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(54) Titre : COMPOSITIONS BIODEGRADABLES TRAITABLES A LA CHALEUR ET ARTICLES EN CONTENANT
(54) Title: MELT PROCESSABLE BIODEGRADABLE COMPOSITIONS AND ARTICLES MADE THEREFROM

(57) Abrégé/Abstract:
The invention presents classes of thermoplastic, biodegradable compositions. Tests indicate that these compositions exhibit good mechanical properties, and readily degrade in the presence of microorganisms. The compositions of this invention are useful for producing injection-molded, thin-walled articles that are capable of appreciably degrading in the sewage system within thirty (30) days.

ABSTRACT

The invention presents classes of thermoplastic, biodegradable compositions. Tests indicate that these compositions exhibit good mechanical properties, and readily degrade in the presence of microorganisms. The compositions of this invention are useful for producing injection-molded, thin-walled articles that are capable of appreciably degrading in the sewage system within thirty (30) days.

Melt Processable Biodegradable Compositions and Articles Made Therefrom

Background of the Invention

This invention is related to the development and use of environmentally friendly materials that can alleviate the growing environmental problem of excessive trash. This invention relates to the development of compositions that degrade rapidly by microorganisms. These compositions can be used in a variety of consumer disposable products. For example, the materials can be fabricated into films, fibers and molded parts for the manufacturing of disposable products such as diapers, sanitary napkins, adult incontinence products, and particularly tampon applicators.

Many natural polymers are known to degrade rapidly by microorganisms but most of them are not useful in fabricating articles because they lack the properties typical to plastic materials. In addition, they are not melt processable. One such material is natural starch. Being cheap and readily available, starch has become the leading component in many developments of biodegradable compositions. The challenge has always been to convert this heat sensitive powder into a melt processable composition that has good mechanical properties while maintaining its high rate of biodegradation.

Many natural and synthetic materials are also known to undergo a rapid digestion by microorganisms. Their chemical structures vary from hydrocarbons and carbohydrates to molecules with ester or amide linkages. Encyclopedia of Chemical Technology, *Plastic, Environmentally Degradable, Supp. Vol.*, 626-68 (Kirk-Othmer, 3d ed.). Most of these materials are not useful in fabricating articles because they lack the mechanical properties typical to plastic materials, in addition to being difficult to process.

The use of starch as a low cost biodegradable filler in certain polymeric systems is known. A fairly high concentration of starch filler is required to achieve biodegradation. At the same time, the mechanical properties of the compositions deteriorate sharply with increasing starch content. The first breakthrough in making high starch content materials was the discovery that starch can be melt processed in the presence of water, heat, and pressure. *See* U.S. Patent Numbers 4,133,784 and 4,337,181 ("the USDA patents").

The USDA patents describe the use of starch filled poly(ethylene-acrylic acid) (EAA) and polyethylene (PE) as a biodegradable film for packaging and agricultural mulch. These patents describe a process where the starch is first gelatinized in the presence of water at elevated temperatures. Under such conditions the highly hydrogen bonded natural structure is destroyed and melt flow is attained. The resulting mixture is then blended with EAA and PE. Large amounts of water are used (20%-50%) and the final starch content is as high as 60 wt. %, after the water is removed.

Tests have indicated that the biodegradation rate of the materials prepared according to these patents displayed unsatisfactory biodegradation properties. The injected molded parts containing PE/EAA with 40 wt. % starch did not degrade at all in the sewage system (0 to 5 % weight loss) after 30 days. This time period was selected for testing because water treatment facilities typically had sewage in residence for about 30 days, but in modern facilities the in residence time is less than a week. However, sanitary protection devices may end up in septic tanks as well so to avoid accumulation and clogging in the plumbing it is reasonable to require a maximum 30 days for degradation.

A starch based blown film is also described in an article by Felix Otey. *Ind. Eng. Chem. Res.*, **1987**, *26*, 1659-1663.

U.S. Patent Number 3,949,145 describes a method to prepare polyvinyl alcohol films filled with starch for agricultural applications. This composition is highly water sensitive, making the composition highly unsuitable for disposable products such as diapers and sanitary napkins. Also, polyvinyl alcohol-containing samples degrade very slowly under simulated anaerobic sewage treatment conditions making compositions formulated according to this patent unsuitable for disposable products.

Injection molded starch capsules are described in U.S. Patent Number 6,673,438. These capsules are made from pure starch in the presence of 5% to 30% water and heat. The structure of the strongly hydrogen bonded starch is believed to be destroyed under these conditions, creating a melt flow. The resulting material is stiff and extremely water sensitive, which make the compositions a poor candidate for biodegradable products such as disposable diapers and sanitary napkins.

Recent improvements in producing starch based biodegradable articles have been reported. *See* U.S. Patent Number 4,673,438; U.K. Patent Number 2,190,093; and European Publications 282,451, 298,920, 304,401, 326,517, and 327,505.

U.S. Patent Number 5,095,054 discloses polymer blends that can be transformed by heat and under pressure to form products having dimensional stability. These compositions comprise destructurized starch, and at least one substantially water insoluble polymer; the composition may optionally contain another water-insoluble polymer and a plasticizer. The starch used in these compositions has a relatively high water content that significantly modifies the starch's dimensional and mechanical properties; although the destructurized starch is thermoplastic, it is not water resistant. This starch composition is an unsuitable substrate for manufacturing disposable products such as tampon applicators, disposable diapers, and sanitary napkins.

U.S. Patent Number 5,087,650 discloses biodegradable plastic compositions comprising unmodified starch and thermoplastic polymers. The starch too has a high water content that causes the starch to become destructurized when heated under pressure. This affects the starch's dimensional and mechanical properties and makes the compositions unsuitable for biodegradable thermoplastic compositions.

GB 2,190,093 describes starch compositions that consist of at least 72 wt. % starch and, optionally, a second hydrophilic polymer. The presence of at least 10 wt. % water is also essential in that process which makes the compositions unsuitable for consumer products.

PCT Application, International Publication Number WO91/02025, discloses a starch-polymer alloy comprising destructurized starch and an ethylene copolymer. Tests have indicated that compositions prepared according to this patent lacked the necessary biodegradation properties required to be suitable for consumer products.

The use of poly(3-hydroxybutyrate) (PHB) and poly (3-hydroxyvalerate) (PHV) copolymer blends are described in Dave. *et al.*, *Polym. Mater. Sci.*, **1990**, *62*, 231-35. Degradation studies of polycapralactone/PHBV compositions yielded relatively low weight loss under lab enzymatic hydrolysis.

A molded tampon applicator from poly(3-hydroxybutyrate) and poly(3-hydroxyvalerate), a plasticizer, and a nucleating agent is described in U.S. Patent Number 4,900,299, assigned to McNeil. Also disclosed is the optional use of a biodegradable filler as hydroxyalkyl cellulose or starch.

The use of starch filled polymers is the cheapest and most convenient route for producing functional biodegradable materials. But the starch content in such compositions must be very high (>50 wt. %) to achieve a reasonable rate of biodegradation. Further, starch powder typically contains 10% to 40% by weight moisture. This starch is generally charged into an extruder where the combination of heat and pressure is sufficient to destructurize and melt the starch. Because starch becomes the major phase, the resulting materials are brittle and require further modifications.

