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(54) Title: MOULDABLE BIODEGRADABLE POLYMER

(57) Abstract: A biodegradable injection mouldable polymer having the composition a) from 50 to 85% by weight of a starch and or a modified high amylose starch b) from 4 to 13% by weight of a water soluble polymer selected from polyvinylacetate, polyvinyl alcohol and copolymers of ethylene and vinylalcohol which have a melting point compatible with the molten state of the starch components c) from 10 to 35% by weight of a polyol plasticizer d) from 0.5 to 10% of a polyethylene oxide or polyethylene glycol e) from 0 to 1.5 % by weight of a C₁₂₋₂₂ fatty acid or salt and f) from 0.25% to 3% of a food grade emulsifier. The polymers are suitable for biodegradable, flushable tampon applicators and other medical or industrial products where flushability and bio degradability are desirable.



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Mouldable Biodegradable Polymer

This invention relates to improvements in biodegradable polymeric products particularly injection mouldable starch based polymers.

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Background to the invention

There is an increasing demand for many plastic products to be biodegradable. One product that has been the subject of attention is the tampon applicator which conveniently should be water flushable water dispersible and biodegradable.

10 Difficulties have been encountered in producing starch based polymers particularly for injection moulding. The molecular structure of the starch is adversely affected by the shear stresses and temperature conditions needed to plasticise the starch and pass it through the extrusion die. For most products foaming has to be avoided and this generally requires attention because of the water content of the starch. Foaming has been avoided by degassing the melt prior to exiting the die as suggested in USA patents 5314754 and 5316578. The latter patent also avoids adding water to the starch. As explained in USA patent 5569692 by not drying starch and avoiding the addition of water the starch can be processed at temperatures between 120°C and 170 °C because the water bound to the starch does not generate a vapour pressure such as to require high pressures.

20 Another approach to improving the melt processability of starch is to provide an additive as in USA patent 5362777 which reduces the melting point of the starch. The additive is selected from dimethyl sulfoxide, a selection of polyols and amino or amide compounds.

25 USA patent 5043196 discloses a high amylose starch for injection moulding. USA patent 5162392 to an injection moldable corn starch and LDPE biodegradable polymer.

In order to produce starch polymers for particular applications they have been blended with a range of other polymers. Biodegradable blown films are disclosed 30 in USA patent 5322866 which blends raw starch, polyvinyl alcohol and talc with glycerol and water. USA patent 5449708 discloses compositions of starch ethylene acrylic acid and a salt of stearic acid plus a glycerol based lubricant. Flexible and clear transparent sheets are disclosed in USA patent 5374304. These are

composed of a high amylose starch and a glycerol plasticizer. The use of starch in conjunction with high amylose or modified starches has also been proposed. USA patents 5314754, and 5316578 both suggest the use of modified starches including hydroxypropyl substituted starches. Hydroxypropylation reportedly
5 increases elongation at break and burst strength and improved resilience in the polymers.

Patent WO00/36006 discloses biodegradable water soluble formulations using a major amount of modified starch and a minor amount of a water soluble poly vinyl alcohol. These formulations are thermo formable but there are no examples of
10 injection mouldable compositions.

Biodegradable tampon applicators are the subject of a number of patents.

Patent 5759569 discloses trans polyisoprene as biodegradable polymer for diaper top sheets and tampon applicators.

Patent applications 2003/0036721 and 2003/0040695 relate to flushable tampon
15 applicators comprised of polyethylene oxides and other components.

USA patent 5002526 discloses a polyvinyl alcohol tampon applicator.

USA patent 5350354 discloses a tampon applicator composed of starch or modified starch, at least 5% of a plasticizer such as glycerol and water.

USA patent 5804653 to a moldable polyvinyl alcohol composition for tampon
20 applicators.

It is an object of this invention to provide an injection mouldable biodegradable polymer which can be processed have acceptable properties for intended uses such as tampon applicators.

25 **Brief Description of the Invention**

The present invention provides a biodegradable injection mouldable polymer having the composition on a dry weight basis of

- a) from 50 to 85% by weight of a starch and/or a modified high amylose starch
- 30 b) from 4 to 13% by weight of a water soluble polymer selected from polyvinyl alcohol, polyvinyl acetate and copolymers of ethylene and vinyl alcohol which have a melting point compatible with the molten state of the starch components
- c) from 10 to 35% by weight of a polyol plasticizer

- d) from 0.5 % to 10% of a polyethylene oxide or polyethylene glycol
- e) from 0 to 1.5 % by weight of a C₁₂₋₂₂ fatty acid or salt and
- f) from 0.25 % to 3% of a food grade emulsifier

- 5 The compositions defined are suitable for forming injection moulded products including medical devices such as urine sample collectors and tampon applicators. The upper limit to the content of the modified starch is determined by its cost. This component contributes structural benefits to the resulting material including good cohesive and elongational properties, good optical properties, and resistance to
- 10 retrogradation. The term retrogradation has been applied to describe the return to crystallinity by the starch components during storage after the heating and cooling operations. This process is what is generically referred to as staling and explains the hardening (or stiffening) of starch-based foods during extended storage. Hydroxypropylation helps to inhibit crystallinity. Typical modified starches include
- 15 those having an hydroxyalkyl C₂₋₆ group or starch modified by reaction with an anhydride of a dicarboxylic acid. A preferred component is hydroxypropylated amylose. Other substituents can be hydroxyethyl or hydroxybutyl to form hydroxyether substitutions, or anhydrides such as maleic phthalic or octenyl succinic anhydride can be used to produce ester derivatives. The degree of
- 20 substitution (the average number of hydroxyl groups in a unit that are substituted) is preferably 0.05 to 2. The preferred starch is a high amylose maize starch. A preferred component is a hydroxypropylated high amylose starch A939 marketed by Penford Australia. The minimum level of hydroxypropylation used is 6.0%. Typical values are 6.1 to 6.9%.
- 25 For cost savings and for property optimisation reasons one may substitute part of this starch with:
- 1) Higher or lower levels of hydroxypropylation
 - 2) A higher level of unmodified starch. This may be possible in particular if the level of hydroxypropylation of the modified starch is increased;
 - 30 3) A starch modified with octenyl succinic anhydride (OSA), which has a higher degree of hydrophobicity. The addition of this modified starch increases water resistance with increasing degree of substitution. The acetyl linkages in the OSA

starch ensure that the material retains biodegradability upon access to water and a biologically active environment.

4) A starch co-polymer, preferably consisting of a styrene butadiene grafted with starch. This material improves impact resistance of the product.

5 The other starch component is any commercially available starch. This may be derived from wheat, maize, potato, rice, oat, arrowroot, and pea sources. Generally the moisture content (wet basis) is about 5 to 15 %. Unmodified starch is a cheap biodegradable raw material from renewable resources that contributes to the barrier properties of the final product, therefore highly attractive for this application. However, its use is limited by the occurrence of retrogradation (crystallisation resulting in brittleness), limited optical clarity of the resulting formed products, limited film-forming properties and limited elasticity for stretching. High-amylose starch is less sensitive to retrogradation (because it is found to be predominantly associated with the crystallization of Amylopectin within the cooked starch). A preferred concentration range for unmodified starch as a fraction of the total amount of starch is 0 to 50%.

