

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



DELEGATURA PROPIEDAD INDUSTRIAL

División de Nuevas Creaciones

PCT
SOLICITUD

PATENTE DE INVENCION

ENTRADA EN FASE NACIONAL

07-45686

21. **EXPEDIENTE No.**

54. **TITULO** COMPOSICIONES DE ALMIDON PLASTIFICADO MODIFICADO QUIMICAMENTE
POR PROCESAMIENTO CON EXTRUSION

51. **CLASIFICACION INTERNACIONAL**

71. **SOLICITANTE** MICHIGAN STATE UNIVERSITY

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74. **APODERADO** JUAN PABLO CADENA SARMIENTO

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FW 19-06-2007

Cadena

AS: 103.671



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 07-045888-00000-0000
Fecha: 2007-05-08 15:58:42 Dep: 2020 NUECREACIONE
Tra 11 PATENTEIYII Evs: 378 FASENACIONALI
Act 411 PRESENTACION Folios: 131

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FORMULARIO ÚNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL

1

SOLICITUD DE:



Patente de Invención.



Patente de Modelo de Utilidad.



Capítulo I.



Capítulo II.

2

SOLICITANTE
(71)

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Cual _____

Número _____

3

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Número 80.410.337 TP 57492

4

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(US), (Respectivamente)

Nacionalidad o Domicilio: Estados Unidos de América, Korea y Bélgica (Respectivamente)

5 PCT (86)

Solicitud Internacional No. PCT/US2005/041237 Fecha 15-11-2005Publicación Internacional No. WO 2006/055504 A2 Fecha 26-05-2006

Título (54): COMPOSICIONES DE ALMIDÓN PLASTIFICADO, MODIFICADO QUÍMICAMENTE, POR
PROCESAMIENTO CON EXTRUSIÓN

7 Clasificación Internacional (51) _____

8 Prioridad

(33) País de Origen

(32) Fecha

(31) Número de Solicitud

US

19-11-2004

10/993,309

SI ☒NO ☐9 Comprobante de pago No. 07-23.449Fecha 07-05-2007

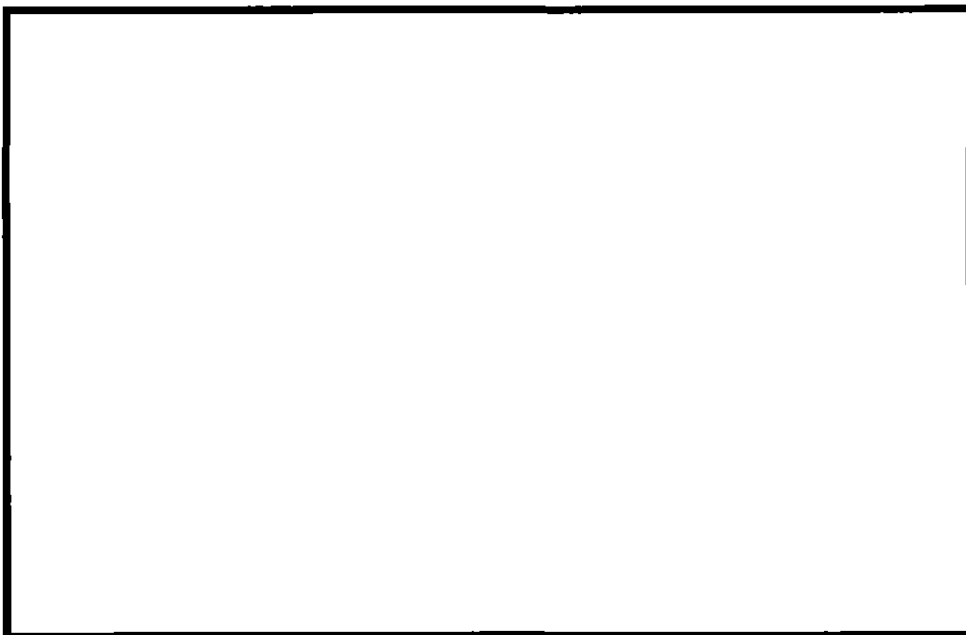
Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página.

10

ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud. \$482.000
- ☒ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☒ Poderes, si fuere el caso. **Fotocopia autenticada**
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones.
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano (Resumen, descripción, reivindicaciones, dibujos)
- ☐ Copia del examen preliminar efectuado por la IPEA.
- ☐ Traducción del examen preliminar efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☐ Arte final 12x12.
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☒ Otros: Tarjeta de Propietarios
Documentos PCT

11 FIGURA CARACTERÍSTICA:



12 Solicito la concesión de la patente,

NOMBRE: JUAN PABLO CADENA SARMIENTO

FIRMA:

Juan Pablo Cadena
C.C. 80.410.337 de Usaquén TP 57492 del C.S.J.

Instrucciones para la presentación de los anexos, ver reverso de esta página.

