</tr>
<tr>
<td>Yield Strength (MPa)</td>
<td>MD</td>
<td>13.5</td>
<td>8.7</td>
<td>8.3</td>
<td>7.3</td>
<td>7.2</td>
<td>7.4</td>
<td>9.2</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>4.3</td>
<td>3.2</td>
<td>3.3</td>
<td>4.0</td>
<td>4.4</td>
<td>6.6</td>
<td>4.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>MD</td>
<td>15.5</td>
<td>10.5</td>
<td>10.3</td>
<td>8.5</td>
<td>7.2</td>
<td>12.8</td>
<td>10.8</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>8.4</td>
<td>6.7</td>
<td>6.6</td>
<td>5.8</td>
<td>5.8</td>
<td>10.4</td>
<td>4.0</td>
<td>5.2</td>
</tr>
<tr>
<td>Percentage of Elongation (%)</td>
<td>MD</td>
<td>282</td>
<td>333</td>
<td>161</td>
<td>104</td>
<td>180</td>
<td>224</td>
<td>187</td>
<td>247</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>273</td>
<td>317</td>
<td>304</td>
<td>174</td>
<td>230</td>
<td>232</td>
<td>55.7</td>
<td>202</td>
</tr>
<tr>
<td>Film processability</td>
<td>o</td>
<td>o</td>
<td>Δ</td>
<td>o</td>
<td>Δ</td>
<td>o</td>
<td>Δ</td>
<td>Δ</td>
<td>x</td>
</tr>
<tr>
<td>Film surface</td>
<td>Smooth</td>
<td>Smooth</td>
<td>Small Particles</td>
<td>Smooth</td>
<td>Small Particles</td>
<td>Smooth</td>
<td>Big particles</td>
<td>Big particles, unable to blow film</td>
<td></td>
</tr>
</tbody>
</table>
As seen from Table 3, film compositions added with the chain extender show good mechanical properties and processability as compared with the Examples without (such as comparative Examples 4, 5 and 6).

As can be seen from Example 2 and Comparative Examples 4 and 5, film compositions prepared with the chain extender (Reagent D) showed better processability than the compositions prepared without the chain extender (such as in the comparative Examples 4 and 5); Furthermore, the film composition prepared according to Example 5 (i.e. addition of reagent E only but without adding the chain extender) shows better elongation than Example 4. However, the film of Example 5 nevertheless suffered from containing big particles and possessed inferior processability as compared to Example 2.

Particularly, as can be seen from Example 3, even with a starch content as high as 70%, the film composition can nonetheless undergo extrusion blowing. In contrast, the film compositions produced without the chain extender were unable to be blown into film under the same conditions.

**Examples 10-13**

Examples 10-13 demonstrate the biodegradable polymer compositions prepared according to the present invention for forming TPS composition by blending TPS complex and biodegradable polyester in the present of compatibilizer and chain extenders.

**Example IQ-A - Preparation of the TPS Complex**

6.0kg corn starch, 1.6kg glycerine, 1.0kg sorbitol, 700g polyester A, 150g urea, 500g talc powder, 50g calcium stearate are mixed in a high speed mixer (SHR-200A, Zhangjiagang Fanfeng Machinery Co. Ltd). The blend
is then prepared using a 50mm co-rotating twin screw extruder (manufactured by Nanjing Jieya Extrusion Equipment Co., Ltd, China), having a barrel length to diameter ratio of 52 :1 and is divided into 13 zones.

Extrusion is then carried out according to following temperature profile (ºC): 60-90-110-130-140-150-155-150-140-140-135-120; the screw speed is set at 150 rpm. And the extruded polymer strands are cooled using airflow on a conveyor belt, and pelletized in line. The extruded polymer strands are easily pelletized into particles at room temperature, without the need for the provision of a moisture- or temperature-controlled environment.