Typically, a fairly high concentration of starch filler is required to achieve biodegradation. But conventional polymers such as polyethylene, polyurethane, etc. have a limited useful capacity for starch filler, that is, the mechanical properties of the compositions deteriorate sharply with increasing starch content. Further, microorganisms have been shown to selectively digest the starch without degrading the polymeric matrix.

The prior art discloses certain compositions that contain destructurized starch, which is a water soluble material and has a very limited use in consumer products. This starch is formed by exposing starch to heat and pressure in the presence of water, which breaks the hydrogen bonds between the starch molecules and renders the materials thermoplastic but soluble in cold water, and thus, unsuitable for consumer products. For this reason, other water insoluble polymers have been incorporated into such compositions, but this caused poor biodegradation.

Despite advances, there still remained a challenge to find a reasonable trade-off between water resistance and high rate of degradation. The present invention provides compositions that maintain a proper balance between mechanical properties, high biodegradation rate, processability, and low cost.

<u>Summary of the Invention</u>

Tests indicate that compositions of the present invention are thermoplastic, exhibit good mechanical properties, and readily degrade in the presence of microorganisms. The compositions of this invention can be injection molded into thin walled parts which are capable of appreciably degrading in the sewage system in thirty days. These products find utility in flushable disposable products.

This invention provides two classes of thermoplastic biodegradable compositions. In one aspect of the invention, compositions comprising a blend of a thermoplastic and ester containing polymer, a plasticizer, and optionally an inert filler are provided. These compositions comprise (a) 10 to 70 wt. % of one or more thermoplastic polymers or copolymers comprising one or more repeating units of the general formula:

$$[-O-\underset{}{\overset{R}{\overset{|}{C}}}H-CH_2-\overset{O}{\overset{\|}{C}}-]_n$$

(I)

wherein R is independently alkyl having from about 1 to 9 carbon atoms;

b. 5 to 35 wt. % of one or more ester containing polymers, the one or more polymers having a molecular weight greater than about 10,000 and selected from the group consisting of:

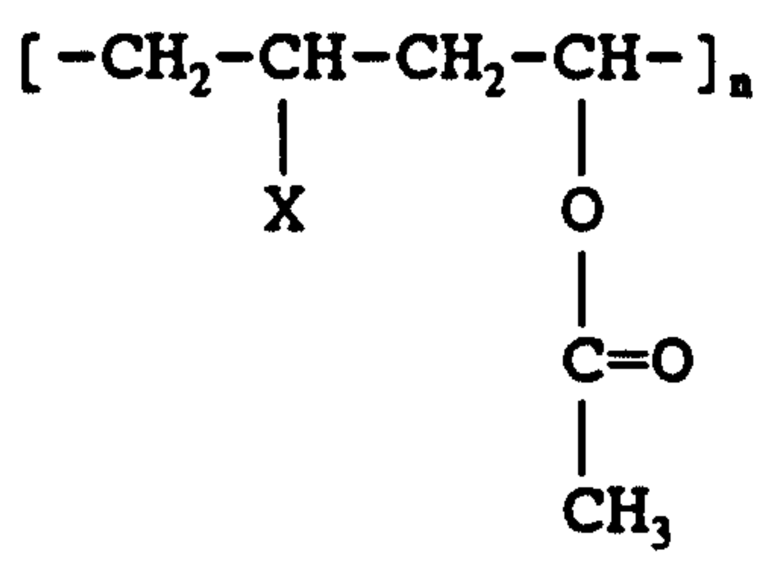
i. polymers with ester linkages in the backbone, the polymers comprising one or more monomeric units of the formula:

$$[-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_1-\overset{\overset{\displaystyle O}{\|}}{C}-O-R_2]_n$$

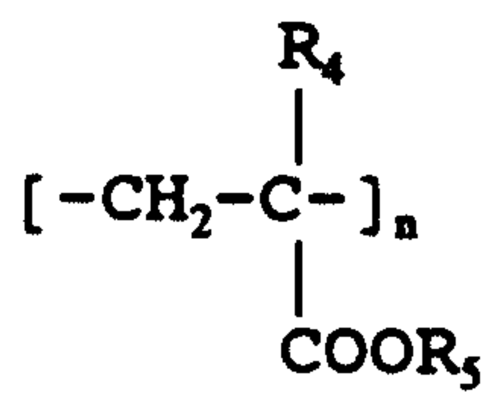
(II)

wherein R_1 may be alkane or alkene having about 2 to 12 carbon atoms; and R_2 is alkane, alkene, or aryl having up to about 12 carbon atoms; and

ii. polymers with pendant ester groups, the polymers comprising one or more monomeric units selected from the group consisting of the units:



and



(III) (IV)

wherein X is independently H, Cl, alkyl having about 1 to 3 carbon atoms, aryl, an acetate or hydroxyl moiety; R_4 is H or alkyl having from about 1 to about 2 carbon atoms; R_5 is alkyl having from about 1 to 4 carbon atoms; and

c. 0 to about 30 wt. % of one or more plasticizers; and

d. 0 to about 50 wt. % of an inert filler.

In another aspect of this invention, a class of starch-based biodegradable compositions are provided. These compositions comprise

a. about 15 to 50 wt. % of a starch-polymer alloy, the starch-polymer alloy comprising:

i. about 50 to 80 wt. % destructurized starch and about 20 to 50 wt. % of a hydrophobic copolymer selected from the group consisting of ethylene-vinyl acetate having a vinyl acetate molar content of from about 5 to 90 %, modified ethylene vinyl-acetate having from about 5 to 90 % of hydrolyzed acetate groups, ethylene-glycidil acrylate, ethylene-methyl methacrylate, ethylene-maleic anhydride, and mixtures thereof;

ii. a plasticizer having a boiling point greater than 150°C selected from the group consisting of glycerine; polyethylene glycol; ethylene glycol; propylene glycol; sorbitol; mannitol; the acetate, ethoxylated and propoxylated derivatives of glycerine, polyethylene glycol, ethylene glycol, propylene glycol, sorbitol, mannitol; and mixtures thereof;

iii. 0 up to about 20 wt. % urea with respect to the weight of the destructurized starch component in (i); and

b. about 30 to 55 wt. % of unmodified starch; and

c. a water soluble plasticizer containing hydroxyl groups and having a molecular weight of less than about 1000.

This invention further relates to articles prepared from the biodegradable compositions disclosed herein, in particular, disposable tampon applicators.

According to one aspect of the present invention, there is provided a composition of matter comprising: a. about 15 to 50 wt. % of a starch-polymer alloy, the starch-polymer alloy comprising: i. about 50 to 80 wt. % destructurized starch and about 20 to 50 wt. % of a hydrophobic copolymer selected from the group consisting of ethylene-vinyl acetate having a vinyl acetate molar content of from about 5 to 90%, modified ethylene vinyl-acetate having from about 5 to 90% of hydrolyzed acetate groups, ethylene-glycidil acrylate, ethylene-methyl methacrylate, ethylene-maleic anhydride, and mixtures thereof; ii. a plasticizer present in an amount of about 20 to 60 wt. % of the destructurized starch component of (i) present in the starch-polymer alloy, said plasticizer is selected from the group consisting of glycerine; polyethylene glycol; ethylene glycol; propylene glycol; sorbitol; mannitol; the acetate, ethoxylated and propoxylated derivatives of glycerine, polyethylene glycol, ethylene glycol, propylene glycol, sorbitol, mannitol; and mixtures thereof; and iii. 0 up to about 20% urea with respect to the weight of the destructurized starch component of (i); and b. about 15 to 55 wt. % of unmodified starch; and c. a water soluble plasticizer containing hydroxyl groups and having a molecular weight of less than about 1000.