The polymer component b) of the composition is preferably compatible with starch, water soluble, biodegradable and has a low melting point compatible with the processing temperatures for starch. Polyvinyl alcohol is the preferred polymer but polymers of ethylene-vinyl alcohol, ethylene vinyl acetate or blends with polyvinyl alcohol may be used. Water solubility of the selected polymer should preferably not occur at room temperature conditions. PVOH offers a combination of excellent film forming and binder characteristics, good elasticity and aids processing of starch-based formulations. PVA (Polyvinyl Alcohol) is produced by the hydrolysis of polyvinylacetate which is made by the polymerization of vinyl acetate monomer. The fully hydrolyzed grades contain few, if any, residual acetate groups; while partially hydrolyzed grades retain some of the residual acetate groups. Fully hydrolyzed grades dissolve in hot (200°F) water, and remain in solution when cooled to room temperature. Preferred grades of PVOH include DuPont Elvanol 71-30 and Elvanol 70-62. Their properties are listed in Table 1.

Table 1. Properties of PVOH grades used in this invention

Grade	71-30	70-62
Weight Average MWt	93,700	107,000-112,000
Intrinsic viscosity (mPa·s)	27-33	58.0-68.0
Hydrolysis (%)	99.0-99.8	99.4-99.8

The higher molecular weight grade appears to reduce brittleness and potentially also water sensitivity. The maximum level is mainly determined by costs.

Increasing the level of PVOH significantly decreases Young's modulus. Film forming may be difficult below 6%. A preferred concentration range for injection moulding material is 6 to 13%.

The preferred plasticiser is a mixture of polyols, in particular sorbitol, and one or more other polyols particularly maltitol, glycerol, mannitol and xylitol, although erythritol, ethylene glycol and diethylene glycol are also suitable. The plasticizer plays a triple role: it provides suitable rheology for the extrusion compounding process and for the injection moulding process whilst also positively affecting the mechanical properties of the product. Cost, food-contact or skin/mucosal membrane contact are important issues in choosing the appropriate plasticizer. Processing performance, mechanical properties and shelf life of the end product depend on the exact composition of the polyol mixture. At zero or very low water content, the plasticizer content is preferably 10% to 35%, more preferably 20%. Dependent on the type of plasticizer(s) used, the equilibrium moisture content of the injection moulded product, as measured by standard moisture balance method, is around 2-5%.

Sorbitol, Maltitol and Glycerol blends are particularly suitable for modifying the mechanical properties of the formulation, as is Xylitol and blends of Xylitol with Sorbitol and Glycerol. Sorbitol and Xylitol are particularly good humectants. However, when using Glycerol in particular below a certain threshold, an anti-plasticisation may occur, where due to the temporary increased mobility of the polymer chains due to the presence of the plasticiser, crystallisation or at least a high degree of ordering may occur causing an increased stiffness and brittleness of these formulations compared to the un-plasticised starch formulation. Furthermore crystallisation is observed when Sorbitol is used on its own. Some polyols (Sorbitol and Glycerol in particular) may exhibit migration to the surface, where either an opaque crystalline film may form in the case of Sorbitol, or an oily

film in the case of Glycerol. Blending various polyols inhibits this effect to varying degrees. Stabilisation may be enhanced with the addition of glycerol monostearate and sodium stearoyl lactylate as emulsifiers. Furthermore, synergistic effects with salt result in stronger effects on mechanical properties.

- 5 An alternative plasticiser is epoxidised linseed oil at 5% to 10%. This plasticiser, preferably stabilised with an emulsifying system aids processing but does not result in a significant further reduction in Young's modulus.

- Water is present during the compounding process to ensure appropriate starch gelatinization. Excess water may be removed during compounding by means of
10 venting or on/off line pellet drying, and may be further regulated to desired levels prior to injection moulding by means of e.g. hopper drying. The humectant properties of the selected blend of polyols will dictate the suitable and stable moisture content of the product. Depending on the polyol blend utilized, the plasticizer content is preferably 10 to 35% and the water content is 10 to 0%. For
15 highly flexible injection moulding components the plasticizer content is preferably higher than for rigid injection moulding or sheet products.

- The polyethylene oxide and polyethylene glycol alternately or together ensure that the composition is biocompatible and can be used in medical devices that have contact with mucosal tissues, including urine sample collectors and tampon
20 applicators. The preferred polyethylene oxide is one having a molecular weight above 20,000. For medical applications the formulations must pass Cytotoxicity (ISO 10993-5), Sensitisation (ISO 10993-10) and Irritation (ISO 10993.10) tests. A preferred additive is Polyethylene oxide (PEG-5000 with a Mw of 210,000) added at 0.57% or 2 % instead of stearic acid results in zero lysis in the cytotoxicity test and
25 when added at 5 % in addition to stearic acid at 0.57% it also results in zero lysis. Polyethylene oxide and polyethylene glycol alternately or together furthermore provide an increased water resistance to the formulation, to prevent excessive swelling which may result in delamination in particular in multi-layer structures (MLS).

- 30 The fatty acid or fatty acid salt component is preferably present in concentrations of 0.5 to 1.5%. Stearic acid is the preferred component. Sodium and potassium salts of stearic acid can also be used. Again cost can be a factor in the choice of this component but lauric, myristic, palmitic, linoleic and behenic acids are all

suitable. Stearic acid is preferred as a lubricating agent because it has shown better compatibility with starches. As well as stearic acid, the salts such as calcium stearate may be used. The stearic acid appears to migrate to the surface of starch-based polymers.

- 5 It is thought that starch may form complexes with fatty acids. The starch glucopyraniside (glucose) is a six-membered ring in the "chair" configuration. The perimeter of the ring is hydrophilic, while the faces are hydrophobic. The starch chain forms a helix, with about six residues per turn. The result is a hollow cylinder with a hydrophilic outer surface and a hydrophobic inner surface. The inner space
- 10 is about 4.5Å in diameter and straight chain alkyl molecules like stearic acid can fit into it. In the same manner, the fatty acid part of emulsifiers such as GMS can form a complex with gelatinized starch, retarding starch crystallization, thereby slowing the process of staling. The amount of monoglyceride that complexes with amylose (the linear component in starch) and with amylopectin (the branched
- 15 component in starch), is dependent upon the degree of saturation of the fatty acid portion of the emulsifier. Unsaturated fatty acids have a bend produced by the double bond in the fatty acid chain that limits their ability to form a complex. Stearic acid is particularly useful as a processing aid, however in the presence of PEO or PEG it may not be necessary. The choice of appropriate processing aid is
- 20 largely limited by the required resistance to delamination in MLS. The emulsifier is preferably a food grade emulsifier and assists in maintaining the lipid and hydrophilic components homogenously dispersed in the composition. Typically the selection is dependent on the HLB (hydrophilic lipophilic balance) value. The preferred emulsifiers are selected from food grade emulsifiers with HLB
- 25 numbers between 2 and 10 and include Propylene glycol monostearate, Glycerol Monoleate, Glycerol monostearate, Acetylated monoglycerides (stearate), Sorbitan monooleate, Propylene glycol monolaurate, Sorbitan monostearate, Calcium stearoxyl-2-lactylate, Glycerol monolaurate, Sorbitan monopalmitate, Soy lecithin, Diacetylated tartaric acid esters of monoglycerides, Sodium Stearoyl lactylate ,
- 30 Sorbitan monolaurate. Sodium Stearoyl Lactylate and Glycerol Monostearate are commonly used in starch systems.