Example IQ-B - Preparation of biodegradable film composition

3.0kg of the TPS complex prepared in Example 1-A is mixed with 7.0kg of polyester A (which is pre-blended with 100g ADR4385, 100g ADR4368c, 200g maleic anhydride and 50g Perbutyl Z) in a high speed mixer. The blend is subsequently prepared using a 38mm co-rotating twin screw extruder (Nanjing Jieya Extrusion Equipment Co., Ltd), having a barrel length to diameter ratio of 40:1 and is divided into 6 zones. A typical extrusion has the following temperature profile (ºC): 60-90-130-150-130-120, and the screw speed is set at 120 rpm. And the extruded copolymer strands are cooled using a water bath, and thereafter pelletized in line. The pellets were dried in a vacuum oven at 70ºC for 5 hours, to remove the surface moisture.

Example IQ-C - Film blowing

The biodegradable film composition prepared by Example 10-B is blown into film using a blow film machine
The blow film machine consists of a single extruder and a film tower. The pellets (of Example 10-B) are compacted and heated into molten polymer and extruded through the single extruder according to the following temperature profile (°C): 100-150-150-160-160. The extruded polymer is then inflated in the film tower to form a thin film bubble. The bubble film is thereafter cooled and undergoes solidification. The bubble film is received by a set of rollers which keeps the bubble and collects it into thin film layers.

**Examples 11-13**

The procedure of preparing TPS complex, biodegradable film composition, and film blowing in Example 10 was followed by examples 11-13. Different ratios of TPS complex and biodegradable polyester are used in examples 11-13. Table 4 summarizes the compositions and testing results for examples 10-13.

**Comparative Example 14-17**

Examples 14-17 demonstrate the biodegradable polymer compositions that are free of TPS complex and chain extenders and are formed by blending starch, biodegradable polyester, plasticizer and other additives, but without compatibilizer and chain extender.

Corn starch, glycerine, sorbitol, polyester A, urea, talc powder, and calcium stearate are mixed in a high speed mixer (SHR-200A, Zhangjiagang Fanfeng Machinery Co. Ltd). The blend is then prepared using a 50mm co-rotating twin screw extruder (manufactured by Nanjing Jieya Extrusion Equipment Co., Ltd, China), having a barrel length to diameter ratio of 52:1 and is divided into 13 zones.
Extrusion is then carried out according to following temperature profile (°C): 60-90-110-130-140-150-155-155-150-140-140-135-120; the screw speed is set at 150 rpm. And the extruded copolymer strands are cooled using air-flow on a conveyor belt, and pelletized in line. The extruded polymer strands are pelletized into particles at room temperature, and the pellets were dried in a vacuum oven at 70°C for 5 hours, to remove the surface moisture.

The biodegradable film compositions were blown into film using a blow film machine according to the protocol described above. Film blowing is carried out according to the following temperature profile (°C): 100-140-140-150-150. Table 4 summarizes the compositions and testing results for examples 14-17.

**Comparative Example 18-21**

Examples 18-21 demonstrate the compositions that are free of TPS complex by blending starch, biodegradable polyester, plasticizer and other additives in the present of chain extenders and compatibilizer.

Corn starch, glycerine; sorbitol, polyester A, urea, talc powder, calcium stearate, 100g ADR4385, 100g. ADR4368c, maleic anhydride and Perbutyl Z are mixed in a high speed mixer (SHR-200A, Zhangjiagang Fanfeng Machinery Co. Ltd). The blend is then prepared using a 50mm co-rotating twin screw extruder (manufactured by Nanjing Jieya Extrusion Equipment Co., Ltd, China), having a barrel length to diameter ratio of 52 :1 and is divided into 13 zones.

Extrusion is then carried out according to following temperature profile (°C): 60-90-110-130-140-150-155-155-150-140-140-135-120; the screw speed is set at 150 rpm. And the extruded polymer strands are cooled using air-flow on a conveyor belt, and pelletized in line. The
extruded polymer strands are pelletized into particles at room temperature, and the pellets were dried in a vacuum oven at 70°C for 5 hours, to remove the surface moisture.

The biodegradable film composition was blown into film using a blow film machine according to the protocol described above. Film blowing is carried out according to the following temperature profile (°C): 100-140-140-150-150. Table 4 summarizes the compositions and testing results for examples 18-21.
Table 4.

