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CASE #1969.PGG

Process Tolerant Low Amylose Tapioca Distarch Adipates

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BACKGROUND OF THE INVENTION

The present invention relates to low amylose tapioca distarch adipates and compositions containing such starch.

10 Starch, in general, contains two types of polymers, amylose which is essentially linear and amylopectin which is branched. Tapioca starch, obtained from cassava, has been known for many years. Regular tapioca starch typically has an amylose content of about 20-23% by weight; the balance being amylopectin. It has been used in a variety of industrial applications, including papermaking, food products, pharmaceuticals, and personal care products. It is often used instead of the more traditional corn starches for a
15 variety of reasons, including low protein content and bland flavor relative to corn.

To meet the demanding needs of the food industry, starch is often modified by numerous techniques known in the industry to change the behavioral characteristics from that of the unmodified starch. Although native tapioca starch and its derivatives are adequate for many applications, it would be desirable to have a tapioca starch which is low
20 in amylose and would thus have different properties which would result in improved functionality when used in industrial applications.

Low amylose starches are known in the art. Low amylose, or waxy, corn has been used for many years for a variety of applications. Low amylose rice starch is gaining importance, particularly in Asia. Low amylose potato starch has also been disclosed in
25 WO 92/11376.

Starches which are crosslinked by using a bi- or poly-functional chemical reagent that is able to react with two or more different hydroxyl groups on the same or different starch molecule are also well known in the art. This type of chemical modification controls

granular swelling and produces a starch that is process tolerant; that is, one that can tolerate high temperature, high shear and/or acidic conditions.

Distarch adipates, prepared by crosslinking with mixed adipic and acetic anhydride reagents, and the methods of producing them are also known in the art. The mixed
5 anhydride reagent used creates organic ester linkages that are relatively stable under many typical processing conditions. See for example U.S. Patent No. 2,461,139 (Caldwell, 8 February, 1949).

When an aqueous dispersion of native tapioca starch is heated, the starch granules begin to swell, and the dispersion develops a short, salve-like texture which is
10 important in imparting palatability and thickening in systems. However, during the process of cooking native starches, this textural state rapidly changes to an elastic, rubbery state in which the swollen granules rupture. Minor variations in cooking time, temperature, and concentration as well as shear and pH are sufficient to effect this transformation. Cross-
linking acts to strengthen the granules by reinforcing the hydrogen bonds which are
15 responsible for holding the granules intact and thus are used to overcome the extreme sensitivity of the swollen starch granules to handling and processing conditions.

Surprisingly, it has now been determined that adipic/acetic crosslinked low amylose tapioca starches have superior process tolerance compared to similarly crosslinked regular tapioca starches as well as similarly crosslinked regular and waxy
20 maize starches.

SUMMARY OF THE INVENTION

The present invention relates to a low amylose tapioca starch crosslinked using mixed adipic and acetic anhydride reagents, and compositions containing such starch.
25 The starch is useful in a wide variety of food, pharmaceutical, and industrial applications to increase the process tolerance of such compositions.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 depicts the relative molecular weight distribution by GPC of the regular and low amylose tapioca starches.

Figure 2 depicts the Brabender viscosity of distarch adipates prepared from regular and low amylose tapioca starches, corn starch and waxy maize starch.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a low amylose tapioca starch crosslinked using mixed adipic and acetic anhydride reagents, and compositions containing such starch.

10 The starch is useful in a wide variety of food, pharmaceutical, and industrial applications to increase the process tolerance of such compositions.

Low amylose starch, as used herein, is intended to mean a starch or flour which has an amylose content substantially lower than that of regular tapioca starch, particularly less than about 10%, more particularly less than about 5%, most particularly less than
15 about 3% amylose by weight.

Low amylose tapioca starch may be obtained by the method of U.S. Application Number 09/832,626, herein incorporated in its entirety by reference.

Also included in this invention are low amylose tapioca starches derived from low amylose cassava plants which may be found in nature, obtained by standard breeding and
20 crossbreeding techniques, or obtained by translocation, inversion, transformation or any other method of gene or chromosome engineering to include variations thereof, whereby the properties of the starch of this invention are obtained. In addition, starch extracted from a plant grown from artificial mutations and variations of the above generic composition which may be produced by known standard methods of mutation breeding is
25 also applicable herein.

The substantially pure starch may be extracted from the root of a low amylose cassava plant. Extraction may be by any method known in the art, including but not limited

to pulverizing the root and separating the starch from the remaining components by water extraction.

The native low amylose tapioca starch is crosslinked using mixed adipic and acetic anhydride reagents. Such reagents and the crosslinking reaction are well known in the art
5 for making distarch adipates using other native starches. For example, the low amylose tapioca distarch adipates may be prepared by reacting starch in an aqueous slurry with an adipic/acetic mixed anhydride reagent. The bound acetyl of the resultant starch may be adjusted by one skilled in the art to any level necessary for the amount of stability desired, particularly in the range of up to about 2.5% bound acetyl. The amount of adipic/acetic
10 mixed anhydride used in the reaction may also be adjusted by one skilled in the art to provide the desired inhibition effect (degree of crosslinking) in the resultant starch. Typically, the amount of mixed anhydride used is less than about 1%.