Table 2. Hydrophobic / Hydrophilic Balance (HLB) Values for some Emulsifiers

	Emulsifier	HLB Value
	Sodium Stearoyl Lactylate (SSL)	21.0
5	Polysorbate 80 (Sorbitan Monooleate)	15.4
	Polysorbate 60 (Sorbitan Monostearate)	14.4
	Sucrose Monostearate	12.0
	Polysorbate 65 (Sorbitan Tristearate)	10.5
	Diacetyl Tartaric Ester of Monoglyceride (DATEM)	9.2
10	Sucrose Distearate	8.9
	Triglycerol Monostearate	7.2
	Sorbitan Monostearate	5.9
	Succinylated Monoglyceride (SMG)	5.3
	Glycerol Monostearate (GMS)	3.7
15	Propylene Glycol Monoester (PGME)	1.8

Glycerol monostearate added at levels ranging from 1-1.5% acts as an emulsifier to stabilise mechanical properties and increase homogeneity of the blend. Sodium Stearoyl Lactylate at 0.25% to 1.5% added to a plasticiser system further stabilizes mechanical properties and increases homogeneity of the blend. Stearoyl Lactylate (as the sodium or calcium salt) is also commonly used as a dough strengthener and may hence act as an anti-retrogradation agent. Combinations of glycerol monostearate and sodium stearoyl lactylate result in faster stabilisation of properties. The HLB value follows the additive rule and is of order 4 to 10 for a suitable mixture of SSL and GMS.

Water is added for the purpose of "gelatinising" (also called deconstructuring or melting) the starch into a polymeric gel structure. Water also may act like a plasticiser in the end-product in that it softens the material or reduces the modulus. The moisture contents of the material may vary at water activities or relative humidities (RH) below 30% or superior to 75%. In many applications, the local RH to which the material is exposed may reach values of up to 90%. For stable mechanical, lamination properties and for ease of processing at all temperatures, non-volatile plasticisers are preferred. Therefore some or all of the water may be dried off during or after the compounding stage and/or in the feeding stage of the

subsequent injection moulding or film forming. This may be achieved with venting the extruder barrel, and/or on-line drying of the pellets. Extrusion processing of unplasticised formulations is possible with water concentrations as low as 10% and formulations with Polyol plasticisers may be dried to 0% free water before injection moulding. The preferred moisture content is the equilibrium moisture content of the formulation at the in-use RH range of the end product as determined by moisture sorption experiments. This depends on the specific composition of the formulation but is in the range of 3-12%.

For a tampon applicator a more preferred formula on a dry weight basis is

- a) from 50 to 70% by weight of starch, of which 50-100% is modified
- b) from 5 to 13% by weight of a water soluble polymer selected from polyvinylacetate, polyvinyl alcohol and copolymers of ethylene and vinylalcohol which have a melting point compatible with the molten state of the starch components
- c) from 15 to 35% by weight of a polyol plasticizer
- d) from 0.5 to 5% of a polyethylene oxide of molecular weight above 20,000
- e) from 0 to 1 % by weight of a C₁₂₋₂₂ fatty acid or salt and
- f) from 0.25% to 1.5% of a food grade emulsifier

The moisture content of the tampon applicator is about 2 to 4 %.

Detailed description of the invention

In the drawings:

Figure 1 illustrates mechanical properties as a function of the type of plasticiser;

Figure 2 illustrates mechanical properties as a function of the amount of plasticiser;

Figure 3 illustrates the Young's modulus as a function of amount of PVOH;

Figure 4 illustrates the Elongation at break as a function of amount of PVOH;

Figure 5 illustrates the equilibrium moisture content of injection moulded tensile bars as a function of granulate moisture content.

A preferred formulation will be described with reference to a preferred application of the formulation to products such as tampon applicators which need to be injection moulded in large quantities and be inexpensive, disposable by means of the waste water system (e.g. flushing), suitable for food contact or medical devices

and biodegradable. Formulations meeting all these criteria are not currently available in the market.

Tampon applicators are usually made by injection moulding low density polyethylene (LDPE) in a multi cavity tool typically with more than 100 cavities.

- 5 Tampon applicators are usually a two part product comprising a barrel with an optional rounded tip consisting of flexible wings that open up when the tampon is pushed forward and an inner plunger which are assembled with the tampon and packed in flow wrap. The typical desirable mechanical properties for the polymer to be used in a tampon applicator are Young's modulus less than 400MPa, elongation at break greater than 30% and tensile stress at break greater than 10 MPa. The applicator should not show instantaneous tackiness on contact with water and should be resistant to mould growth.

- 15 A preferred tampon applicator contains 55 to 65 % of hydroxypropylated high amylose starch; 11 to 13% polyvinyl alcohol; 18 to 21 % of a polyol mixture containing sorbitol, and at least two of maltitol, glycerol and xylitol; 1.5 to 2.5% of polyethylene oxide with a molecular weight in the range of 100,000 to 400,000; 0.5 to 1.5% of glycerol monostearate and sodium stearyl lactylate; 0.7 to 0.9% of stearic acid.

- 20 Based on cost and performance considerations a suitable formulation for a tampon applicator is (on dry and wet basis):

Table 3

Hydroxy propylated high-amylose starch	Polyol plasticizer mixture	PVOH	PEO	Glycerol monostearate	Stearic Acid	Sodium stearyl lactilate	Moisture Content
63.5%	19.8%	12.7%	1.98%	0.99%	0.79%	0.25%	Dry basis
62.8%	19.6%	12.6%	1.96%	0.98%	0.78%	0.25%	3% Injection moulding product
58.36%	18.2%	11.7%	1.82%	0.91%	0.73%	0.23%	10% max granulate moisture content

- 25 In this formulation the polyol composition is preferably [Sorbitol] > 2[Maltitol] ≥ [Glycerol]. Dependent on the composition of plasticizer(s) used, the equilibrium moisture content of the injection moulded product, as measured by standard

moisture balance method, is of order 2-5%, see Figure 5. This equilibrium is reached within 24h, or even instantly after processing, as long as the granule moisture content is below 10%. This formulation has a Young's modulus of 165 MPa, a stress at break of 13.7 MPa, and an elongation at break of 112%.

- 5 The applicators are biodegradable and have strength and flexibility properties comparable to the non biodegradable materials currently used. The costs of production are also comparable.