<table>
<thead>
<tr>
<th>Examples</th>
<th>TPS Complex + Chain Extenders</th>
<th>No TPS Complex + No Chain Extenders</th>
<th>No TPS Complex + Chain Extenders</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>TPS Complex</td>
<td>3kg</td>
<td>4kg</td>
<td>5kg</td>
</tr>
<tr>
<td>Starch</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Glycerine</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Urea</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CaSt</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Tale</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polyester A</td>
<td>7kg</td>
<td>6kg</td>
<td>5kg</td>
</tr>
<tr>
<td>Reagent D (ADR)</td>
<td>200g</td>
<td>200g</td>
<td>200g</td>
</tr>
<tr>
<td>Reagent E (Compatibilizer)</td>
<td>200g</td>
<td>200g</td>
<td>200g</td>
</tr>
<tr>
<td>Yield Strength (MPa)</td>
<td>MD</td>
<td>16.3</td>
<td>12.5</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>TD</td>
<td>4.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Percentage of Elongation (%)</td>
<td>MD</td>
<td>17.3</td>
<td>14.2</td>
</tr>
<tr>
<td>MFR(g,165°C/5KG)</td>
<td>4.43</td>
<td>2.86</td>
<td>1.68</td>
</tr>
<tr>
<td>Film processability</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Film surface</td>
<td>Smooth</td>
<td>Smooth</td>
<td>Smooth</td>
</tr>
</tbody>
</table>
Mechanical Properties

Tensile properties of the film samples prepared from Examples 10-21 are shown in the Table 4. As seen from Table 4, the films of examples 10-13 are within the scope of the invention and it will be observed that they displayed the best mechanical strength as compared to comparative examples 14-17 which had no TPS complex and no chain extenders and comparative examples 18-21 which had no TPS complex. Notably, the tensile strength of films of examples 10-13 is about 2-3 times higher than comparative examples 14-17, and about 2 times as high as comparative examples 18-21.

Referring to Table 4, when the starch content is 36%, the composition of comparative example 17 shows very low melt strength in blow film process and it is very difficult to obtain film samples. Similarly, it is almost impossible to blow film using the composition of comparative example 21 due to its poor processability and its unstable melt. Accordingly, it can be seen that with increasing the starch content in the biodegradable film composition, film processability becomes worse.

However, as seen from Table 4, the film sample prepared by example 13 with the same starch content as compared to comparative examples 17 and 21 shows better processability and mechanical strength. This can be attributed to the formation of TPS complex resulting in a stable composition and the presence of chain extenders in the film composition which increases the melt strength of the film sample.

Rheological Properties

The rheological test was carried out by using Anton Paar Physica MCR 301 rheometer, at a temperature of 180°C,
and with test angular frequency from 0.01s\(^{-1}\) to 1000s\(^{-1}\). All the biodegradable compositions of examples 10-21 were tested to compare the rheological properties. The test results are shown on Fig. 1.

The rheological curves for composition of examples 10-13 and comparative examples 14-17 are shown in Fig. 1(A). As seen from Fig. IA, the compositions of comparative examples 14-16 have relatively higher shear viscosity at low shear rate than examples 10-12. This is because the starch in the compositions of comparative examples 14-16 is not completely plasticized and is present in the form of particles, acting only as a filler to increase shear viscosity.

Notably, only the composition of example 13 shows higher shear viscosity at low shear rate compared to comparative example 17. This relatively higher shear viscosity may be the result of the formation of a large amount of TPS-polyester copolymer due to the addition of chain extenders and consequently, more branching of the polymer chains. The rheological curves demonstrate that the compositions prepared according to the comparative examples are not well plasticized and very difficult to blow film.

The rheological curves for composition of examples 10-13 and comparative examples 18-21 are shown in Fig. 1B. Referring to Fig.IB, the compositions of examples 10-13 (containing TPS complex) have relatively narrow molecular distribution and have higher shear viscosity at low shear rate than comparative examples 18-20 (does not contain TPS complex).

The rheological curves in Fig. 1 also indicate that the compositions prepared by the TPS complex method may facilitate the formation of intermolecular and intramolecular bonds between the TPS complex and
polyester chains, thereby resulting in improvements to the processability and stability when compared to compositions prepared without providing a TPS complex.