According to another aspect of the present invention, there is provided a method of preparing a biodegradable composition comprising: a. blending about 50 to 80 wt. % of destructurized starch with a hydrophobic copolymer selected from the group consisting of ethylene-vinyl acetate having a vinyl acetate molar content of from about 5 to 90%, modified ethylene vinyl-acetate having from about 5 to 90% of hydrolyzed acetate groups, ethylene-glycidil acrylate, ethylene-methyl methacrylate, ethylene-maleic anhydride, and mixtures thereof; b. blending the product of step (a) with a plasticizer selected from the group consisting of glycerine; polyethylene glycol; ethylene glycol; propylene glycol; sorbitol; mannitol; the acetate, ethoxylated and propoxylated derivatives of glycerine, polyethylene glycol, ethylene glycol, propylene glycol, sorbitol, mannitol; and mixtures thereof, said plasticizer is present in an amount of about 20 to 60 wt. % of the destructurized starch component of step (a); c. optionally blending the product of step (b) with up to about 20% urea with respect to the weight of the destructurized starch component of step (a); d. blending the product of step (c) with about 15 to 55 wt. % of unmodified starch; and a water soluble plasticizer containing hydroxyl groups and having a molecular weight of less than about 1000.

According to still another aspect of the present invention, there is provided a shaped article formed from the composition described herein.

According to yet another aspect of the present invention, there is provided a shaped article formed from the composition described herein which is a tampon applicator.

According to a further aspect of the present invention, there is provided a composition of matter made by the process of combining: a. about 15 to 50 wt. % of a starch-polymer alloy, the starch-polymer alloy comprising: i. about 50 to 80 wt. % destructurized starch and about 20 to 50 wt. % of a hydrophobic copolymer selected from the group consisting of ethylene-vinyl acetate having a vinyl acetate molar content of from about 5 to 90%, modified ethylene vinyl-acetate having from about 5 to 90% of hydrolyzed acetate groups, ethylene-glycidil acrylate, ethylene-methyl methacrylate, ethylene-maleic anhydride, and mixtures thereof; ii. a plasticizer present in an amount of about 20 to 60 wt. % of the destructurized starch component of (i) present in the starch-polymer alloy, said plasticizer is selected from the group consisting of glycerine; polyethylene glycol; ethylene glycol; propylene glycol; sorbitol; mannitol; the acetate, ethoxylated and propoxylated derivatives of glycerine, polyethylene glycol, ethylene glycol, propylene glycol, sorbitol, mannitol; and mixtures thereof; and iii. 0 up to about 20% urea with respect to the weight of the destructurized starch component of (i); and b. about 15 to 55 wt. % of unmodified starch; and c. a water soluble plasticizer containing hydroxyl groups and having a molecular weight of less than about 1000.

Brief Description of the Drawings

Figure 1 is a graphical representation illustrating that modifying the pre-made starch-polymer alloy (AIO6H resin) with 20 wt. % glycerin and 40 wt. % starch resulted in a higher viscosity, whereas with 40 wt. % $CaCO_3$ a significant lower viscosity was achieved.

Figure 2 is a graphical representation demonstrating the simplicity of viscosity control by varying the starch and $CaCO_3$ content.

Detailed Description of the Invention

This invention provides classes of thermoplastic biodegradable compositions. One class of compositions comprises a blend of a thermoplastic and ester containing polymers, a plasticizer, and optionally an inert filler.

The thermoplastic polymer component in these compositions contains the monomeric unit represented by the following general Formula I:

$$[-O-\overset{\overset{\displaystyle R}{|}}{C}H-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-]_n$$

(I)

wherein R is independently alkyl having from about 1 to 9 carbon atoms (i.e., homologous hydrocarbon series from methyl to nonyl). In broader terms, all biodegradable poly(3-hydroxyalkanoates) are suitable polymers for this invention. The thermoplastic polymers of Formula I may include copolymers where R differs in the repeating monomeric units. This family of polymers has been described. Gross, *et al.*, *Macromolecules*, **1989**, *22*, 1106; Brandl,, *et al.*, *Applied and Environmental Microbiology*, **1988**, *58*, 1977. These polymers are generally produced by microorganisms and several variants have been synthesized in laboratories. Bloembergen, *et al.*, *Macromolecules*, **1987**, *20*, 3089-91; Shelton, *et al.*, *Polymer Letters*, **1971**, *9*, 173-78. These polymers may be synthesized according to methods known to those skilled in the art. The aforementioned publications describe exemplary synthetic techniques.

In accordance with a preferred embodiment, the polymer (I) possesses a methyl or ethyl sidechain, R, (i.e., poly(3-hydroxybutyrate)(PHB) and poly(3-hydroxyvalerate) (PHV), respectively). In a more preferred embodiment, a copolymer of PHB and PHV will be used (PHBV), wherein the valerate content is between about 5 to 25%.

Thermoplastic polymer (I) is present in the compositions in an amount of about 10 to 70 wt. %. Preferably, the thermoplastic polymer content will be about 20 to 50 wt. %.

Thermoplastic polymers such as PHBV are stiff and brittle and are difficult to process due to their low rate of crystallization. Blending PHBV with certain ester containing polymers overcomes these drawbacks permitting the synthesis of strong and useful materials that degrade rapidly in the presence of microorganisms.

Ester containing polymers suitable for inclusion in the first class of compositions of the invention will have ester linkages in the backbone or contain pendant ester groups. These polymers should have a molecular weight greater than about 10,000.

Polymers containing ester linkages in the backbone contain one or more monomeric units of the following general Formula II:

$$[-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_1-\overset{\overset{\displaystyle O}{\|}}{C}-O-R_2]_n$$

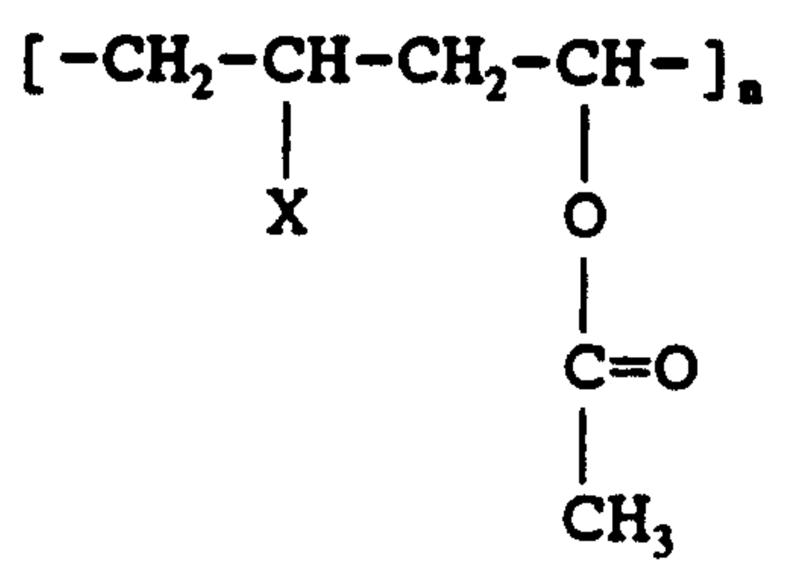
(II)

wherein R_1 may be alkane or alkene having about 2 to 12 carbon atoms; and R_2 is alkane, alkene, or aryl having up to about 12 carbon atoms.