The material is manufactured by means of extrusion compounding, using co- or counter-rotating twin screw or selected design single screw extruders. The
10 preferable process is twin screw co-rotating compounding, with an extrusion pressure of at least 20 Bar and with a screw speed of at least 100 RPM. Water may be added to the process (by means of liquid injection together with the plasticisers) dependent on the level and nature of other plasticisers. Removal of water may be carried out by means of convective drying for the extrudate strands,
15 a centrifuge and a fluidised bed for granulate, or barrel venting or both. Granulate may be obtained by means of underwater pelletising, die face cutting or strand cooling and cutting.

A suitable process involves compounding and injection moulding in tandem, where the extrudate is accumulated in a shooting pot and injected into the mould. Here
20 the injection moulder inlet moisture content is optimised for best processing conditions and minimal shrinkage.

If required, further drying of the injection moulded parts may occur in a drying tunnel, drum, or fluidised bed.

The material may be injection moulded using conventional screw driven or
25 injection driven processes with hot or cold runner systems. The viscosity of the formulation given above is comparable or lower than that of LDPE at shear rates typical for the injection moulding process. This means that pressures for multi-cavity processing will be comparable to the conventional process. For single-cavity injection moulding conditions for selected formulations of this invention, injection
30 pressures are of order 50-500 Bar, barrel temperatures 90-180°C, nozzle temperature 80-120°C, mould temperature 25-90°C. The other key aspect affecting injection moulding efficiency is cycle time which is dominated by the time taken for the part to become sufficiently solidified after moulding. The low processing

temperature for the formulations of this invention, and the absence of an actual molten state, results in short solidification time, hence short cycle time comparable to polyethylene. This makes the formulation suitable for high volume injection moulding operations.

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Control Example To illustrate how the formulations of this invention achieve properties specific for the application of this invention, the listed Examples are compared to a Control example which is a biodegradable starch-PVOH based material suitable for thermoforming applications, described in patent specification WO00/36006.

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Example 1 A formulation was developed which contained the same grades and relative proportions of starch, PVOH and stearic acid as the "Control" formulation but 23% plasticizer (on dry basis). The plasticizer system consist of a mixture of glycerol, maltitol and sorbitol in the ratios 3.3:1.5:1. In addition this formulation contains 1% of a polyethylene oxide for biocompatibility and 1.7% glycerol monostearate as emulsifier. It meets all the mechanical property requirements for the tampon applicator, as illustrated in Table 5.

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Example 2 The second formulation is identical to Example 1 with the exception of the composition of the plasticizer, which consists of glycerol, maltitol and sorbitol in ratios 4.3:1:3.5. This significantly higher sorbitol level results in a higher Young's modulus as illustrated in Table 4.

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Example 3 The Control formulation is not suitable for tampon applicators, because it fails the Cytotoxicity test required to ensure biocompatibility to the level required of a medical device class IIA. In this Example, stearic acid which is instrumental in the cytotoxicity was removed and PEO added at a level of 0.6%.

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Example 4 Also developed to verify the determining factors in cytotoxicity, this Example has a 5.5% level of PEO, whilst maintaining the same level of stearic acid as the Control formulation.

Example 5 For comparative purposes with the Control, Example 3 and Example 4 this formulation contains no stearic acid, and a 2% level of PEO. The biocompatibility of these formulations is discussed later and tabulated in table 8. Furthermore this formulation is comparable to Example 2, except for a higher level of PVOH. The ratio PVOH to (dry) starch is 0.20 compared to a ratio of 0.11 for

30

Example 2. This results in a significant reduction in Young's modulus, and a significant increase in elongation at break, as illustrated in Figure 3 and Figure 4 respectively and in Table 4.

Example 6 This formulation is plasticized to 21% with the Glycerol, Maltitol, Sorbitol, mixture of Example 1. It contains an emulsifier system of 1% GMS and 0.28% SSL, and 0.5% PEO. It meets all the mechanical property requirements for the tampon applicator, as illustrated in Table 5.

Example 7 This formulation is comparable to Example 1, except for a higher level of PVOH. The ratio PVOH to (dry) starch is 0.23 compared to a ratio of 0.11 for Example 1. This results in a significant reduction in Young's modulus, and a significant increase in elongation at break, as illustrated in Figure 3 and Figure 4 respectively and in Table 4.

Example 8 This formula is plasticized to 32% with the polyol mixture of Example 1. The higher level of plasticization significantly reduces the Young's modulus, the tensile strength, and increases elongation at break dramatically. The properties are stabilized with a GMS/SSL mixture at 1% and 0.25% respectively, and cytotoxicity is overcome by 1% PEO.

Example 9 The following three examples were developed to quantify the dependence of mechanical properties on the level of plasticizer used, illustrated in Figure 2 and Table 4. The plasticizer polyol mixture is that of Example 1. This formula contains 14% plasticizer. The GMS/SSL emulsifier is incorporated at a 0.3%/0.1% level, PVOH at the same ratio as the Control example and no PEO is added.

Example 10 This formula has the same PVOH/Starch ratio, and the same type and level of emulsifier, and the same type of plasticizer as Example 9, but with a plasticizer level of 23% instead of 14%. At the equilibrium 4% moisture content, the resulting tensile test bars meet all the mechanical property requirements for the tampon applicator, as illustrated in Table 5.

Example 11 This formula has the same PVOH/Starch ratio, and the same type and level of emulsifier, and the same type of plasticizer as Example 9, but with a plasticizer level of 32%. This formulation is also comparable to Example 8, except for a lower level of PVOH. The ratio PVOH to (dry) starch is 0.11:1 compared to a ratio of 0.18 for Example 8. This results in a significant reduction in Young's

modulus, and a significant increase in elongation at break, as illustrated in Figure 3 and Figure 4 respectively, and in Table 4.

Example 12 The following four examples were developed to quantify the dependence of mechanical properties on the type of polyol plasticizer used, illustrated in Figure 1 and table 4. The GMS/SSL emulsifier is incorporated at a 1%/0.25% level. The PVOH to starch ratio is 0.21, and no PEO is added. Each of the four formulas contains 35% plasticizer (on dry basis). The plasticizer polyol mixture in this formulation consists of a Glycerol, Maltitol, Sorbitol mixture with ratios 4:2:1. As discussed later and tabulated in table 6, these formulations show a different humectant behaviour, which is believed to be instrumental in the mechanical properties and their stability.

Example 13 To compare polyol plasticizers this material contains 35% Sorbitol. Sorbitol is the strongest humectant of the three compared plasticizer systems, resulting in the lowest moisture loss measurement at 130°C as shown in Table 6. The humectant behaviour as well as the higher melting temperature of Sorbitol results in the highest Young's modulus, as illustrated in Figure 1. It meets all the mechanical property requirements for the tampon applicator, as illustrated in Table 5. However, pure sorbitol exhibits a bloom effect, causing an opaque white crystalline layer on the injection moulded object surface, which may be eliminated by mixing sorbitol with minor amounts of maltitol and glycerol as in the preferred formulation of this invention.