**First Moulau Test**

A first set of Molau tests are performed at room temperature by stirring about 0.50g of three distinct samples produced according to Comparative Examples 4, 5 and Example 2 respectively. Each sample is mixed in 100 ml of chloroform and stored in a test tube for one week to allow settling to occur. The turbidity of the samples was subsequently measured. The results of the first set of Molau tests are shown in Fig. 2.

Fig 2A shows the test result for a TPS complex/polyester A sample prepared according to Comparative Example 4;

Fig. 2B shows the test result for a TPS complex/polyester A/Reagent E sample prepared according to Comparative Example 5;

Fig. 2C shows the result for a TPS complex/Polyester A/Reagent E/Reagent D sample prepared according to Example 2.

As can be seen from Fig. 2A, the sample prepared without reagent D and reagent E revealed a clear separation of a transparent Polyester A layer from an upper layer of starch particles.

Fig. 2B (sample containing Reagent E), displayed a less distinct upper layer as compared to Fig. 2A. This is because some co-polymerisation between the TPS and polyester may have taken place as a result of adding reagent E. Consequently, there was a lower degree of separation of starch particles (upper layer) from the polyester in Fig 2B as compared to Fig 2A.
Fig. 2C (sample containing both reagent D and reagent E) showed almost no separation between the starch particles and the polyester. The sample displayed a substantially uniform turbid layer, resulting from a large amount of starch-polyester copolymer being produced in the sample. As can be deduced from the Molau tests, the addition of Reagent D (as compared to simply adding E alone or none of D or E) may be partly responsible for the superior stability of TPS/polyester copolymer in Fig. 2C.

**Second Molau Test**

The second set of Molau tests are performed at room temperature by stirring about 0.50g of three distinct samples produced according to Comparative Examples 16 and 20 and Example 12 respectively. Each sample is mixed in 100 ml of chloroform and stored in a test tube for one week to allow settling to occur. The turbidity of the samples was subsequently measured. The results of the second set of Molau tests are shown in Fig. 3.

Fig 3A shows the test result for a sample prepared according to Comparative Example 16, Starch/Polyester A/Reagent E/Reagent D =30/53.5/0/0;

Fig 3B shows the test result for a sample prepared according to Comparative Example 20, Starch/Polyester A/Reagent E/Reagent D =30/53.5/2/2;

Fig 3C shows the test result for a sample prepared according to Comparative Example 12, TPS complex/Polyester A/Reagent E/Reagent D =50/50/2/2;

In the above three samples, comparable masses of starch, polyester A and additives were used to obtain a meaningful comparison.

As can be seen from Fig. 3A, the sample prepared without reagent D and reagent E revealed a clean
separation of an almost transparent Polyester A from the down layer of starch particles.

Fig. 3B (sample containing reagent D and reagent E), displayed a more turbid upper layer as compared to Fig. 3A. This is because some amounts of starch-polyester copolymer may be produced. It is postulated that Reagent D (a chain extender) is capable of reacting with the end groups of TPS and polyester to introduce chain extension therein and form a TPS-polyester copolymer. Consequently, there was a lower degree of separation of starch particles (lower white layer) from the polyester in Fig 3B as compared to Fig 3A.

Fig. 3C (sample containing TPS complex, reagent D and reagent E) showed almost no separation between the starch particles and the polyester. The solution became homogeneous and more turbid, which may be the result of the formation of starch-polyester copolymer between almost all the polyester and TPS complex.

**Storage stability test**

The storage stability test is carried out in the thermo-hygrostat laboratory, maintained at 25°C and 100% relative humidity. Film samples from Example 2 and Comparative Example 4 are kept in the thermo-hygrostat laboratory; Tensile tests are conducted every three months, and calculated for their percentage changes with respect to initial yield strength, tensile strength and percentage of elongation.
The result of the stability test is tabulated on Table 5 below.