The resultant low amylose tapioca distarch adipates have properties and functionality which are unique and desirable in many applications. The low amylose
15 tapioca distarch adipates have a peak viscosity which is higher than that of regular tapioca, corn or waxy maize starches which have been modified in the same manner. Under acid conditions, viscosity breakdown is minimal and occurs slowly after the peak viscosity is reached. This is indicative of process tolerance in low pH systems such as a cherry pie filling or fruit prep. Yet, the viscosity onset and rise to peak of the low amylose tapioca
20 distarch adipates are similar to that of regular tapioca distarch adipates. Further, the low amylose distarch adipates reach peak viscosity quickly. Such viscosity profiles are highly desirous in many industrial applications.

The presently disclosed low amylose tapioca distarch adipates may be further modified to enhance their properties and functionality. In particular, the starch diadipates
25 may be physically modified, such as by thermal inhibition described in WO 95/04082 (published February 9, 1995) or by shear.

The low amylose tapioca distarch adipates may also be pregelatinized. Exemplary processes for preparing pregelatinized starches are disclosed in U.S. 4,280,851 (Pitchon, et al.), U.S. 4,465,702 (Eastman, et al.), U.S. 5,037,929 (Rajagopalan), U.S. 5,131,953 (Kasica, et al.), and U.S. 5,149,799 (Rubens). Conventional procedures for pregelatinizing starch are well known to those skilled in the art and described in such articles as Chapter XXII- "Production and Use of Pregelatinized Starch", Starch: Chemistry and Technology, Vol. III - Industrial Aspects, R.L. Whistler and E.F. Paschall, Editors, Academic Press, New York 1967.

The low amylose tapioca starch adipates may be purified by any method known in the art to remove off-flavors and colors that are native to the starch or created during starch modification processes. Purification processes preferred for treating the present starches are disclosed in U.S. Serial No. 07/832,838 filed February 7, 1992, by Kasica, et al. Alkali washing techniques, for starches intended for use in either granular or pregelatinized form, are also useful and described in the family of patents represented by U.S. 5,187,272 (Bertalan, et al.). Purification can either be done to the native low amylose tapioca starch prior to crosslinking or to the distarch adipate.

One skilled in the art is capable of using any single or combination of modifications known in the art in order to obtain the desired starch properties and functionality. These modifications are well known in the art and the resulting starch properties and functionality will vary depending, *inter alia*, on the type of modification employed, the degree of modification, and the reaction conditions.

The low amylose tapioca distarch adipates of the present invention may be used in a variety of industrial applications, including without limitation paper products, food products, pharmaceutical and nutritional products, personal care products and other industrial products.

Paper products is intended to include, without limitation, paper, paperboard, linerboard, corrugating, cardboard, bags, and envelopes.

Food products is intended to mean any edible product and includes, without limitation, cereals, breads and bread products, cheese and imitation cheese products, condiments, confectioneries, dressings including pourable dressings and spoonable dressings, pie fillings including fruit and cream fillings, sauces, including white sauces and
5 dairy-based sauces such as cheese sauces, gravies, imitation and lite syrups, puddings, custards, yogurts, sour creams, pastas, beverages including dairy-based beverages, glazes, soups and baby food.

Pharmaceutical and nutritional products is intended to include pharmaceutical excipients, tablets including effervescent tablets, dusting starches and powders, and
10 prebiotics products.

Personal care products is intended to include without limitation deodorants and antiperspirants, hair fixatives including sprays, gels, mousses, lotions and pomades, soaps and cleansers, makeup including eye shadow, powders, foundations, and blushers, shampoos and conditioners, and mouthwashes, breath fresheners and toothpastes.

15 Other industrial products is intended to include without limitation detergents, and biodegradable foamed products including loosefill, sheets and shapes.

The low amylose tapioca distarch adipates may generally be used at any desired level, the amount being dependent upon the functionality to be obtained. In general, the starch will be used in an amount of from about 1% to about 95%, particularly from about
20 5% to about 60%, more particularly in an amount of about 10% to about 40% by weight of the product.

EXAMPLES

The following examples are presented to further illustrate and explain the present
25 invention and should not be taken as limiting in any regard. All percents used are on a weight/weight basis.

In the examples below, the tapioca samples used are as follows:

Tapioca = regular tapioca starch commercially available from National Starch and Chemical Company (Bridgewater, NJ, USA).

LATS = low amylose tapioca starches genetically produced by introducing the GBSS gene

5 in the antisense mode and using FEC from which cassava plants are regenerated.

Corn = regular corn starch commercially available from commercially available from National Starch and Chemical Company (Bridgewater, NJ, USA).

Waxy = waxy maize starch commercially available from National Starch and Chemical Company (Bridgewater, NJ, USA).