7 3

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-046688-00000-0000

Fecha 2007-05-08 15:58.42 Dep 2020 NUECREACIONE
Tra 11 PATENTEIYII Eve: 379 FASENACIONALI
Act 411 PRESENTACION Folios: 131

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176009-2

RECIBO OFICIAL DE CAJA : 07 - 23,449
FECHA : MARZO 21 DE 2007

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	050-00110-6	59310980	21/03/2007	16,740,000.00

***** CONCEPTO *****

CANT. REMISTICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	482,000.00
	TOTAL :	\$ 482,000.00

SON: CUATROCIENTOS OCHENTA Y DOS MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

4

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES

PATENTE ☒ PCT/US2005/041237 MODELO DE UTILIDAD ☐ DISEÑO INDUSTRIAL ☐

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DOMICILIO EAST LANSING, MI 48824, ESTADOS UNIDOS DE AMERICA

APODERADO JUAN PABLO CADENA SARMIENTO

TITULO COMPOSICIONES DE ALMIDON PLASTIFICADO, MODIFICADO QUIMICAMENTE, POR PROCESAMIENTO
CON EXTRUSION CLASIFICACION

EXPEDIENTE No. FECHA DE SOLICITUD ROLLO MICROFILM

CERTIFICADO No. FECHA DE CONCESION VIGENCIA DESDE HASTA

PRORROGA CAMBIO DE NOMBRE

TRASPASO A

INVENTOR (ES) RAMANI NARAYAN, SUNDER BALAKEISHNAN, YOGARAJ NABAR, BOO-YOUNG SHIN,

OTROS PHILLIPPE DUBOIS, JEAN-MARIE RAQUEZ

OFICINA DE COMUNICACIONES

From the INTERNATIONAL BUREAU

PCTNOTIFICATION CONCERNING
TRANSMITTAL OF COPY OF INTERNATIONAL
APPLICATION AS PUBLISHED OR REPUBLISHED

To:

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JUN 02 2006

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Date of mailing (day/month/year)

26 May 2006 (26.05.2006)

Applicant's or agent's file reference

MSU 4.2-724 PCT

IMPORTANT NOTICE

International application No.

PCT/US2005/041237

International filing date (day/month/year)

15 November 2005 (15.11.2005)

Priority date (day/month/year)

19 November 2004 (19.11.2004)

Applicant

MICHIGAN STATE UNIVERSITY et al

The International Bureau transmits herewith the following documents:

copy of the international application as published by the International Bureau on 26 May 2006 (26.05.2006) under
No. WO 2006/055504copy of international application as republished by the International Bureau on under
No. WOFor an explanation as to the reason for this republication of the international application, reference is made to INID codes (15), (48)
or (88) (as the case may be) on the front page of the attached document.The International Bureau of WIPO
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1211 Geneva 20, Switzerland

Authorized officer

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Form PCT/IB/311 (January 2004)

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
26 May 2006 (26.05.2006)

PCT

(10) International Publication Number
WO 2006/055504 A2(51) International Patent Classification:
C08B 30/12 (2006.01) C09J 103/06 (2006.01)(74) Agent: MCLEOD, Ian, C.; McLeod & Moyne, P.C., 2190
Commons Parkway, Okemos, MI 48864 (US).(21) International Application Number:
PCT/US2005/041237(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV,
LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI,
NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG,
SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US,
UZ, VC, VN, YU, ZA, ZM, ZW.(22) International Filing Date:
15 November 2005 (15.11.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/993,309 19 November 2004 (19.11.2004) US(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LI, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CHEMICALLY MODIFIED PLASTICIZED STARCH COMPOSITIONS BY EXTRUSION PROCESSING

(57) Abstract: A chemically modified plasticized starch (CMPS) is prepared by reacting starch with an organic dibasic acid or an anhydride of the acid in the presence of a plasticizer using optional free radical initiators, and optionally with the incorporation of nano clays in the reactive extrusion process. The starch is thermoplastic and has a lower viscosity than the traditional thermoplastic starch. The CMPS is useful in preparing starch polymer compositions which are at least partially biodegradable.

WO 2006/055504 A2

**CHEMICALLY MODIFIED PLASTICIZED STARCH
COMPOSITIONS BY EXTRUSION PROCESSING**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not Applicable

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable

STATEMENT REGARDING GOVERNMENT RIGHTS

[0003] Not Applicable

BACKGROUND OF THE INVENTION

(1) Field of the Invention

[0004] The present invention relates to a biodegradable chemically modified plasticized starch (CMPS) composition, and a chemically modified starch-nanoclay CMPS composition, and to a process for the preparation thereof. The invention preferably relates to a twin screw extrusion process for manufacturing the chemically modified starch composition by reacting starch with a dibasic acid or anhydride of the acid as a modifier in the presence of plasticizer and an optional free radical initiator for the acid or anhydride to provide the plasticized starch compositions which have improved processability and reduced viscosity, and is particularly useful when combined with other thermoplastic polymers.

(2) Description of Related Art

[0005] In the last two decades, considerable effort has gone into the development of biodegradable polymers and blends using starch. The processing characteristics and mechanical

properties of unmodified starch polymers are very poor compared to typical synthetic polymers.