<table>
<thead>
<tr>
<th>Duration (Days)</th>
<th>1st day</th>
<th>90th day</th>
<th>180th day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Results</td>
<td>Change (%)</td>
<td>Results</td>
</tr>
<tr>
<td>Example 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yield Strength (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>8.7</td>
<td>9.8</td>
<td>+13</td>
</tr>
<tr>
<td>TD</td>
<td>3.3</td>
<td>4.4</td>
<td>+33</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>10.5</td>
<td>13.4</td>
<td>+28</td>
</tr>
<tr>
<td>TD</td>
<td>6.7</td>
<td>9.5</td>
<td>+42</td>
</tr>
<tr>
<td>Percentage of Elongation (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>333</td>
<td>324</td>
<td>-2.5</td>
</tr>
<tr>
<td>TD</td>
<td>317</td>
<td>415</td>
<td>+31</td>
</tr>
<tr>
<td>Comparative Example 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yield Strength (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>9.2</td>
<td>5.8</td>
<td>-47</td>
</tr>
<tr>
<td>TD</td>
<td>4.0</td>
<td>2.3</td>
<td>-43</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>10.8</td>
<td>8.6</td>
<td>-20</td>
</tr>
<tr>
<td>TD</td>
<td>4.0</td>
<td>3.3</td>
<td>-18</td>
</tr>
<tr>
<td>Percentage of Elongation (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>187</td>
<td>276</td>
<td>+47</td>
</tr>
<tr>
<td>TD</td>
<td>55.7</td>
<td>329</td>
<td>+490</td>
</tr>
</tbody>
</table>

Table 5.

As seen from Table 5, the film produced with the addition of the chain extender and the compatibilizer (Example 2) show good storage stability as compared to the film produced without adding either (Example 4). Particularly, the film samples of Example 2 show good retention of mechanical strength and a stable percentage of elongation. Notably, the yield strength and tensile strength remained relatively unchanged in the first half year. For example, the percentage yield strength (TD) remain relatively unchanged after six months whilst the tensile strength (TD) changed by less than 30%. The change in percentage elongation was also less than 50% in the transverse direction.

In contrast, the film samples of comparative example 4 showed dramatic deterioration in properties over half a year. Notably, yield strength reduced from about 50% to about 70%, tensile strength decreased about 40%, whilst percentage of elongation varied- significantly from +200%
to +600%. Over a relatively short storage period of half a year, it becomes clear that the strength of the film in Example 4 undergoes large reductions and displays a high degree of instability. This is indicative that such films (Example 4) may not be useful for practical applications that span a substantial period of time.

Without being bound by theory, it is believed that the reason for good storage stability and hydrolysis resistance of Example 2 is attributable to the chain extender which helped to increase the molecular weight of the TPS/polyester copolymer, inhibit reactivity of the end groups and repair the broken molecular chains. Additionally, the stable TPS complex comprising the aliphatic-aromatic co-polyester provided the strong "bone" for the TPS and facilitated the formation of a stable, amorphous TPS having excellent processability. Consequently, the produced TPS-polyester copolymer is able to tolerate higher moisture content and possesses improved resistance to chemical degradation. Lastly, the compatibilizer provided the two phases (TPS complex and polyester) with excellent reactivity by facilitating formation of intermolecular and intramolecular chemical bonds between the starch and polyester chains. In summary, the film composition of Example 2 displayed good storage stability and enhanced resistance to hydrolysis and demonstrates the technical superiority of the film composition produced by the present invention.

The polymer composition of the present invention may be applied in numerous commercial applications, not least in the manufacture of biodegradable plastic films for storage and packaging purposes. In particular, the present biodegradable film composition possesses high molecular weight and good resistance to hydrolysis, which
is highly advantageous to its applicability in such forms.

The polymer composition of the present invention is a highly cost effective alternative as compared to presently known forms of film compositions. Particularly, the present TPS-polyester composition comprises of starch as a major component without compromising the mechanical strength of a film produced from the composition. This allows manufacturers to produce much cheaper compositions owing to the reduced usage of expensive biodegradable polyesters.