In a preferred embodiment, the polymers containing ester linkages in the backbone (II) may be polycapralactone, ethylene glycol adipate, propylene glycol sebacate, ethylene glycol adipate, propylene, glycol sebacate, ethylene glycol phthalate. In a more preferred embodiment, the polymer (II) is polycapralactone. Other suitable polymers and copolymers of Formula II will be apparent to those skilled in the art and may be used without detracting from the spirit of the invention.

Polymers comprising pendant ester groups have one or more monomeric units represented by the following general

Formulas III and IV:



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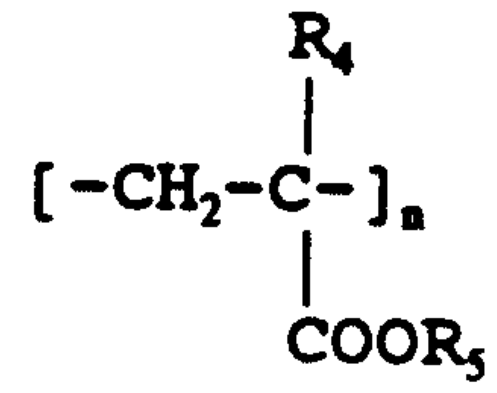

(III) (IV)

wherein X is independently H, Cl, alkyl having from about 1 to 3 carbon atoms, aryl, an acetate or hydroxyl group; R_4 is H or alkyl having from about 1 to about 2 carbon atoms; R_5 is alkyl having from about 1 to 4 carbon atoms.

In certain preferred embodiments, the polymers with pendant ester groups may be polyvinyl acetate, ethylene vinyl acetate copolymers, vinyl chloride-vinyl acetate copolymers, described in Formula III; or methacrylate copolymers, described in Formula IV. Other suitable polymers of Formulas (III) and (IV) will be apparent to those skilled in the art and may be used without detracting from the spirit of the invention.

The ester-containing polymers (II), (III), and/or (IV) are present in the composition in an amount of about 5 to 35 wt. %. In a preferred embodiment, the ester-containing polymer content will be about 10 to 25 wt. %.

Generally, the ester-containing polymers used in practicing this invention are commercially available or may be synthesized according to conventional methods known to those skilled in the art.

The first class of compositions of the invention may also contain up to about 30 wt. % of a plasticizer, preferably about 5 to 20 wt. %. Suitable plasticizers include liquid esters of dibasic aliphatic acids having a molecular weight of less than about 4000 and having between 2 to 12 carbon atoms, or polyesters represented by Formula II above, and are predominantly liquids or wax-like materials with molecular weights of less than 2000, or the acetate esters of glycerine.

In a preferred embodiment, the plasticizer is selected from the group including triacetate ester (triacetin), poly(propane sebacate), poly(hexamethylene succinate), poly(hexamethylene fumarate), poly(dodecane sebacate), and poly(tetramethylene azelate). In a more preferred embodiment, the plasticizer is triacetate ester (triacetin). Other suitable plasticizers will be apparent to those skilled in the art and may be used without detracting from the spirit of the invention. Generally, the plasticizers are commercially available or may be synthesized according to conventional methods known to those skilled in the art.

To accelerate degradation and reduce the cost of the compositions, fillers (up to 50 wt. %, preferably about 20 to 40 wt. % of the composition) may be added to the first class of compositions to control the compositions' melt viscosity. Starch and calcium carbonate are particularly useful and are preferred, with starch being the preferred filler. Preferably, the starch will have a water content of less than 2%, preferably no more than about 0.1%. It is also preferred that the starch have a particle size of less than about 15 microns, and preferably less than about 5 microns.

Starches suitable for fillers include, but are not limited to, natural or vegetable starches such as those extracted from corn, maize, potatoes, rye, oats, or wheat.

This invention relates to a second class of degradable thermoplastic compositions comprising a premade starch-hydrophobic polymer alloy, blended with unmodified starch and a liquid plasticizer.

The starch-polymer alloy comprises about 50 to 80 wt. % destructurized starch and 20 to 50 wt. % of a water insoluble polymer. In the context of this invention, "destructurized starch" has its conventional meaning, i.e., starch that has been formed by thermoplastic melt formation in the presence of water; this process disrupts the starch's hydrogen bonds, and, thus, the starch's crystalline structure. The water insoluble polymer is selected from the group consisting of ethylene-vinyl acetate having a vinyl acetate molar content of from about 5 to 90 %, modified ethylene vinyl-acetate having from about 5 to 90 % of hydrolyzed acetate groups, ethylene-glycidil acrylate, ethylene-methyl methacrylate, ethylene-maleic anhydride, and mixtures thereof. In certain preferred embodiments, the polymer will be ethylene-vinyl acetate, preferably with a vinyl acetate content of about 12 to 80%.

The starch-polymer alloy further comprises a plasticizer selected from the group consisting of glycerine; polyethylene glycol; ethylene glycol; propylene glycol; sorbitol; mannitol; the acetate, ethoxylated and propoxylated derivatives of glycerine, polyethylene glycol, ethylene glycol, propylene glycol, sorbitol, mannitol; and mixtures thereof. In certain preferred embodiments, the plasticizer will be glycerine. Generally, the plasticizer comprises between about 20 to 60 wt. % of the destructurized starch component present in the alloy.

The alloy further comprises 0 up to about 20 wt. % urea with respect to the weight of the destructurized starch component; that is, if the composition contains 60 grams of destructurized starch the composition will contain 12 grams of urea.

The content of the above-described premade starch-polymer alloy in the biodegradable composition is about 15 to 50 wt. %, preferably about 15 to 30 wt. %.

This starch-polymer alloy is further blended with unmodified starch having a low water content. In the context of this invention, "unmodified starch" means starch that has not been melt processed, and, thus, its crystalline structure has not been disrupted. In certain preferred embodiments, the starch content has no more than about 2 wt. % water. In a more preferred embodiment, the starch has no more than about 0.1 wt. % water. In a preferred embodiment, the particle size of the starch will be less than about 15 microns, preferably about 5 to 10 microns, and more preferably less than about 5 microns.

The unmodified starch content of the biodegradable composition is about 30 to 55 wt. %, preferably about 40 to 50 wt. %. In a preferred embodiment, the total starch content of the biodegradable composition (i.e., the destructurized plus the unmodified starch) will be about 55 to 70 wt. %, more preferably about 60 to 65 wt. %.