[0006] The prior developments in the area of biodegradable materials from starch involve the use of an external plasticizer to solvate the starch granules and impart melt processability and enhance the room-temperature flexibility of the final product. Some of the earliest efforts on such materials were discussed in U.S. Pat. No. 3,312,641 (A. E. Staley Mfg. Co.) and Canadian Patent Appl. No. 838,572 (USDA, Lincoln, Nebr.). The subject of these patents was the extrusion of amylose primarily using water as a plasticizer. In addition, poly (vinyl alcohol), glycerol and other related materials were also incorporated in the system. Cast films from water-based dispersions of starch, glycerol and other polymers were evaluated in U.S. Pat. Nos. 3,949,145, 4,133,784, and 4,337,181 (USDA, Peoria, Ill.). More recently, extruded compositions using water were discussed in Eur. Pat. Appl. EP 282,451, 304,401, 327,505, 404,723, 404,728, and 408,503 (Warner Lambert Co.); water-free systems using glycerol were discussed in PCT Int. Appl. WO 90/05,161 (Tomka); and formulations using both water and other plasticizers like glycerol were the subject of PCT Int. Appl. WO 92/19680 (Novamont S.p.a.), Eur. Pat. Appl. EP 400,531 (Butterfly S.r.l.), and PCT Int. Appl. WO 90/14,388 (Agri-Tech Industries, Inc.).

[0007] WO92/19680 (Novamont) describes the use of undried starch (about 12% moisture) in biodegradable polymeric compositions. These compositions produce films whose properties are sensitive to moisture. WO93/00116 (P&G) describes plastic compositions, which use "destructurized" starch, a form where the crystallinity of the starch has been destroyed by heating. The term "destructurized starch" refers to starch in which the granular, crystalline structure is destroyed resulting in the

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formation of a homogeneous, amorphous material that melts and flows like a thermoplastic. The "destructurization" process is accomplished by heating starch granules in the presence of water at elevated temperatures and pressures in a closed volume like an extruder. The higher the amount of water used, the lower the temperature needed for "destructurization" to be completed. Typical compositions for the "destructurization" processes include extruding starch with about 15-20% water by weight along with other additives. It has been argued that the concept of "destructurization" is just a new name ascribed to an old concept of gelatinization and/or plasticization of starch that first originated in the food industry. The term gelatinization refers to the process of disruption of the granular structure of starch by heating a starch suspension at temperatures in the range of 50°-80°C. Traditional processing in the food industry involves further heating and mixing of starches to result in the formation of a homogeneous plasticized mass as discussed by Shogren, R. L., et al., Starch/Stärke 45, 276-280 (1993). The plasticization of starch using water and glycerol has been reported as early as 1947 for pharmaceutical applications ("The Pharmacopoeia of the United States of America", XIII, p. 513-514, 1947).

[0008] The principal difference between the various applications has to do with the ratios of starch and plasticizer (water, glycerol or both) used in the composition. This leads to differences in the rheological and final characteristics of each composition that is suited to the specific application. A high proportion of plasticizer (70-90% by weight) results in a jelly-like material. Medium plasticizer contents (40-70% by weight) are more suited for food applications that have good elasticity combined with reasonable rigidity to be able to form and shape various products. Low

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plasticizer contents (10-40% by weight) are appropriate for plastics applications that require greater rigidity and better mechanical strength characteristics. More recently, plasticization of starch in the absence of water, using polyhydric alcohols like glycerol and sorbitol has been reported. The term plasticization in the classical sense as used in the polymer industry involves transformation of a rigid, crystalline material into a pliable, less crystalline (if not amorphous) material with a lowered glass transition temperature. Japanese Patent No. 04-48,851 discloses the manufacture of biodegradable sheets based upon mixtures of starch and biodegradable polyesters derived from reactions of diols and acids. The starch has normal moisture content of about 10 to 12% by weight.

[0009] In a typical plasticized system with starch, the diffusion of plasticizer out of the product when exposed to low humidity conditions and diffusion of water into the product under high humidity conditions is an inevitable result. This causes embrittlement of the product due to loss of plasticizer (low humidity) and problems associated with retention of product shape, texture, and form due to excess absorbed water (high humidity). These effects are detrimental especially when water is used as a plasticizer, but are prevalent even in non-water based starch formulations that incorporate hygroscopic plasticizers. In general, due to the poor durability of plasticized starch upon exposure to different environments (due to its hydrophilic nature) there is likely to be very little commercial use of plasticized native or unmodified starch by itself.

[0010] Physical or chemical modifications of the starch are a viable alternative to solving some of these problems. Physical modifications include coating the starch granules with

hydrophobic sizing agents and binders similar to those used in the paper industry, like rosin, proteins, like soy proteins and silanes or physically coating the end product with hydrophobic materials like low molecular weight waxes, and natural resins (zein, rosin, shellac and the like) and higher molecular weight non-polar polymers. Cross-linking of the starch granules or plasticized starch is another physical modification route to improving the hydrophobicity of starch-based materials. Chemical modifications include grafting reactions and non-degradative substitution of the hydroxyls on the starch with functional groups like esters, ethers, isocyanates and the like. Cyclic dibasic acid anhydrides such as succinic anhydride yield starch esters containing a free carboxylate group that increases the water-holding capacity of the product (U.S. Patent No. 2,461,139; 1949). The same chemistry can be carried out with maleic anhydride to yield the maleate half ester. Treatment of a starch suspension with a cyclic dicarboxylic acid anhydride containing a hydrophobic substituent group yields products with emulsion stabilizing properties (U.S. Patent No. 2,661,349; 1953). These starch esters have value as dispersants in coatings replacing commercially available paint containing dispersants. U.S. Patent 3,732,207 discusses the production of starch esters by heating starch with maleic or succinic anhydride at 100-155 °C in a batch process with reaction times of 10 hours in the presence of 0.5-15% moisture to give a product with degree of substitution (DS) 0.02 to 0.04.