Advantageously, through the formation of a TPS-polyester complex, the disclosed method is further capable of incorporating a higher loading of starch relative to polyester without compromising on the film processability and mechanical strength of the polymer composition. It can therefore be envisaged that the disclosed method and composition could be used for the production of cost-effective plastics, wherein starch or thermoplastic starch forms the major component, but at the same time, the disclosed composition can be processed into film with relative ease and the resultant film possesses adequate mechanical strength as may be required.
Claims

1. A composition for making a biodegradable polymer comprising:
   a thermoplastic starch (TPS) that is grafted, or capable of being grafted, to an aliphatic-aromatic co-polyester, said aliphatic-aromatic co-polyester being present in a continuous phase in amounts sufficient to disperse said TPS therein;
   a biodegradable polyester in the continuous phase; and
   a chain extender having epoxy functionality capable of reacting with the end groups of said TPS and biodegradable polyester to introduce chain extension therein and form a TPS-polyester co-polymer.

2. The composition as claimed in claim 1, wherein the chain extender comprises epoxy-functional (meth) acrylic monomers and at least one of non-functional (meth) acrylic and styrenic monomers.

3. The composition as claimed in claim 1 or claim 2, wherein the weight amount of TPS in said composition is greater than the amount of biodegradable polyester.

4. The composition as claimed in claim 1 or claim 2, wherein the weight ratio of the biodegradable polyester to TPS is from about 1:1.5 to about 1:4.

5. The composition as claimed in claim 2, wherein each of said epoxy-functional (meth) acrylic monomers comprises at least two epoxy functional groups.
6. The composition as claimed in claim 5, wherein said epoxy-functional (meth) acrylic monomers comprises at least three epoxy functional groups.

7. The composition as claimed in claim 2, wherein said epoxy-functional (meth) acrylic monomers contain 1,2-epoxy groups.

8. The composition as claimed in claim 7, wherein said 1,2-epoxy groups are selected from the groups consisting of glycidyl acrylate, glycidyl methacrylate, glycidyl esters and glycidyl ethers.

9. The composition of any one of claims 1 to 8, wherein the amount of said chain extender in said composition is in the range 0.1% to 10% by weight.

10. The composition as claimed in claim 1, wherein the weight amount of said biodegradable polyester in said composition is in the range of 20 to 40% by weight.

11. The composition as claimed in claim 1, wherein the weight amount of said TPS in said composition is in the range of 50 to 80% by weight.

12. The composition of claim 1, wherein said TPS further comprises a plasticizer selected from alcohols, diols, triols, sugar alcohols, polyvinyl alcohol, hydroxy acids, salts of hydroxy acids, hydroxy acid oligomers, salts of hydroxy acid oligomers, low molecular weight polyesteramides, alkyl citrates and mixtures thereof.
13. The composition as claimed in claim 12, wherein said plasticizer is selected from the group consisting of: glycerol, polyethylene glycol, ethylene glycol, sorbitol, acetyltributylcitric acid and triethyleneglycol diacetate.

14. A composition as claimed in claim 1, further comprising a compatibilizer capable of promoting coupling reaction between the biodegradable polyester and the TPS.

15. The composition as claimed in claim 14, wherein said compatibilizer is selected from the group consisting of anhydrides, carboxylic acids, alkyl carbamates, isocyanates, oxazoline and olefins.

16. The composition as claimed in claim 15, wherein said compatibilizer is maleic anhydride (MAH).

17. The composition as claimed in any one of the preceding claims, wherein said biodegradable polyester is selected from the group consisting of: polylactic acid (PLA), polybutylene succinate (PBS), polybutylene adipate co-terephthalate (PBAT), poly (lactic-co-glycolic acid) (PLGA), polycaprolactone (PCL) and polyglycolide (PGA).

18. The composition as claimed in claim 17, wherein said biodegradable polyester is PBAT.

19. The composition as claimed in any one of the preceding claims, wherein said aliphatic-aromatic co-polyester is PBAT.
20. The composition as claimed in any one of the preceding claims, wherein said TPS-polyester co-polymer has a molecular weight of from about 20,000 to about 500,000 Daltons (Da).

21. The composition as claimed in any one of the preceding claims, wherein the weight ratio of TPS to aliphatic-aromatic co-polyester is from about 1:1 to about 10:1.