To arrive at the composition of the invention the starch-polymer alloy is further blended with a water soluble plasticizer containing hydroxyl groups. This plasticizer should have a molecular weight of less than about 1000. In certain preferred embodiments, the plasticizer may be glycerin, trimethylpropane, sorbitol, erythritol, or polyethylene glycol. In a more preferred embodiment, the plasticizer is glycerin. Other suitable plasticizers will be apparent to those skilled in the art, and the use of other plasticizers will not depart from the spirit of the invention. The amount of the plasticizer utilized is an amount effective to render the composition thermoplastic and to reduce the composition's sensitivity to water. Generally, the plasticizer is present in an amount about 15 to 30 wt. % of the composition, preferably 20 to 30 wt. %.

In addition to unmodified starch other inert additives, such as calcium carbonate ($CaCO_3$) can be incorporated into the formulation. In certain preferred embodiments, the amount of additional inert filler is about 2 to 20 wt. %, more preferably about 5 to 10 wt. %.

The following table summarizes the preferred utilization ranges:

Table 1

MATERIAL	RANGE, WEIGHT %	PREFERRED RANGE, %
Total pre-made alloy	15-50	15-30
Unmodified starch	30-55	40-50
Plasticizer	15-30	20-30
$CaCO_3$	2-20	5-10
Calculated Values:		
Modified starch	9-30	9-18
Hydrophobic water insoluble compatible polymer	6-20	6-12
Total Starch	55-70	60-65

The thermoplastic compositions of this invention are useful for producing injection-molded, thin-walled articles which have the advantage of being biodegradable. Thus, the compositions are particularly useful for preparing flushable, disposable products such as tampon applicators. Shaped articles such as films, fibers, and molded parts can be made from the claimed compositions not only by injection molding processes but also by melt-processes such as melt-extrusion, and compression molding.

EXAMPLES

EXAMPLE 1

a. Preparation

PHBV (15% hydroxyvalerate), obtained from ICI, England and the ester containing polymers were melted and blended with plasticizer and fillers using a Brabender Plasti-Corder™ mixer. The ester-containing polymers, plasticizer, and amounts of the components are set forth in Table 2. The mixing was carried out at 160°C and 50 rpm. The uniform blends were removed from the bowl and pressed into 10 - 20 mil thick films (5000 psi, 160°C) for characterization and biodegradation testing.

Materials

G-30 - Paraplex™ G-30, a low molecular weight liquid aliphatic polyester (C.P. Hall).

PEG - 4000 molecular weight polyethylene glycol (Carbowax™ 3600 Union Carbide.

Triacetin™ (triacetate ester of glycerol) - technical grade (Celanese).

EVA - Ethylene-vinylacetate copolymer, 28 % acetate (UE-634, USI).

PCL - Polycapralactone (Tone™ 700 Union Carbide).

PHBV - Polyhydroxybutyrate-polyhydroxyvalerate copolymer (ICI).

Starch - 5 to 10 microns powder (ADM).

$CaCO_3$ - Calcium carbonate.

b. Mechanical and Dimensional Properties

The compositions prepared and studied are described in Table 2 along with test results.

In the context of this invention " tensile strength," means the maximum stress a material subjected to a stretching load can withstand without breaking. The term "elongation" refers to the fractional increasing a material's length due to stress in tension; also referred to as elasticity. The tensile strength/elongation of the compositions was determined using an Instron at 10 inch/minute with crosshead speed and a 1 inch gap. "Flex modulous" describes the polymer's stiffness. It was measured using an Instron at 2 inch/minute. The term "melt index," as used in the context of this invention, means the number of grams of thermoplastic resin that can be forced through a specified opening under a certain pressure; this is a very important property for thermoplastic compositions. The melt index was determined at 5000 psi and at 160°C.

Biodegradable Compositions Based On PHBV

Table 2

Sample	Tensile Strength PSI	Elong. %	Flex Modu Kpsi	Melt Index 160°C	% Weight loss 30 days	Composition A/B/C/D A=PHBV D=STARCH
						B=PCL C=Triacetin
1	814	41	118	6	-	46/23/10/20
2	504	46	98	7	79.5	38/17/15/30
3	674	7	134	11	85.3	27/13/20/40
4	489	172	122	9	-	43/22/15/20
5	342	23	138	5	83	30/15/15/40
6	654	11	83	13	71.8	40/20/20/20
7	504	47	165	4.2	100	50/0/25/25
8	581	18	222	2.8	100	45/0/20/35
9	1570	15	331	39	100	70/30/0/0
10	849	114	131	12	51.7	35/35/10/20
11	325	70	110	13	69	27.5/27.5/5/15/30
12	400	15	85	20	76.8	20/20/20/40
14	347	20	108	11	74.1	22.5/22.5/15/40
15	452	71	102	28	69.3	30/30/20/20
16	597	57	107	22	72.2	25/25/20/30
17	514	36	133	9	64.2	30/30/10/30
18	1057	9	185	7	71.5	25/25/10/40
19	1154	115	150	21	24.9	23/47/10/20
20	933	23	99	25	46.1	17/38/15/30
21	341	19	97	30	68.6	13/27/20/40
22	1086	126	99	28	36.1	22/43/15/20
23	615	11	134	18	65.6	15/30/15/40
24	881	65	128	42	45.9	20/40/20/20
25	583	32	96	37	60	16/34/20/30
26	755	41	127	16	44	20/40/10/30
27	695	16	111	13	59.4	16/34/10/40
						B=EVA C=TRIACETIN
28	512	49	64	5	75	46/23/10/20
29	386	78	66	4.6	100	38/17/15/30
30	304	12	51	10	87	27/13/20/40

Sample	Tensile Strength PSI	Elong. %	Flex Modu Kpsi	Melt Index 160°C	% Weight loss 30 days	Composition A/B/C/D A=PHBV D=STARCH
41	270	270	12.5	9.9	26	23/46/10/20
42	158	277	14.7	19.1	60	16/34/10/40
43					70	13/27/20/40
						B=TONE 700 C=G-30
44	1077	83	218	7	58.8	46/23/10/20
45	926	13	182	8	65(70)	38/17/15/30
46	596	8	156	16	67.6	27/13/20/40
47	736	7	138	7	73.4	30/15/15/40
48	1022	38	150	15	63.9	40/20/20/20
						B=EVA C=PEG
49	506	18	95.6	3.4	75	46/23/10/20
50	682	2.7	153	4.2	100	38/17/15/30
						B=EVA C=Triacetin D=$CaCo_3$
51	1096		111.4	12.4	100	50/10/20/20
52	837		66.7	8	100	40/10/25/25
53	882		74.5	9	85	40/20/20/20

As can be seen in Table 2, a fairly wide range of mechanical and processing properties can be obtained from the ranges discussed in the preferred embodiments.

The type and concentration of the plasticizer (C) has a great impact on the melt flow index of the blend (i.e., processability) and on the flexibility and degradation rate. See Table 2.

In certain preferred embodiments, the ratio of the PHBV to the ester containing polymer (i.e., PCL, EVA) may range from 2:1 to 1:2. The rate of degradation is dependent on this ratio and the PHBV rich compositions degrade faster. For rapid degradation, the ester containing polymer should preferably not be present in levels greater than about 20 wt. % where the PHBV content is less than about 50 wt. %. For example, compare the percent weight loss of samples 2, 3, 5, and 6 with samples 19, 20, 22, 24, 26, and 41 as reported in Table 2.

c. Biodegradation tests

The biodegradation of the compositions described in Table 2 was tested in simulated water treatment plant conditions. The samples were exposed to municipal sludge microflora kept at 35°C. These conditions provide a representative anaerobic environment for the degradation of flushed disposable materials. The degradation was followed by monitoring gas evolution and weight loss for thirty days.