Example 14 To compare polyol plasticizers this material contains 35% Xylitol.

Example 15 To compare polyol plasticizers this material contains 35% Glycerol.

Advantageous properties of this formulation that make it particularly suitable for ISO standard 10993 class 2A medical devices such as tampon applicators are:

1. Low Youngs Modulus (<400MPa)

The stiffness of the material may be manipulated with the level and composition of polyol plasticiser and may range from 1145 MPa for unplasticised formulations, to 10 MPa for the examples with the highest levels of plasticiser. This makes these grades suitable for a wide range of injection moulding applications.

As shown in Table 4, using a range of plasticiser systems, the Young's modulus (of compression moulded dogbones) has been reduced significantly from the base case formulation, which only contains water as plasticizer (Test method ASTM638).

5

Table 4 . Mechanical properties of plasticised formulations

Example	PVOH / starch ratio	Emulsifier		Plasticiser system				PEO	Young's Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)		
		(% wt on dry basis)											
		GMS	SSL	Glycerol	Maltitol	Sorbitol	Other						
control	0.12								mean (stdev)				
1	0.11	1.7%		13%	6%	4%		1%	1145 (143)	24.8 (4.5)	29.2 (5.1)		
2	0.11	1.7%		11%	2.6%	9%		1%	375 (12)	9.6 (0.3)	36 (10.7)		
5	0.20	1.1%		11%	2.6%	9%		2%	449 (13)	10.5 (0.5)	30.1 (8.5)		
6	0.12	1.1%		11%	2.6%	9%		2%	230 (16)	6.9 (0.1)	117 (7.3)		
7	0.12	1.1%	0.28%	12%	5%	3.5%		0.5%	111 (6.2)	11.1 (0.8)	186 (24)		
8	0.23	1.1%		13%	6%	4%		2%	53.6 (6.5)	8.8 (0.5)	284 (38)		
9	0.18	0.9%	0.23%	19%	8%	6%		1%	10.6 (1.2)	4.5 (0.1)	389 (29)		
10	0.11	0.3%	0.1%	8%	3.5%	2%			418 (2.3)	18.4 (0.6)	101.5 (5.1)		
11	0.10	0.3%	0.1%	13%	6%	4%			103 (11)	8.1 (0.4)	105 (5.4)		
12	0.11	0.3%	0.1%	18%	8%	5%			42.9 (7.6)	5.4 (0.2)	127 (7.6)		
13	0.21	1.0%	0.25%	20%	10%	5%			19.3 (1.5)	6.4 (0.3)	254 (34)		
14	0.21	1.0%	0.25%			35%			74.5 (5.9)	11.8 (0.2)	291 (22)		
14	0.21	1.0%	0.25%			Xylitol	35%		49.4 (5.5)	8.3 (0.3)	336 (20)		

10 2. Strain at break (> 30%)

The extensional behaviour of the material may be manipulated with the level of plasticiser and may range from 30% minimum, for unplasticised formulations, to 390% for the examples with the highest levels of plasticizer and PVOH. This makes these grades suitable for a wide range of injection moulding applications.

15

3. Tensile strength (> 10MPa)

The tensile strength of the material may be manipulated with the level of plasticiser and may range from 4.5MPa for highly plasticised formulations to 25MPa for the examples with low levels or zero plasticizer. Hence, grades may be prepared suitable for a wide range of injection moulding applications.

20

Table 5 summarises the formulations that meet all the mechanical property requirements simultaneously. Here the listed moisture contents is measured using a Perkin elmer HB43 moisture balance at 130°C after conditioning the specimens for 40h as per ASTM638.

25

Table 5. Formulas that meet mechanical requirements for tampon applicator

Example	MC (%) ¹	Young's Modulus (MPa) mean (stdev)	Tensile strength (MPa) mean (stdev)	Elongation at break (%) mean (stdev)
Example 1	3.0%	375 (12)	9.6 (0.3)	36 (10.7)
Example 6	2.5%	111 (6.2)	11.1 (0.8)	186 (24)
Preferred formula	3.3%	165 (31)	13.7 (2.6)	112 (9.5)
Example 10	1.8%	84.9 (11)	10.2 (0.4)	232 (27)
Example 13	1.4%	74.5 (5.9)	11.8 (0.2)	291 (22)

An issue with starch-based polymers has been in the past that mechanical properties alter over time, as a result of moisture loss and/or crystallisation effects. Many of the compositions developed here show sustainable, non-hardening, mechanical properties. The time required for reaching equilibrium properties depends on the drying stages in the process as well as the plasticizer and emulsifier system used, and its humectant properties. Table 6 illustrates the superior humectant properties of the plasticizer system used in Example 13 (Sorbitol) and Example 14 (Xylitol) compared to Example 12 (mixture of glycerol>maltitol>sorbitol) and Example 15 (Glycerol). The table shows the measured moisture contents by means of a halogen moisture balance at 130°C, compared to the actual water content in the compounded formulas, which were not dried for the purpose of this test.

Table 6. Moisture loss at 130°C of undried granulates with different humectant composition

Example	Plasticiser at 35%	Moisture content in compounded formula (%)	Measured moisture loss (%)
Example 12	Glycerol/Maltitol/Sorbitol	17.58%	16.55%
Example 13	Sorbitol	18.82%	5.53%
Example 14	Xylitol	20.13%	7.83%
Example 15	Glycerol	18.76%	16.72%

A combination of barrel venting and granulate drying is recommended to reach equilibrium moisture content in the injection moulded part on-line. Formulations made without granulate drying/venting show a significant hardening within the first 100h. Any subsequent hardening would then be due to crystallisation and/or antiplasticisation effects. Formulations with the preferred polyol composition processed at the appropriate moisture contents do not show aging of mechanical properties, as shown in Table 7. Any observed changes do not follow repeatable

trends across the Examples, and are most likely due to the small sample size and the experimental scale of the part manufacture.

Table 7. Mechanical property stability as function of storage conditions

	Example 9	Example 10	Example 11
Temperature	23°C	37°C	23°C
Time lapse	2 months	3 weeks	2 months
Change in Tensile Strength (MPa)	2.80	0.17	1.01
Tensile Strength (% change)	18%	2%	14%
Change in Elongation at Break (%)	2.53	-4.12	-13.0
Elongation at Break (% change)	3%	-3%	-11%

4. Shrinkage comparable to conventional LDPE

Shrinkage of injection moulded tensile test bars was observed. Many formulations showed comparable or lower shrinkage than for LDPE, even before any process optimisation. Others showed higher shrinkage and would require further optimization, but shrinkage behaviour was found controllable for all grades.

Example Shrinkage (machine direction)

Example 6	6.6% $\pm$ 1.3% (N=11)
Example 12	4.5% $\pm$ 0.5% (N=40)
Example 14	2.9% $\pm$ 0.4% (N=9)
Example 13	2.6% $\pm$ 0.2% (N=10)

5. Biodegradable

The compositions of this invention are biodegradable and compostable according to international standards, in particular EN13432:2000 for commercial composting facilities and waste water management systems. Biodegradation tests were carried out according to EN13432 requirements, in particular ISO 14855 in compost and ISO 14851 or ISO 14852 in aqueous medium. EN13432-specified disintegration tests demonstrated the required levels of disintegration in simulated conditions for commercial composting.