22. The composition as claimed in claim 21, wherein said TPS to aliphatic-aromatic co-polyester weight ratio is 5:1.

23. The composition as claimed in claim 1, further comprising a free radical initiator capable of promoting grafting, cross-linking and/or coupling reactions between the TPS and the biodegradable polyester.

24. A process for producing a biodegradable film composition comprising:

   providing a thermoplastic starch (TPS) that is grafted, or capable of being grafted, to an aliphatic-aromatic co-polyester;

   blending said TPS with a biodegradable polyester and a chain extender to form a TPS-polyester co-polymer;

   extruding the TPS-polyester co-polymer to produce said biodegradable film composition.

25. The process according to claim 24, characterized in that the weight amount of TPS is
greater than the weight amount of biodegradable polyester.

26. The process of any one of claims 24 or 25, wherein the weight ratio of the biodegradable polyester to TPS is from about 1:1.5 to about 1:4.

27. The process according to any one of claims 24 to 26, wherein said chain extender comprises epoxy-functional (meth)acrylic monomers and at least one of non-functional (meth)acrylic and styrenic monomers.

28. The process according to claim 27, wherein said epoxy-functional (meth)acrylic monomer contains at least two epoxy functional groups.

29. The process according to claim 27, wherein said epoxy-functional (meth)acrylic monomer contains at least three epoxy functional groups.

30. The process according to claim 27, wherein said epoxy-functional (meth)acrylic monomers contain 1,2-epoxy groups.

31. The process according to any one of claims 24 to 30, wherein said chain extender is selected from the group consisting of: glycidyl acrylate, glycidyl methacrylate, glycidyl ethers, glycidyl esters and mixtures thereof.

32. The process according to any one of claims 24 to 31, wherein the amount of said chain extender is in the range of 0.1% to 10% by weight.
33. The process according to any one of claims 24 to 32, wherein the weight amount of said biodegradable polyester is in the range of 20% to 40% by weight.

34. The process according to any one of claims 24 to 33, wherein the weight amount of said TPS is in the range of 50% to 80% by weight.

35. The process according to claim 24, further comprising the addition of a plasticizer selected from alcohols, diols, triols, sugar alcohols, polyvinyl alcohol, hydroxy acids, salts of hydroxy acids, hydroxy acid oligomers, salts of hydroxy acid oligomers, low molecular weight polyesteramides, alkyl citrates and mixtures thereof.

36. The process according to any one of claims 24 to 35, further comprising the addition of a compatibilizer for promoting coupling reaction between the biodegradable polyester and the TPS.

37. The process according to claim 36, wherein said compatibilizer is selected from the group consisting of: anhydrides, carboxylic acids, alkyl carbamates, isocyanates, oxazoline and olefins.

38. The process according to claim 29, wherein said compatibilizer is maleic anhydride.

39. The process according to claim 21, wherein further comprising the addition of a free radical initiator.
40. The process according to claim 24, wherein said biodegradable polyester is selected from the group consisting of: polylactic acid (PLA), polybutylene succinate (PBS), polybutylene adipate co-terephthalate (PBAT), poly (lactic-co-glycolic acid) (PLGA), polycaprolactone (PCL) and polyglycolide (PGA).

41. The process according to claim 40, wherein said biodegradable polyester is PBAT.

42. The process according to claim 24, wherein said aliphatic-aromatic co-polyester is PBAT.

43. The process according to claim 24, characterized in that said TPS-polyester co-polymer has a molecular weight of from about 20,000 Da to about 500,000 Da.

44. The process according to claim 24, wherein the TPS and the biodegradable polyester are in a weight ratio of from about 1:1 to about 10:1.

45. The process according to claim 44, wherein the TPS and the biodegradable polyester are in a weight ratio of from about 5:1.