EXAMPLE 2

a. Preparation

Materials

AIO6H - Mater Bi® molding grade, a starch-polymer alloy (Novamont).

Starch - Clinton 400 corn starch, 1 wt. % moisture (ADM, Decture IL).

$CaCO_3$ - Calcium Carbonate - Supermite, 1 micron particle size, untreated (ECC International, Syalacauga, Alabama).

Glycerin - 99% pure.

PEG - Carbowax™, 600 MW (Union Carbide).

Atmer™ 129 - glycerol monostearate mold release agent (ICI).

Injection molding grade Mater-Bi® (AIO6H) was obtained from Novamont in 50kg sealed bags. The pellets were mechanically mixed with the modifying powders (starch, calcium carbonate) and liquids (polyethylene glycol, Carbowax™, glycerin) and fed into a twin screw Brabender mixer. The barrel temperature was kept at 160°C to avoid thermal degradation of starch. Screw speed was 50 RPM and the total throughput reached 15-20 lb/hr. The strands were air cooled on a conveyor prior to entering the pelletizer. The melt rheology of each composition was determined at various shear rates using a capillary rheometer from Keyaness (Honey Brook PA, model Galaxy IV #0052). Films were made by compression molding the pellets into 10-20 mil thick films (5000 psi, 160°C in a Pasadena Press) for characterization and biodegradation testing. Selected compositions were injection molded into a tampon applicator using an Engle 80 ton machine with 5.2 ounce barrel extruder.

b. Biodegradation Tests

Bench scale digestion units were set up in one incubator. Each unit contained a mixture of freshly collected digested and raw sludges from a waste treatment facility. Previous acclimated sludge (seed) was also added at about 1.5% level. The anaerobic digesters were placed in an incubator at 35°C. Each test material (1 gram film, 10-20 mil thick) was wrapped in a nylon mesh containing glass weight to assure contact with bottom of the sludge. Weight loss and gas evolution was monitored for 30 days.

Glycerin and starch are highly compatible with Mater-Bi resin and their blends produced clear films. In the biodegradation tests, it appeared that the synthetic polymer portion of the Mater-Bi® did not degrade and this preserved the film integrity. The addition of glycerin and starch reduced the synthetic resin content in the composition and increased the degradation rate. In the unmodified starch alloys, around 55% weight loss was measured, which is also the nominal concentration of starch in Mater-Bi®. The modified resins, have shown weight losses of up to 88%.

An empirical correlation can be drawn between the rate of degradation and the hydrophobic resin content in the continuous phase. The modified compositions' concentration in the continuous phase can be calculated as follows:

$$\%\ \text{Synthetic resin} = \frac{[\text{Mater-Bi® concentration}] \times 0.4}{[\text{Mater-Bi® concentration}] + [\text{Starch added}]}$$

In Table 3, the calculated portion of the synthetic resin and the corresponding weight losses are shown.

Biodegradation of Mater-Bi®(AIO6H) Formulations

Table 3

Example #	A	B	C	D	E	F	G
AIO6H	40	45	50	40	45	45	100
Glycerin	20	20	20	20	20	20	-
Starch	40	35	30	20	15	-	-
$CaCO_3$	-	-	-	20	20	35	-
Synthetic resin, % -calculated	20	22.5	25	27	30	40	40
30 days weight loss, %	88	80.4	76.6	70.1	68.5	54	55

The results also indicate that the presence of $CaCO_3$ has no effect on the biodegradation. In comparing samples F and G with samples A - E, it is evident that to achieve a higher rate of degradation, the continuous phase may be diluted with starch.

c. Melt Flow Characteristics

The starch compositions must meet certain melt flow requirements for producing injection molded parts with thin walls, such as a tampon applicator. The rheology measurements also suggest that the starch has a strong interaction with Mater-Bi®. This was manifested in a very sharp increase in the melt viscosity. Such phenomenon was not observed with inert fillers, i.e., calcium carbonate.

As expected, the addition of glycerin caused a significant reduction in the melt viscosity. At the same time, glycerin rendered the composition soft and pliable. Although this had facilitated the mold filling process, it also necessitated a very long cooling period to prevent distortion of the part upon ejection. It was found that the softening effect of glycerin can be offset by the addition of starch powder but not calcium carbonate. Hence, for a given amount of glycerin and added powder, both the stiffness and the melt viscosity can be determined by the ratio of starch to $CaCO_3$.

This effect is illustrated in the attached figures. Figure 1 shows that modifying the AIO6H resin with 20 wt. % glycerin and 40 wt. % starch resulted in a higher viscosity, whereas with 40 wt. % $CaCO_3$ a significant lower viscosity was achieved. Figure 2 demonstrates the simplicity of viscosity control by varying the starch and $CaCO_3$ content. The various formulations and their measured properties are listed in Table 4.

Table 4

Exam. #	AIO6H	GLYCERIN	STARCH	$CaCO_3$	ATMER -129	VISCOSITY 1000/sec	Degradation, % loss, 30 days
Mater-Bi® (AIO6H unmodified alloy)						4854	55.1
A1	50	20	30			3511	76.6
A2	45	20		35		2210	53.9
A3	45	20	35			5409	80.4
A4	45	20	15	20		2524	68.5
A5	40	20	40			5639	88.1
A6	40	20	20	20		3009	70.1
A7	45	20	30	5		3479	
A8	45	20	25	10		3213	
A9	45	15	35	5	0.4	6360	
A10	40	15	30	15	0.4	6187	
A11	45	15	30	10	0.4	6442	
A12	45	15	25	15	0.4	5748	
A13	40	15	25	20	0.4	5517	
A14	40	15	20	25	0.4	4736	

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Exam. #	AlO6H	GLYCERIN	STARCH	$CaCO_3$	ATMER™ -129	VISCOSITY 1000/sec	Degradation, % loss, 30 days
A15	40	17	20	23	0.4	4080	
A16	38	17	25	20	0.4	4763	
A17	35	20	40	5	0.4	4827	
A18	35	20	35	10	0.4	5115	
A19	35	23	42		0.4	4810	84.6
A20	30	25	45		0.4	4059	
A21	35	23	40	2	0.8	4222	
A22	35	23	40	2	1.2	3843	
A23	35	23	40	2	1.6	3523	
A24	30	25	45		1.0	4124	
A25	25	25	50		1.0	4903	
A26	22	28	50		1.0	4100	

A critical balance was identified between the components that would enable a short cycle molding. A desired viscosity range of 3300-4200 poise at 100 sec^{-1} shear rate and 160°C was identified. Incomplete parts were produced with higher viscosities and soft distorted parts were obtained at the lower end. The addition of the flow modifier, Atmer™ 129 from ICI proved beneficial since it can reduce the viscosity without decreasing the modulus (i.e., stiffness) of the alloy. The effect of Atmer™ on viscosity can be seen in Table 4, experiments A21, A23, and A23.