6. Flushable

The compositions of this invention disintegrate substantially in simulated conditions for waste water treatment and may therefore be considered flushable. Two example materials (control formula as a 1mm thick sheet and formula Example 5

as a 1mm thick injection moulded part) were tested for flushability in comparison to toilet paper.

For flushability testing, a modified version of standard method CEN TC 249 WI 249510 ("Plastics — Evaluation of disposability in waste water treatment plants —

- 5 Test scheme for final acceptance and specifications") was used. Modifications to the method were: a) Sample drying was eliminated because complete drying of natural materials may change the microstructure and hence moisture sorption behaviour of the material; b) Different vessel and agitation conditions were used to better mimic the turbulent conditions experienced by flushed materials; c) The
- 10 residue collected on the sieve was washed with excess water to better replicate the screening procedures at waste treatment plants. A 'flushability factor' was defined as the fraction of material that passes a 10mm mesh sieve after 16 hours agitation in water.

- It was found that both the Control and the formula of Example 5 achieved a
- 15 flushability factor of 1.0, indicating that these materials may be considered flushable.

7. Biocompatible

- Biocompatibility testing was conducted as required for medical devices of Class 2A according to ISO standard 10993 "Biological evaluation of medical devices". This
- 20 class represents devices suitable for contact with mucosal membranes with single or multiple use or contact likely to be up to 24 h. Devices of this type must pass the following tests:

Cytotoxicity (ISO 10993-5)

- With the use of cell culture techniques, these tests determine the lysis of cells (cell
- 25 death), the inhibition of cell growth, and other effects on cells caused by medical devices, materials and/or their extracts. There are two methods that may be used to determine Cytotoxicity. One is the ISO Elution method, the other an Agar Overlay method. The former is a more sensitive test and was used for the evaluation of this invention.

- 30 **Sensitisation (ISO 10993-10)**

These tests estimate, using an appropriate model, the potential of medical devices, materials and/or their extracts for contact sensitization. These tests are appropriate because exposure or contact to even minute amounts of potential leachables can

result in allergic or sensitization reactions. Sensitization tests are described in ISO 10993-10.

The formulations of this invention comply with this test.

Irritation (ISO 10993-10)

- 5 These tests estimate the irritation potential of medical devices, materials and/or their extracts, using appropriate sites for implant tissue such as skin, eye and mucosal membrane in a suitable model. Irritation tests are described in ISO 10993-10.

Biodegradable starch-PVOH material (Control) is not biocompatible, in that it fails
10 the cytotoxicity test, likely due to the effect of stearic acid which acts as a surfactant on the exposed cells. In order to ensure biocompatibility of the formulations of this invention, polyethylene oxide (or polyethylene glycol) was added at various levels and is shown to be effective both in the presence and absence of stearic acid. Table 8 summarises the formulation Examples that were
15 submitted to biocompatibility testing.

Table 8. Biocompatibility test results

Example	Stearic acid (%wt dry basis)	PEO (%wt dry basis)	Cytotoxicity	Irritation	UPS Systemic toxicity
Control	0.6%	0%	fail	pass	pass
Example 3	0%	0.6%	pass	Not carried out	
Example 4	0.6%	5.5%	pass		
Example 5	0%	2.1%	pass		

The Cytotoxicity test was passed by the formulation Example 3, Example 4 and Example 5 of this invention (ISO Elution method IX Minimal Essential Media Extract (MEM) which is conducted at 37°C). Furthermore, the Irritation test, and a
20 USP systemic toxicity test in mouse, which was suggested to us as a screening test for the Sensitisation test, was passed by the control formulation of this invention, which does not include additives intended to increase biocompatibility, therefore it was not deemed necessary to test the biocompatibilised Example 3, Example 4 and Example 5.

25 **8. Low cost.**

The current formulations are significantly lower in cost than any biodegradable materials that meet some of the key criteria for this application, and not inhibitive more expensive to current non biodegradable or non-flushable tampon applicators (at most a factor 2-3 compared to current LDPE prices). This kind of formulation
30 does not experience the level of price fluctuation that oil-derived polymers do.

The combination of low Young's modulus, high elongation at break, suitable tensile strength, biocompatibility, biodegradability, flushability and injection mouldability make these formulations ideally suitable for pharmaceutical and hygiene devices such as tampon applicators.

- 5 The performance and appearance of tampon applicators are acceptable and as good as conventional non – biodegradable applicators. Whilst not qualified at this stage, the material has a softer, more natural, feel than many conventional polymers. The significant advantage of the applicators made from the composition of this invention is that disposal is much simpler, more convenient and hygienic.
- 10 From the above description and examples it can be seen that the present invention provides a biodegradable starch polymer that is comparable in price and performance characteristics to conventional non-biodegradable injection moldable polymers. Consequently tampon applicators can be just as presentable and attractive with the added benefit of being environmentally friendly.
- 15 Those skilled in the art will realize that although the present invention has been illustrated in relation to tampon applicators the injection moulding compositions of this invention can also be used for other applications by tailoring the specific composition content to the desired properties of the product. The composition may be used to mould other medical or food associated products, including cotton
- 20 buds, urine collection aids, cutlery, scoops and spatulas where flushability and biodegradability are desirable. These properties also make the composition useful in products which currently represent a litter or waste management problem including toilet roll cores, toilet brush heads, clips and ties used in packaging, oesophagus clips used in meat processing, temporary sewer plugs in buildings,
- 25 inert ammunition simulators, mosquito repellent buckets.

CLAIMS

1. A biodegradable injection mouldable polymer having the composition on a dry weight basis of
 - a) from 50 to 85% by weight of a starch and/or a modified high amylose starch
 - 5 b) from 4 to 13% by weight of a water soluble polymer selected from polyvinylacetate, polyvinyl alcohol and copolymers of ethylene and vinylalcohol which have a melting point compatible with the molten state of the starch components
 - c) from 10 to 35% by weight of a polyol plasticizer
 - 10 d) from 0.5 to 10% of a polyethylene oxide or polyethylene glycol
 - e) from 0 to 1.5 % by weight of a C₁₂₋₂₂ fatty acid or salt and
 - f) from 0.25% to 3% of a food grade emulsifier
2. A composition as claimed in claim 1 or claim 2 wherein component b) is a
15 polyvinyl alcohol.
3. A composition as claimed claim 1 wherein the polyol plasticiser is a mixture sorbitol and at least one other polyol.
- 20 4. A composition as claimed in claim 3 in which the other polyol is selected from the group consisting of glycerol, maltitol, xylitol, erythritol, mannitol, ethylene glycol, diethylene glycol, and polyethylene glycol.
5. A composition as claimed in claim 1 in which component d) is a polyethylene
25 oxide with a molecular weight in the range of 100,000 to 400,000.
6. A composition as claimed in claim 1 in which the food grade emulsifier has a hydrophobic lipophilic balance number from 2 to 10.
- 30 7. A composition as claimed in claim 6 in which the emulsifier is selected from glycerol monostearate, sodium stearyl lactylate or mixtures thereof.
8. A composition as claimed in claim 1 in which component e) is stearic acid.