[0011] Tomasik et al., Starch 47 96 (1995) reacted corn starches in extruders containing varying amounts of moisture (18, 20 and 30%) with succinic, maleic and phthalic anhydrides to form starch esters. Carbonate buffer, either pH 8 or pH 9 was added as a medium during extrusion. It is demonstrated that

extrusion of starch with cyclic anhydrides in alkaline medium presents a facile method of preparation of anionic starches of hydrophobic character based. However, this method has several serious limitations resulting from the chemistry and the extrusion process. For example, it is extremely difficult to extrude these samples at temperatures of around 130°C due to the resultant high viscosity of the starch melt. Also, the use of water is extremely problematic in processing and quality of the final product.

[0012] Related prior art is described in:

- (1) Ramani Narayan, Steven Bloembergen and Amit Lathia, A Method of Preparing Biodegradable Modified-Starch Moldable Products and Films, U.S. Patent 5,869,647, February 9, 1999 , July 1993;
- (2) Narayan, R., Biodegradable Multi-Component Polymeric Materials Based on Unmodified Starch-Like Polysaccharides, U.S. Patent 5,500,465, October 31, 1995;
- (3) Narayan, R., Krishnan, M., DuBois, P., Polysaccharides Grafted With Aliphatic Polyesters Derived From Cyclic Esters, U.S. Patent 5, 540, 929, July 30, 1996;
- (4) Narayan, R., Krishnan, M., DuBois, P., Polysaccharides Grafted With Aliphatic Polyesters Derived From Cyclic Esters, U.S. Patent 5,578,691, November 26, 1996;
- (5) Narayan, R., Krishnan, M., DuBois, P., Polysaccharides Grafted With Aliphatic Polyesters Derived From Cyclic Esters, U.S. Patent 5, 616,671, April 1, 1997;
- (6) U.S. patent application co-filed with the present application.

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OBJECTS

[0013] It is an object of the present invention to provide a chemically modified plasticized starch and plasticizer compositions which have improved properties. It is further an object of this invention to provide a process which is economical and reproducible. These and other objects will become increasingly apparent by reference to the following description.

SUMMARY OF THE INVENTION

[0014] The present invention relates to biodegradable, reactive, chemically modified plasticized starch (CMPS) compositions with low viscosity and good processability. Further, the present invention relates to a continuous reactive extrusion process for manufacturing the compositions. An important aspect of this invention is that the process uses no added water, and prevents problems such as high viscosity, clogging of the thermoplastic starch melt at the die or foaming of the thermoplastic starch melt. Furthermore, the resulting chemically modified starch composition is highly reactive to yield graft copolymers with polyesters as described in detail in our co-pending patent application, which is incorporated herein by reference. These starch-polyester graft copolymers are readily processable into films, and molded products using conventional plastics processing equipment, and the resultant product has the most preferred balance in mechanical properties, water resistance, processability and the rate of biodegradation. The invention also describes a new chemically modified starch-nano clay composition with improved dispersability of the nano clay in the matrix, reactivity and processability for subsequent reaction with polyesters as described in our co-pending patent application.

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[0015] In accordance with the present invention, there is provided a biodegradable, reactive low viscosity chemically modified plasticized starch composition (CMPS) prepared by the reactive blending or extrusion processing of starch in the presence of chemical modifiers, a plasticizer and an optional free-radical initiator.

[0016] The present invention also provides a biodegradable chemically modified starch-nano clay product prepared by reactive extrusion processing of starch in the presence of modifiers, plasticizers and nanoclay material.

[0017] The present invention also relates to a composition which comprises a mixture of starch esters of a dibasic acid or an anhydride of a dibasic acid, wherein the mixture has reduced viscosity from a natural starch in dimethyl sulfoxide.

[0018] The present invention also relates to a starch based composition which comprises a reacted mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, and anhydride of the dibasic organic acid, or mixtures thereof, and a plasticizer.

[0019] In particular the present invention relates to a starch based composition which comprises a reactively extruded mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer and, optionally a free radical initiator for the reaction, wherein the mixture has been extruded with heating and venting of water from the mixture.

[0020] Further, the present invention relates to a biodegradable, chemically modified starch based composition which comprises a reactively extruded mixture comprising a biodegradable starch polymer, a chemical modifier selected from

the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer optionally a free radical initiator for the reaction and a nanoclay, wherein the mixture has been extruded with heating and venting of water from the mixture.

[0021] Preferably the starch polymer is selected from the group consisting of cornstarch, potato starch, tapioca starch, rice starch, wheat starch, and cassava starch. Preferably the starch polymer in the mixture is present in an amount between about 5% to 90% by weight of the mixture. Preferably the starch polymer is an unmodified, oxidized or thin boiling starch of 0 to 95 degree fluidity. Preferably the starch polymer has moisture content of about 0.5% to 15% by weight. Preferably the starch polymer is in a pulverized form. Preferably the plasticizer is a polyhydric alcohol. Preferably the plasticizer is present in an amount between about 10 to 50 wt% of the mixture. Preferably the chemical modifier is present in an amount between about 0.5% to about 10% by weight of the starch polymer. Preferably the nanoclay is selected from a group consisting of montmorillonite; smectite, hectorite and mixtures thereof. Preferably the nanoclay is present in an amount between about 0.5 to 25 wt% of the mixture. Preferably the free radical initiator is 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane or other organic peroxide. Preferably the free radical initiator is present in the mixture in an amount between about 0.01 to 2.0 wt% of the mixture. Preferably the mixture is processed in a twin-screw extruder at a temperature in the range of about 100°C to 200°C.