EXAMPLE 3

Preparation of Articles from the Biodegradable Compositions

The following composition was first compounded in a 30 mm corotating Werner & Pfleiderer twin screw extruder:

	% weight
PHBV (7% valerate)	38
Tone 700	16
Triacetin	15
Starch	20
Calcium carbonate	10
Boron Nitride	1

<u>Materials</u>

Triacetin (triacetate ester of glycerol) - technical grade (Celanese).

PHBV - Polyhydroxybutyrate-polyhydroxyvalerate copolymer - (ICI).

Starch - 5 to 10 microns powder (ADM).

$CaCO_3$ - Calcium carbonate.

Tone 700 - Polycapralactone (PCL) (Union Carbide).

The PHBV powder was preblended with the polycaprolactone (Tone 700) pellets and the starch powder. In a cement mixture the solid blend was sprayed with the liquid triacetin and tumbled for 15 minutes to obtain a uniform mixture. The blend was then fed into the back of the twin screw extruder using a volumetric feeder. Screw speed of 300 rpm was used and the temperature profile was gradually increased from 91°C at the back to 135°C at the front. The actual melt temperature was 140°C. The strands were cooled and chopped into 5mm size pellets.

Tampon applicators were molded from the above pellets using an 80 ton Engle machine with 5.2 oz. barrel capacity. The molding cycle time was 14 seconds and the mold temperature was 33°C. The temperature profile in the barrel was from 141°C in the feed zone up to 160°C at the nozzle.

CLAIMS:

1. A composition of matter comprising:

a. about 15 to 50 wt. % of a starch-polymer alloy, the starch-polymer alloy comprising:

i. about 50 to 80 wt. % destructurized starch and about 20 to 50 wt. % of a hydrophobic copolymer selected from the group consisting of ethylene-vinyl acetate having a vinyl acetate molar content of from about 5 to 90%, modified ethylene vinyl-acetate having from about 5 to 90% of hydrolyzed acetate groups, ethylene-glycidil acrylate, ethylene-methyl methacrylate, ethylene-maleic anhydride, and mixtures thereof;

ii. a plasticizer present in an amount of about 20 to 60 wt. % of the destructurized starch component of (i) present in the starch-polymer alloy, said plasticizer is selected from the group consisting of glycerine; polyethylene glycol; ethylene glycol; propylene glycol; sorbitol; mannitol; the acetate, ethoxylated and propoxylated derivatives of glycerine, polyethylene glycol, ethylene glycol, propylene glycol, sorbitol, mannitol; and mixtures thereof; and

iii. 0 up to about 20% urea with respect to the weight of the destructurized starch component of (i); and

b. about 15 to 55 wt. % of unmodified starch; and

c. a water soluble plasticizer containing hydroxyl groups and having a molecular weight of less than about 1000.

2. The composition of claim 1 which comprises about 15 to 30 wt. % of component a.

3. The composition of claim 1 or 2 wherein the unmodified starch, component b, contains no more than about 2 wt. % water.

4. The composition of any one of claims 1 to 3 which comprises about 30 to 55 wt. % of the unmodified starch, component b.

5. The composition of any one of claims 1 to 3 which comprises about 40 to 50 wt. % of the unmodified starch, component b.

6. The composition of any one of claims 1 to 5 wherein the starch content of the total composition is in the range of about 55 to 70 wt. %.

7. The composition of any one of claims 1 to 5 wherein the starch content of the total composition is in the range of about 60 to 65 wt. %.

8. The composition of any one of claims 1 to 7 which further comprises about 2 to 20 wt. % of an inert filler.

9. The composition of claim 8 wherein the inert filler is calcium carbonate.

10. The composition of claim 9 wherein calcium carbonate comprises about 5 to 10 wt. % of the composition.

11. A method of preparing a biodegradable composition comprising:

a. blending about 50 to 80 wt. % of destructurized starch with a hydrophobic copolymer selected from the group consisting of ethylene-vinyl acetate having a vinyl acetate molar content of from about 5 to 90%, modified ethylene vinyl-acetate having from about 5 to 90% of hydrolyzed acetate groups, ethylene-glycidil acrylate, ethylene-methyl methacrylate, ethylene-maleic anhydride, and mixtures thereof;

b. blending the product of step (a) with a plasticizer selected from the group consisting of glycerine; polyethylene glycol; ethylene glycol; propylene glycol; sorbitol; mannitol; the acetate, ethoxylated and propoxylated derivatives of glycerine, polyethylene glycol, ethylene glycol, propylene glycol, sorbitol, mannitol; and mixtures thereof, said plasticizer is present in an amount of about 20 to 60 wt. % of the destructurized starch component of step (a);

c. optionally blending the product of step (b) with up to about 20% urea with respect to the weight of the destructurized starch component of step (a);

d. blending the product of step (c) with about 15 to 55 wt. % of unmodified starch; and a water soluble plasticizer containing hydroxyl groups and having a molecular weight of less than about 1000.

12. A shaped article formed from the composition of any one of claims 1 to 10.

13. A shaped article formed from the composition of any one of claims 1 to 10 which is a tampon applicator.

14. A composition of matter made by the process of combining:

a. about 15 to 50 wt. % of a starch-polymer alloy, the starch-polymer alloy comprising:

i. about 50 to 80 wt. % destructurized starch and about 20 to 50 wt. % of a hydrophobic copolymer selected from the group consisting of ethylene-vinyl acetate having a vinyl acetate molar content of from about 5 to 90%, modified ethylene vinyl-acetate having from about 5 to 90% of hydrolyzed acetate groups, ethylene-glycidil acrylate, ethylene-methyl methacrylate, ethylene-maleic anhydride, and mixtures thereof;

ii. a plasticizer present in an amount of about 20 to 60 wt. % of the destructurized starch component of (i) present in the starch-polymer alloy, said plasticizer is selected from the group consisting of glycerine; polyethylene glycol; ethylene glycol; propylene glycol; sorbitol; mannitol; the acetate, ethoxylated and propoxylated derivatives of glycerine, polyethylene glycol, ethylene glycol, propylene glycol, sorbitol, mannitol; and mixtures thereof; and

iii. 0 up to about 20% urea with respect to the weight of the destructurized starch component of (i); and