9. A medical device formed by injection molding a composition as defined in claim 1 and which has a final moisture content of 2 to 3% by weight.
- 5 10. A tampon applicator made by injection moulding having a composition on a dry weight basis of
- a) from 50 to 70% by weight of starch, of which 50-100% is modified
 - b) from 5 to 13% by weight of a water soluble polymer selected from polyvinylacetate, polyvinyl alcohol and copolymers of ethylene and
 - 10 vinylalcohol which have a melting point compatible with the molten state of the starch components
 - c) from 15 to 35% by weight of a polyol plasticizer
 - d) from 0.5 to 5% of a polyethylene oxide of molecular weight above 20,000
 - e) from 0 to 1 % by weight of a C₁₂₋₂₂ fatty acid or salt and
 - 15 f) from 0.25% to 1.5% of a food grade emulsifier
11. A tampon applicator as claimed in claim 10 which contains 55 to 65 % of an hydroxypropylated high amylose starch; 11to 13% polyvinyl alcohol; 18 to 21 % of a polyol mixture containing sorbitol, and at least two of maltitol,
- 20 glycerol and xylitol; 1.5 to 2.5% of polyethylene oxide with a molecular weight in the range of 100,000 to 400,000; 0.5 to 1.5% of glycerol monostearate and sodium stearyl lactylate; 0.7 to 0.9% of stearic acid.
12. A tampon applicator as claimed in claim 11 in which the product has a
- 25 moisture content of 2-4 %.
13. An Injection moulded product having a composition as claimed in claim 1 which has a Young's modulus between 70 MPa and 400 MPa, a tensile strength between 8 MPa and 15 MPa and an elongation at break between
- 30 30% and 300%.

14. A tampon applicator as claimed in claim 11 which has a Young's modulus between 160MPa and 200MPa, a tensile strength between 10 and 15 MPa and an elongation at break between 50 and 150%.
- 5 15. A tampon applicator as claimed in claim 11 which is biodegradable in waste water and disintegrates so as to not negatively impact waste water management systems