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Example 1 – Amylose content

a. Amylose content was determined by potentiometric titration. Approximately 0.5 g of a starch sample was heated in 10mls of concentrated calcium chloride (about 30% by weight) to 95°C for 30 minutes. The sample was cooled to room temperature, diluted with
15 5 mls of a 2.5% uranyl acetate solution, mixed well, and centrifuged for 5 minutes at 2000 rpm. The sample was then filtered to give a clear solution.

The starch concentration was determined polarimetrically using a 1 cm polarimetric cell. An aliquot of the sample (normally 5 mls) was then directly titrated with a standardized 0.01 N iodine solution while recording the potential using a platinum electrode with a KCl reference
20 electrode. The amount of iodine needed to reach the inflection point was measured directly as bound iodine. The amount of amylose was calculated by assuming 1.0 gram of amylose will bind with 200 milligrams of iodine.

The results of the potentiometric titration are showed in Table I.

Table I

<u>Base starch</u>	<u>Amylose Content (%)</u>
Tapioca	20%
LATS	2.7%

As can be determined from Table I, the low amylose tapioca starches contain significantly less amylose than the regular tapioca starches.

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- b. The amylose contents were checked by gel permeation chromatograph (GPC). Samples were prepared for analysis by slurrying 4 to 8 mg of starch in 4 g of dimethylsulfoxide (DMSO) containing 5mM sodium nitrate and heating to 100°C for 2 hours. The sample was filtered if necessary, and injected (300μl) into a GPC 150C
- 10 chromatograph (Waters Corporation, Amherst, MA). The Gel Permeation Chromatograph utilized 4 columns (guard column, 10⁵, 10³, 10² micron (nominal) pore size columns, all from Polymer Laboratories, Amherst, MA). The mobile phase was dimethyl sulfoxide containing 5 mM of sodium nitrate. The instrument was operated at a temperature of 80°C and a flow rate of 0.7 ml/minute was used. The columns were calibrated with pullulan
- 15 standards (Showa Denko K.K., Japan) ranging in molecular weight from 5800 to 850,000. Figure 1 shows the relative molecular weight distribution by GPC of the regular and low amylose tapioca starches. As can be determined from the figure, the low amylose tapioca starch has significantly more amylopectin as seen by the peak at a relative log (molecular weight) of about 6.83. Further, this is the sole main peak. In contrast, the regular starch
- 20 shows an additional amylose peak at a relative log (molecular weight) of about 6.

Example 2 – Preparation of the Distarch adipates

- a. 100 grams of low amylose tapioca starch was slurried in 150 grams water and brought to a temperature of 27°C. The pH of the slurry was then adjusted to 8.0 using a

3% NaOH solution. The reagent was mixed in a separate flask using 3.9%(wt/wt) acetic anhydride and 0.9%(wt/wt) of a 1:9 adipic:acetic mixed anhydride based on the weight of the starch. This mixture was then added to the starch slurry at a controlled rate during which the pH was kept constant at pH 8.0 until the reaction was complete. The pH was then adjusted to 6.0 using a dilute HCl solution and the starch was washed and dried.

- b. The method of Example 2a was repeated using tapioca starch.
- c. The method of Example 2a was repeated using corn starch.
- d. The method of Example 2a was repeated using waxy maize starch.

10 Example 3- Viscosity

The viscosity of the starches of Example 2 were measured using a Visco/amylo/graph, Model VA-1A (C.W. Brabender Instrument Co., Hackensack, NJ, USA 07606). A slurry of 5% starch on a dry weight basis was prepared and controlled to pH3 using a citric acid/trisodium citrate buffer solution. The total charge weight of 460grams was heated from 50°C to 92°C at a rate of 1.5°C per minute. The slurry was then held at 92°C for 30 minutes. The hot viscosity was measured while heating the paste in the Visco/amylo/graph. The results are shown in Figure 2.

As can be seen from Figure 2, the low amylose tapioca distarch adipate has a peak viscosity which is higher than that of regular tapioca, corn or waxy maize starches which have been modified in the same manner. Under acid conditions, viscosity breakdown is minimal and occurs slowly after the peak viscosity is reached. This is indicative of process tolerance in low pH systems. The viscosity onset and rise to peak of the low amylose tapioca distarch adipate is similar to that of regular tapioca distarch adipate, but the low amylose distarch adipates reach peak viscosity quickly.

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CLAIMS

We claim:

1. A low amylose tapioca distarch adipate.
2. The starch of claim 1, wherein the starch has an amylose content of less than about
5 10% by weight.
3. The starch of claim 1, wherein the starch has an amylose content of less than about
5% by weight.
4. The starch of claim 1, wherein the starch has an amylose content of less than about
3% by weight.
- 10 5. A composition comprising the starch of any one of claims 1-4.
6. The composition of claim 5, wherein the composition is selected from the group
consisting of paper products, food products, pharmaceutical products, nutritional
products, personal care products, detergents, emulsifying agents, encapsulating
agents, and biodegradable foamed products.
- 15 7. A composition comprising tapioca starch, the improvement comprising substituting a
low amylose tapioca distarch adipate for at least a portion of the starch in the
composition.