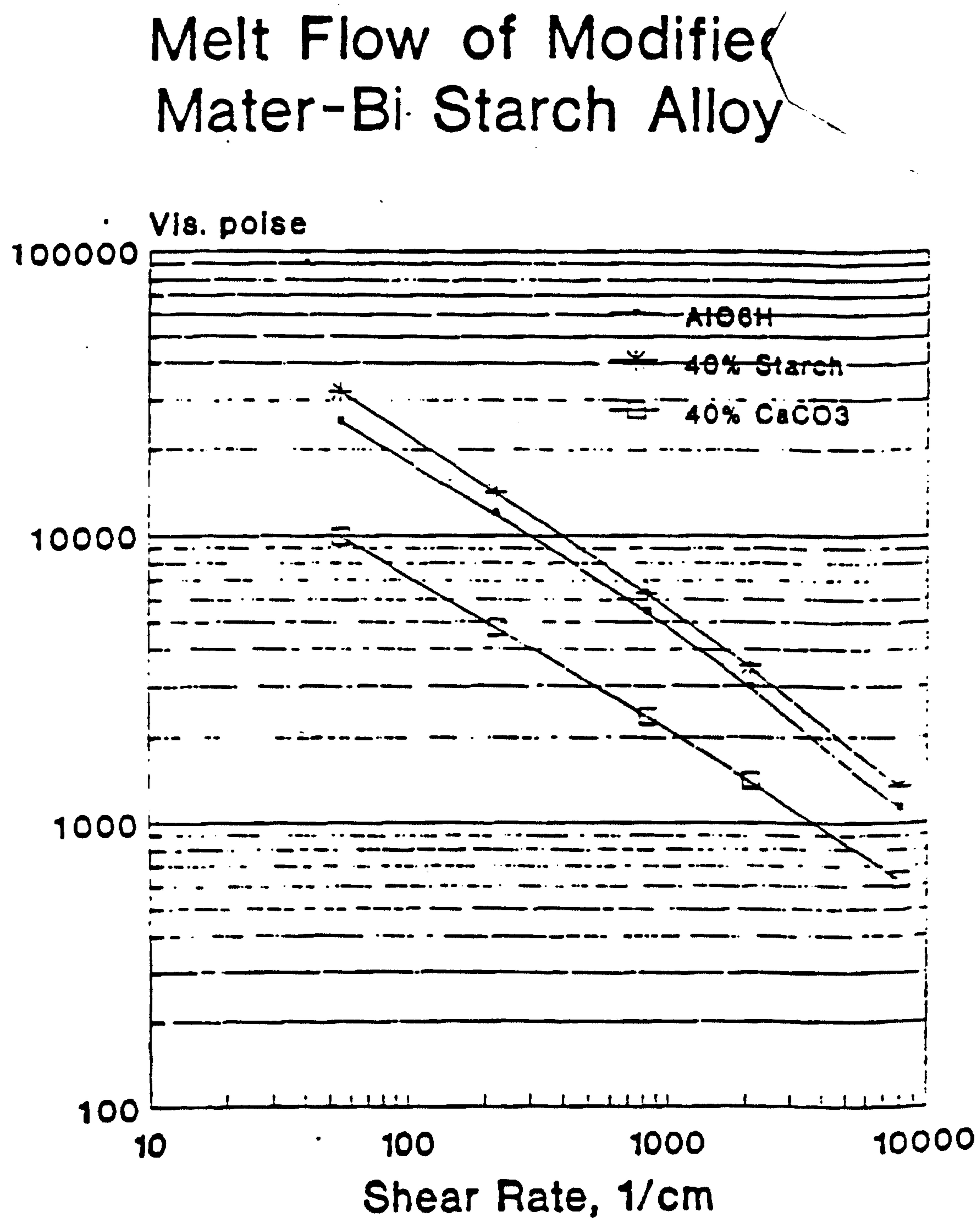
b. about 15 to 55 wt. % of unmodified starch; and

c. a water soluble plasticizer containing hydroxyl groups and having a molecular weight of less than about 1000.

SMART & BIGGAR

OTTAWA, CANADA

PATENT AGENTS



Modified - 20 wt. % glycerin, 40 wt. % powder

FIGURE 1

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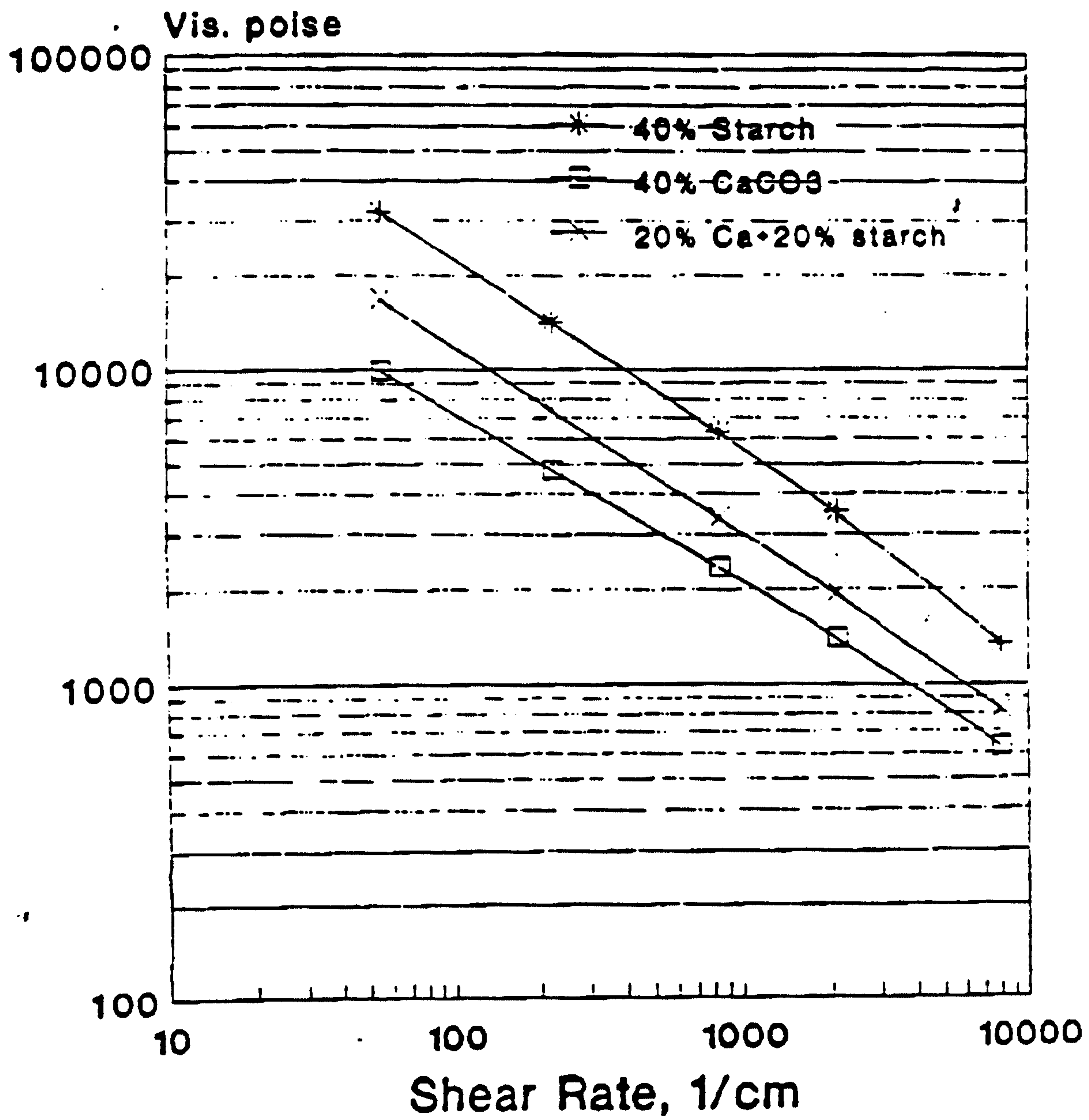
Melt Flow of Modified Mater-Bi Starch Alloy



Modified - 20 wt. % glycerin, 40 wt. % powder

FIGURE 2