Preferably the anhydrides are selected from the group consisting of maleic-, succinic-, itaconic-, phthalic- and mixtures thereof. Preferably the chemical modifier is about 2% to 5% by weight of the starch polymer of the mixture.

[0022] The present invention also relates to a process for preparing a starch based composition which comprises reactively extruding a mixture which comprises a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer and, optionally a free radical initiator wherein the mixture is extruded with heating and venting of water from the mixture. Preferably the starch polymer and modifier are mixed as powders. The processing is preferably at 100-250°C.

BRIEF DESCRIPTION OF THE FIGURES

[0023] Other advantages of the present invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

[0024] FIGURE 1 is a graph which depicts the calibration curve of the glycerol pump used in the synthesis of chemically modified plasticized starch (CMPS); by reactive extrusion processing using maleic anhydride or maleic acid modifier.

[0025] Figure 2 is an extrusion flow apparatus diagram for the preparation of CMPS.

[0026] FIGURES 3A, 3B and 3C show the screw configurations used for reactive extrusion processing in the synthesis of CMPS.

[0027] FIGURE 4 is a graph showing FTIR results of CMPS samples produced using maleic anhydride modifier by the reactive extrusion processing. CMPS samples were extracted in THF solvent using a Soxhlet apparatus. Residue from the thimble of the apparatus was dried to constant weight and FTIR analysis conducted. Solvent was evaporated from the extract and the extract dried to constant weight and FTIR analysis conducted.

[0028] FIGURE 5 is a graph showing the FTIR results of CMPS samples produced using maleic acid modifier by reactive extrusion processing. CMPS samples were extracted in THF solvent using a Soxhlet apparatus. Residue from the thimble was dried to constant weight and FTIR analysis conducted. Solvent was evaporated from the extract and the extract dried to constant weight and FTIR analysis conducted.

DETAILED DESCRIPTION OF THE INVENTION

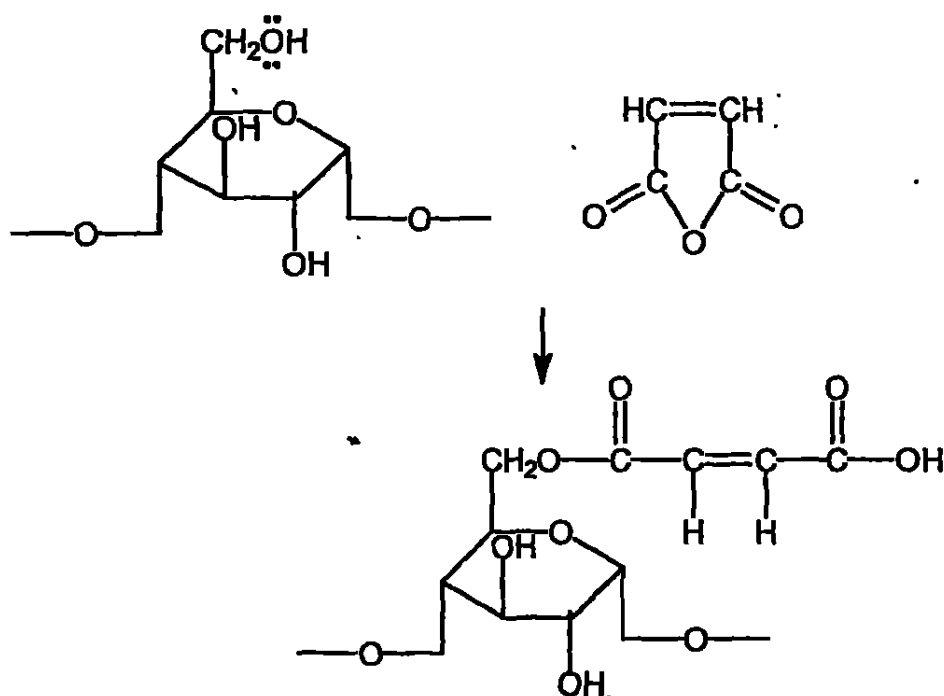
[0029] The present invention provides (i) a biodegradable chemically modified starch composition, (ii) a biodegradable chemically modified starch-nanoclay composition, (iii) and a method for making thereof wherein, generally, the composition is prepared by continuous reactive extrusion processing. Preferably, the present invention concerns a) biodegradable, highly reactive, chemically modified starch composition with low viscosity and high processability, that yields graft copolymers with biodegradable polyesters as described in our co-pending patent application. Another object of the present invention is to provide b) a new chemically modified starch-nanoclay composition with improved dispersability of the nanoclay in the matrix, reactivity and processability for subsequent reaction with polyesters as described in our co-pending patent application.