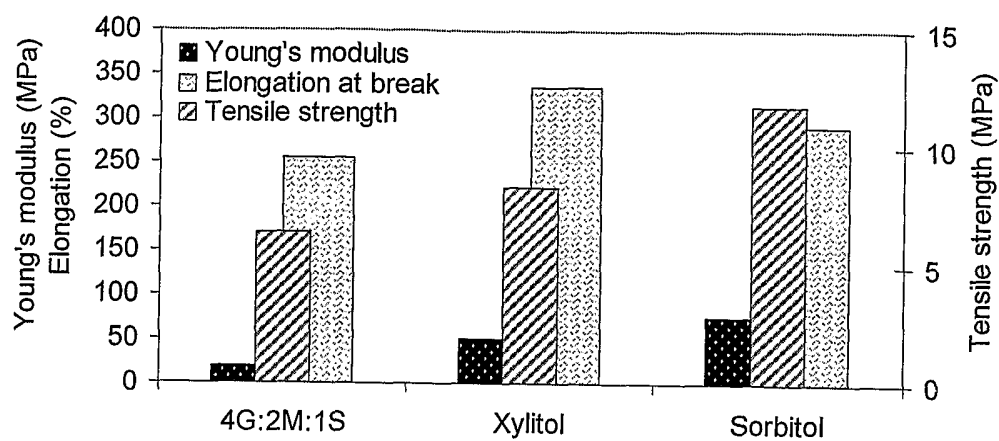


Figure 1

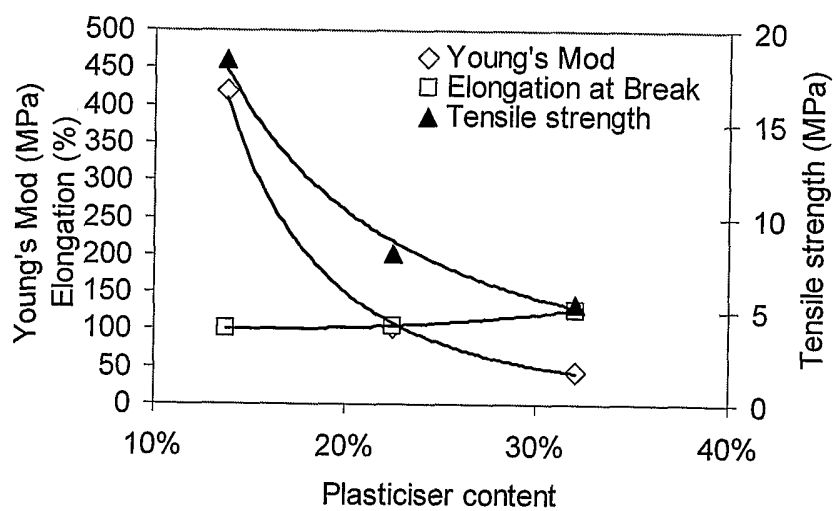


Figure 2

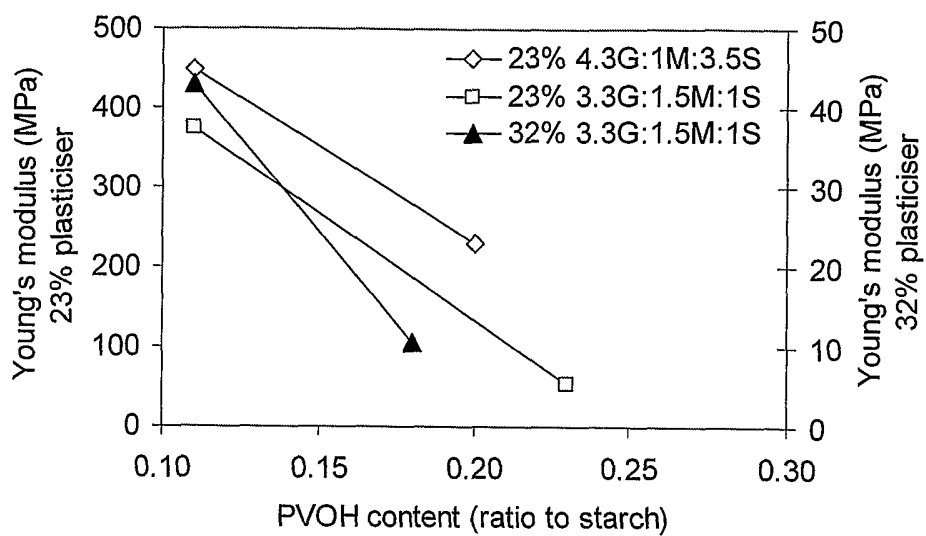


Figure 3

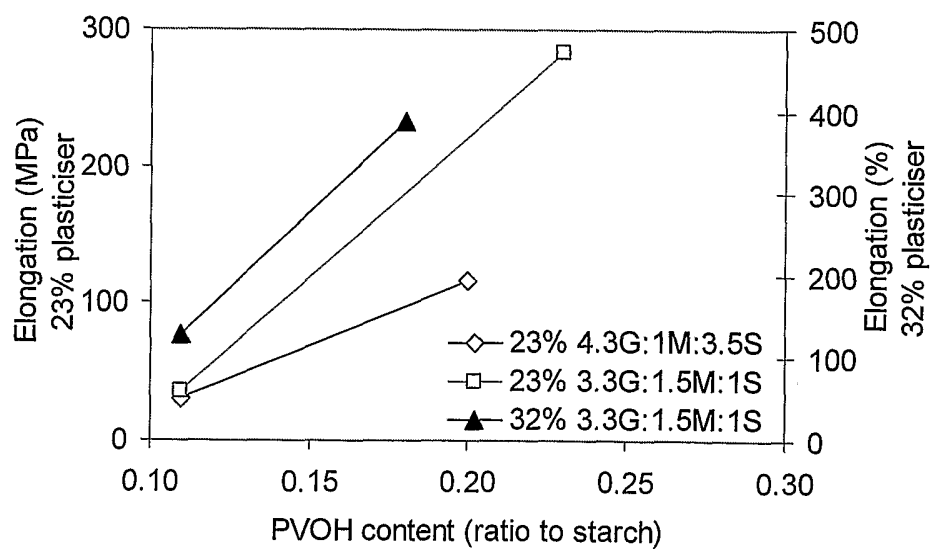


Figure 4

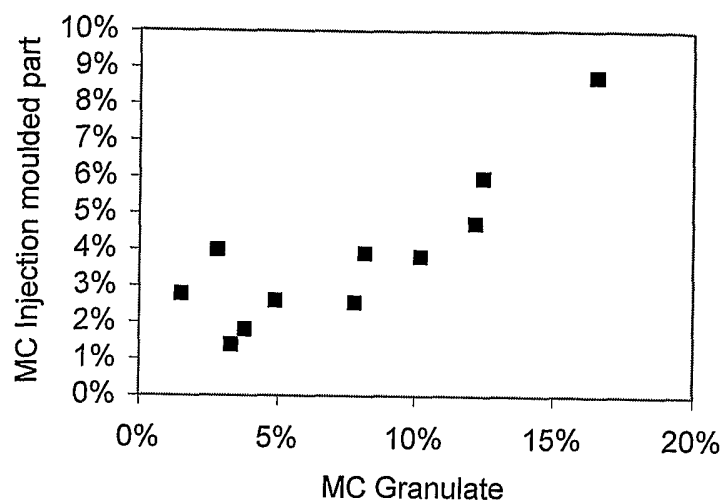


Figure 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2005/001507

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ⁷: C08L 3/02, 3/04; A61F 13/26, 13/15; A61L 15/62; C08L 3/12, 3/14

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: WPAT JAPIO; C08L 3/02, 3/04, 3/06, 3/08, 3/12, 3/14; A61F 13/26, 13/15; A61L 15/62; key words: starch, polyvinyl, plasticizer, polyethylene oxide, stearate, lactylate, oleate, tampon applicator; STN: CaPlus key words: starch, polyvinyl, plasticizer, polyethylene oxide, stearate, lactylate, oleate, tampon applicator

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, Y	WO 2002/074352 A (THE PROCTOR & GAMBLE COMPANY) 26 September 2002 page 17, lines 11-21; page 33, lines 14-36; claims	1-15
X, Y	EP 635545 A (AIR PRODUCTS AND CHEMICALS, INC.) 25 January 1995 page 4, lines 9-19, 30-32; claims	1-15
X, Y	WO 1992/016583 A (PARKE, DAVIS & COMPANY) 1 October 1992 page 17, lines 24-39; page 14, lines 25-29; page 15, lines 7-8; page 16, line 24; page 17, lines 24-39; page 23, line 10 – page 24, line 9; claims	1-8, 9-15
X, Y	US 5393804 A (GEORGE et al.) 28 February 1995 col. 4, lines 7-36; col. 9, lines 1-17, 38-51; claims	1-8, 9-15

☒ Further documents are listed in the continuation of Box C

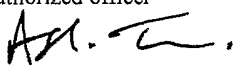
☒ See patent family annex

* Special categories of cited documents:	
"A" 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
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"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
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Date of mailing of the international search report
 24 NOV 2005

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2005/001507

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5512090 A (FRANKE et al.) 30 April 1996 col. 3, lines 8-10; claims	1-8
Y	US 5462981 A (BASTIOLI et al.) 31 October 1995 col. 3, lines 39-53; col. 5, lines 38-42; claims	1-8
Y	WO 2000/036006 A (FOOD & PACKAGING CENTRE MANAGEMENT LIMITED) 22 June 2000 whole document	1-8
Y	WO 1994/003543 A (NOVAMONT S.P.A.) 17 February 1994 page 3, line 20 – page 4, line 13; page 8, lines 5-23; page 9, lines 2-9; claims	1-8
Y	US 5350354 A (BILLMERS) 27 September 1994 col. 3, lines 50-55; claims	1-8
Y	US 6231970 B (ANDERSEN et al.) 15 May 2001 col. 10, lines 16-21; col. 25, lines 14-17; col. 27, lines 30-32; col. 28, lines 28-31; claims	1-8
A	US 5316578 A (BUEHLER et al.) 31 May 1994 col. 3, lines 20-45; col. 4, lines 33-41; claims	1-15
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A	WO 2002/083784 A (FOOD & PACKAGING CENTRE MANAGEMENT LIMITED) 24 October 2002 whole document	1-15
A	EP 613672 A (TAMBRANDS, INC.) 7 September 1994 whole document	1-15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2005/001507

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			
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		BR 9205783	CA 2105479	CA 2105480	
		CN 1066077	CN 1067253	EP 0578759	
		EP 0581843	FI 934094	FI 934095	
		HU 66562	HU 66717	IE 920854	
		IE 920855	MX 9201222	NO 933335	
		NO 933336	PT 100265	PT 100266	
		WO 9216584	ZA 9201958	ZA 9201959	
US 5393804		AU 56780/94	CA 2149139	CN 1089279	
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		ID 28986	NZ 512241	PL 348243	
		SK 7842001	US 2004242732		
WO 9403543		AU 44186/93	CA 2141562	EP 0652910	
		HK 1013302	US 5874486	US 6277899	
US 5350354		CA 2030716	EP 0438672		
US 6231970		AU 15857/01	BR 0016960	CA 2396973	
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2005/001507

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		FI	921264	NO	921139	PL	291195
		TR	25856	WO	9201743	ZA	9105770
WO	9831523	AU	22429/97	EP	0954422	EP	1354685
WO	02083784	EP	1392770	US	2004122135		
EP	0613672	NONE					

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

END OF ANNEX