46. The process according to claim 24, further comprising adding a free radical initiator capable of promoting grafting, cross-linking and/or coupling reactions between the TPS and the biodegradable polyester.
47. A biodegradable film made in a process as claimed in any one of claims 24 to 46.
FIG. 1

Complex Viscosity (Pa·s) vs Angular Frequency (1/s)

FIG. 1A
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

| Int. Cl. | CO8L 67/02 (2006.01) | CO8J 5/18 (2006.01) | CO8B 31/00 (2006.01) | CO8L 3/06 (2006.01) |

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

* 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 database consulted during the international search (name of database and, where practicable, search terms used)

WPI, EPDOC- (THERMOPLASTIC STARCH, ALIPHATIC AROMATIC COPOLYESTER, POLYBUTYLENE ADIPATE TEREPHTHALATE, POLYLACTIC ACID, POLYGLYCOLIC ACID, POLYCAPROLACTONE, DEGRADABLE POLYESTER, POLYBUTYLENE SUCINATE, PLA, PBS, PBAT, PLGA, PGA, PCL, GLICYDYL, EPOXY, CHAIN EXTENDER, ADR 4.3.68)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>(See Abstract; page 2, paragraph 4; page 4, paragraphs 1 &amp; 4; page 5, paragraph 2; page 6, paragraph 2; page 7, paragraph 2; page 9, paragraph 4; page 11, paragraph 4; page 11, last paragraph to page 12, first paragraph; page 14, paragraph 2)</td>
<td>14-16, 23, 36-39 &amp; 46</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C

See patent family annex

Date of the actual completion of the international search: 20 May 2010

Date of mailing of the international search report: 21 MAY 2010

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. +61 2 6283 7999

Authorized officer

BENJAMIN SILVA

AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No: +61 3 9935 961 1
### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 6231970 B1 (ANDERSON et al.) 15 May 2001 (See column 7, lines 5-10; column 11, lines 14-20; column 19, lines 5-7 &amp; 47-50; column 20, lines 47-55; column 22, lines 45-67; column 24, line 45 to column 26, line 20; column 43, lines 10-15; column 45, lines 19-31 &amp; Examples 1 &amp; 30)</td>
<td>1, 3-4, 10-13, 17-22, 24-26, 33-35, 40-45 &amp; 47, 14-16, 23, 36-39 &amp; 46</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>WO 2009053383</td>
<td>DE 102007050769</td>
</tr>
<tr>
<td>US 6231970</td>
<td>AU 15857/01</td>
</tr>
<tr>
<td></td>
<td>CN 1451027</td>
</tr>
<tr>
<td></td>
<td>BR 0016960</td>
</tr>
<tr>
<td></td>
<td>CA 2396973</td>
</tr>
<tr>
<td></td>
<td>EP 1265957</td>
</tr>
<tr>
<td></td>
<td>WO 0151557</td>
</tr>
<tr>
<td>EP 0965615</td>
<td>AU 48994/99</td>
</tr>
<tr>
<td></td>
<td>CN 1312838</td>
</tr>
<tr>
<td></td>
<td>IT TO980524</td>
</tr>
<tr>
<td></td>
<td>MX PA00012859</td>
</tr>
<tr>
<td></td>
<td>US 6348524</td>
</tr>
<tr>
<td></td>
<td>WO 9965990</td>
</tr>
<tr>
<td></td>
<td>CA 2334336</td>
</tr>
<tr>
<td></td>
<td>JU 20010041</td>
</tr>
<tr>
<td></td>
<td>JP 2009185305</td>
</tr>
<tr>
<td></td>
<td>KR 20010052952</td>
</tr>
<tr>
<td></td>
<td>NO 20006410</td>
</tr>
<tr>
<td></td>
<td>US 2002006989</td>
</tr>
<tr>
<td></td>
<td>BR PI0506454</td>
</tr>
<tr>
<td></td>
<td>EP 1812508</td>
</tr>
<tr>
<td></td>
<td>KR 20070012629</td>
</tr>
<tr>
<td></td>
<td>US 7629405</td>
</tr>
<tr>
<td></td>
<td>US 2006111458</td>
</tr>
<tr>
<td></td>
<td>US 7638560</td>
</tr>
<tr>
<td></td>
<td>US 2009160095</td>
</tr>
<tr>
<td></td>
<td>WO 2006055505</td>
</tr>
<tr>
<td></td>
<td>WO 2009073197</td>
</tr>
</tbody>
</table>

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.