[0030] The components of the biodegradable chemically modified starch composition that are employed in the process that is within the scope of this invention preferably include the following:

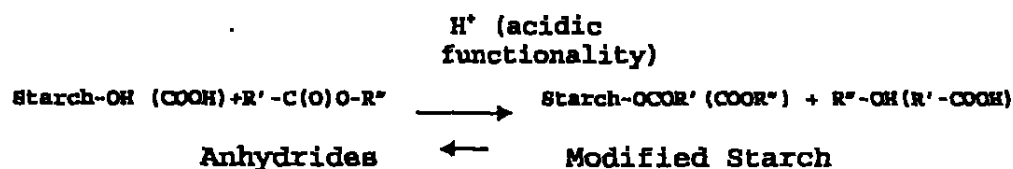
- (I) Starch preferably selected from the group of potato starch, corn starch, waxy starch, tapioca starch, rice starch, wheat starch, and cassava starch and the like

- (II) Plasticizer preferably selected from the group of polyhydroxy compounds including glycerol, ethylene glycol, and the like
- (III) Modifier selected from the group of dibasic acids and their cyclic anhydride compounds; and
- (IV) Optionally, free radical initiator selected from the group of peroxides, and the like.

The proposed reactions are:



Maleation Chemistry



Transesterification Chemistry

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[0031] Starch $(C_6H_{10}O_5)_n$, is a mixture of linear (amylose) and branched (amylopectin) polymers. Amylose is essentially a linear polymer of α -(1 $\rightarrow$ 4) linked D-glucopyranosyl units. Amylopectin is a highly-branched polymer of D-glucopyranosyl units containing α -(1 $\rightarrow$ 4) linkages, with α -(1 $\rightarrow$ 6) linkages at the branch points. The process of the present invention can use various types of starches, such as regular corn starch which contains about 75% amylopectin (higher molecular weight branched starch polymer) and 25% amylose (lower molecular weight linear starch polymer), as well as hybrid corn starch products containing more than 50% amylose, sold by Corn Products, Inc. (Chicago, Illinois). Various other starches, such as potato starch, tapioca starch, rice starch, wheat starch, cassava starch, and other starches familiar to those skilled in the art can be utilized in accordance with the present invention. Compositions having increased levels of linear starch polymers are most likely to be the correct choice in terms of processability, film forming, molding and mechanical properties. The starch component in the chemically modified starch composition is 5% to 90% by weight, preferably from 50% to 80% by weight.

[0032] A plasticizer is added to the inventive compositions to achieve greater material processability and product flexibility, although plasticizers typically soften the compositions in which they are included. The preferred plasticizers are polyhydric alcohols. More preferably, glycerol is used as a suitable plasticizer since it induces high flexibility, is virtually odorless, has a relatively high boiling point, is biodegradable, and is commercially available at a reasonable cost. Plasticizer concentration in the final chemically modified starch product is 15% to 50% by weight and

preferably from 20% to 30% by weight.

[0033] The preferred modifiers that are useful in the present invention are to provide a chemically modified starch ester product. The starch ester product may preferentially be formed by reaction of the starch hydroxyl groups with a dibasic acid or cyclic anhydride to obtain ester linkages with pendant carboxylic groups as shown in Scheme I. The derived pendant carboxylic group can also catalyze the aforementioned reaction between the hydroxyl groups on the starch, and the dibasic acids or their cyclic anhydrides. The more preferred dibasic acids and their cyclic anhydrides include maleic-, succinic-, itaconic-, phthalic- and stearic anhydrides and combinations thereof. The modifier is preferably present in amount of about 0.5% to about 10% by weight of the starch polymer and also provides an acidic environment for the mixture.

[0034] Optionally, a free radical initiator may be used for improving the melt-strength of chemically modified starch product. It is preferred that the free radical initiator be an organic peroxide such as 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane, tert-butylperoctoate, tert-butylperoxypivalate, dicumylperoxide, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, bis(tert-butylperoxyisopropyl)benzene and the like. Azo compounds, such as azobisisobutyronitrile can be also used. The free radical initiator is present in the amount of 0.01 to 2.0 wt percent of the total mass.

[0035] The present invention also relates to a biodegradable chemically modified starch-nano clay product, prepared by reactive extrusion processing of starch in the presence of modifiers, plasticizers, and nanoclay material.

[0036] Nanoclays can be useful to provide an increased mechanical strength, flame retardancy, gas barrier properties,

and improved barrier to water vapor for chemically modified nanoclay starch product (ii). Another preferred embodiment is that the nanoclays useful for the present invention are well-dispersed in the biodegradable chemically modified starch-clay product. The preferred nanoclays are smectite, hectorite clays including phyllosilicates such as smectite clay minerals, e.g., montmorillonite, particularly sodium montmorillonite; bentonite; hectorite; saponite; stevensite; beidellite; and the like. The clays used are typically smectite clays, particularly bentonite and hectorite. Smectite clays possess some structural characteristics similar to the better-known minerals talc and mica. The preferred range of nanoclays is ranging from 0.5 to 25 wt % of the total mass.

[0037] The reactive modification process of starch to form chemically modified plasticized starch (CMPS) in an extruder prevents the traditionally seen problems, such as clogging of the plasticized starch melt at the die or foaming of the plasticized starch melt at the die, observed during the regular thermo-plasticization of starch. The apparatus used in carrying out the extrusion process may be any screw type extruder. While the use of a single or twin screw extruder may be used, it is preferred to use a twin-screw extruder. Such extruders will typically have rotating screws in a horizontal cylindrical barrel with an entry port mounted over one end and a shaping die mounted at the discharge end. When twin screws are used, they may be co-rotating and intermeshing or non-intermeshing. Each screw will comprise a helical flight or threaded sections and typically will have a relatively deep feed section followed by a tapered transition section and a comparatively shallow constant-depth meter section. The motor driven screws, generally fit snugly into the cylinder or barrel to allow mixing, heating and shearing of the material as it passes

through the extruder.

[0038] Control of the temperature along the length of the extruder barrel is important and is accomplished in zones along the length of the screw. Heat exchange means, typically a passage such as a channel, chamber or bore located in the barrel wall, for circulating a heated media such as oil, or an electrical heater such as calrod or coil type heaters, are often used. Additionally, heat exchange means may also be placed in or along the shaft of the screw device.

[0039] Variations in any of the elements used in the extruder may be made as desired in accordance with conventional design practices. A further description of extrusion and typical design variations can be found in "Encyclopedia of Polymer Science and Engineering", Volume 6, 1986, pp. 571 to 631.

[0040] In carrying out the extrusion process, temperatures in the extruder will vary depending on the particular material, desired properties and application. They can generally range from about 100.degree. to 250 degree. C. and preferably will range from about 150.degree. to 200.degree. C.

[0041] Further, the biodegradable chemically modified starch (i), and biodegradable chemically modified starch-nanoclay compositions (ii) can be manufactured in a one-step process; wherein the components were previously mixed together, and were then introduced into the feed throat of a twin-screw extruder (such as a Century ZSK-30 co-rotating twin screw extruder) at a feed rate of 500-9000 g/hr by means of a solid metering. Alternatively, the components may be separately introduced in the case of liquid component by means of a peristaltic pump, and in the case of solid component by means of a solid metering

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at a feed rate of 40-8000 g/hr.

[0042] The biodegradable, chemically modified starch composition and the biodegradable, chemically modified starch-nanoclay compositions are particularly useful for manufacturing starch-polyester graft copolymers as described in our co pending patent application referred to previously.

[0043] The following experimental examples demonstrate the utility of the present invention for forming biodegradable chemically modified starch (i), and biodegradable chemically modified starch-nanoclay (ii) compositions.

[0044] Examples of materials made in accordance with the present invention are biodegradable as demonstrated by standard ASTM test methods.

EXAMPLES

Example 1

[0045] Chemical modification of starch polymer was carried out as follows:

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[0046] Regular silver pearl corn-starch, obtained from Cargill Inc. was reactively modified using maleic anhydride/maleic acid in a twin-screw co-rotating CENTURY extruder with a screw diameter of 30 mm and a L/D ratio of 40. Maleic anhydride (MA) was ground to a fine powder using a mortar and pestle and mixed with the starch (800 gm starch + [20 gm] maleic anhydride) using a kitchen blender for 15 minutes before being fed to the feed port of the extruder. Glycerol was mixed with 2, 5-Bis (tert-butylperoxy)-2, 5-dimethylhexane (Luperox 101) {200 gm glycerol + 1.6 gm Luperox 101} and pumped to the extruder using a peristaltic pump. The relative rates of the starch/MA mixture to the glycerol/Luperox 101 mixtures were maintained at 80:20. The calibration curve for the glycerol pump is shown in Figure 1. The screw configuration used for the maleation consisted of conveying and kneading elements as shown in Figures 3A to 3C. A water vacuum was applied at the vent port to remove the unreacted maleic acid/water mixture. The chemically modified plasticized starch, CMPS, was collected and ground to a fine powder. Ground CMPS was stored in an oven at 50°C. The extrusion processing conditions for the reactive maleation is outlined in Table 1.

TABLE 1: Extrusion Processing conditions in the synthesis of CMPS

ZONE	SET	ACTUAL	UNITS
ZONE1	15	39	°C
ZONE2	95	103	°C
ZONE3	125	122	°C
ZONE4	145	146	°C
ZONE5	160	157	°C
ZONE6	165	161	°C
ZONE7	165	167	°C
ZONE8	165	164	°C
ZONE9	150	156	°C
DIE	145	147	°C
MELT TEMP.		148	°C
MOTOR SPEED		125	RPM
TORQUE		35	%
PRESSURE		92	Psia
FEEDER SPEED, CENTURY		155 (Rate = 12.3 lbs/hr)	%
GLYCEROL PUMP		0.1 (Rate = 3.07 lbs/hr)	%
FEEDER SPEED, EXT		-	%

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[0047] CMPS produced was extracted using tetrahydrofuran (THF) in a Soxhlet apparatus to remove the unreacted maleic anhydride and maleic acid (formed by reaction with water present in starch). FTIR analysis (Figure 4) of the Soxhlet residue (after drying in an oven at 50°C overnight) confirmed grafting of the maleic anhydride onto the starch backbone with the presence of the ester carbonyl peak at 1720 cm⁻¹.

Example 2

[0048] The procedure given in Example 1 was followed using maleic acid modifier instead of maleic anhydride. CMPS produced was extracted using tetrahydrofuran (THF) in a Soxhlet apparatus to remove the unreacted maleic acid. FTIR analysis (Figure 5) conducted on the Soxhlet residue (after drying in an oven at 50°C overnight) confirmed grafting of the maleic acid onto the starch backbone with the presence of the ester carbonyl peak at 1720 cm⁻¹.

Example 3

[0049] The procedure in Example 1 was followed to produce CMPS modified using 2.4-wt%, maleic anhydride, both with and without the initiator. Chemically modified plasticized starch (CMPS) was produced by plasticization of regular corn starch (Corn Products, Inc-Brazil) using 20-wt% glycerol plasticizer in a twin-screw extruder. The intrinsic viscosity of starch, PS, CMPS (2.4-wt% maleic anhydride and 0.1-wt% Luperox 101) and CMPS (no Luperox 101) were determined in DMSO solvent using Cannon Ubbelohde viscometer (0B). The intrinsic viscosity of starch was around 1.6 dl/g while that of PS reduced to 1.2 dl/g. However, on maleation without addition of Luperox 101, the intrinsic viscosity of CMPS drastically dropped to 0.29 dl/g. This reduction is attributed to a decrease in molecular

weight due to the hydrolysis of starch in the presence of maleic acid. However, on addition of Luperox 101, the intrinsic viscosity increased slightly to 0.31 dl/g. This increase is attributed to branching or cross-linking reactions occurring.

Example 4

[0050] Chemical modification of starch polymer to form chemically modified plasticized starch-nano clay products.

[0051] Regular silver pearl corn-starch, obtained from Cargill Inc. was reactively modified using maleic anhydride/maleic acid in a twin-screw co-rotating CENTURY™ extruder with a screw diameter of 30 mm and a L/D ratio of 40 in the presence of BENTONE 166™, which is an alkylaryl ammonium hectorite clay, obtained from Elementis Specialties (Highstown, NJ), with greatly improved dispersability characteristics. Maleic anhydride (MA) was ground to a fine powder using a mortar and pestle and mixed with the starch (800 gm starch + 20 gm maleic anhydride + 150 gm BENTONE 166) using a kitchen blender for 15 minutes before being fed to the feed port of the extruder. 200 gm glycerol was pumped to the extruder using a peristaltic pump. The relative rates of the starch/MA/BENTONE 166 mixture to the glycerol were maintained at 80:20.

Example 5

[0052] The procedure in Example 4 was followed to produce CMPS modified using 2.5-wt%, maleic anhydride and BENTONE 111™, which is an organic derivative of a special smectite clay, obtained from Elementis Specialties. Maleic anhydride (MA) was ground to a fine powder using a mortar and pestle and mixed with the starch (800 gm starch + 20 gm maleic anhydride + 150 gm BENTONE 111) using a kitchen blender for 15 minutes before being fed to the feed port of the extruder. 200 gm glycerol was

pumped to the extruder using a peristaltic pump. The relative rates of the starch/MA/BENTONE 111 mixture to the glycerol were maintained at 80:20.

Example 6

[0053] The procedure in Example 4 was followed to produce CMPS-clay product using 2.5-wt%, maleic anhydride and Cloisite 30B™, which is a montmorillonite clay modified with dihydroxy quaternary ammonium salt obtained from Southern Clay Products.

[0054] Preferably the starch esters with the plasticizer (glycerol) have a viscosity in the range of about 0.15 to 0.3 dl/gram in DMSO. Natural starch has a viscosity of 1.51 dl/gm and plasticized starch has a viscosity of 1.20 dl/gm. Thus there is a significantly reduced viscosity.

[0055] It is intended that the foregoing description be only illustrative of the present invention and that the present invention be limited only by the hereinafter appended claims.

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WE CLAIM:

1. A composition which comprises a mixture of starch esters of a dibasic acid or an anhydride of a dibasic acid, wherein the mixture has reduced viscosity from a natural starch in dimethyl sulfoxide.
2. A starch based composition which comprises a reacted mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of the dibasic organic acid or mixtures thereof and a plasticizer.
3. A starch based composition which comprises a reactively extruded mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer and, optionally a free radical initiator for the reaction, wherein the mixture has been extruded with heating and venting of water from the mixture.
4. A biodegradable, chemically modified starch based composition which comprises a reactively extruded mixture comprising a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer optionally a free radical initiator for the reaction and a nanoclay, wherein the mixture has been extruded with heating and venting of water from the mixture.

5. The composition of any one of Claims 1, 2, 3, or 4 wherein said starch polymer is selected from the group consisting of cornstarch, potato starch, tapioca starch, rice starch, wheat starch, and cassava starch.
6. The composition of any one of Claims 1, 2, 3, or 4 wherein the starch polymer in the mixture is present in an amount between about 5% to 90% by weight of the mixture.
7. The composition of any one of Claims 1, 2, 3, or 4 wherein starch polymer is an unmodified, oxidized or thin boiling starch of 0 to 95 degree fluidity.
8. The composition of any one of Claims 1, 2, 3, or 4 wherein the starch polymer has moisture content of about 0.5% to 15% by weight.
9. The composition of any one of Claims 1, 2, 3, or 4 wherein said starch polymer is in a pulverized form.
10. The composition of any one of Claims 2, 3, or 4 wherein the plasticizer is a polyhydric alcohol.
11. The composition of any one of Claims 2, 3, or 4 wherein the plasticizer is present in an amount between about 10 to 50 wt% of the mixture.
12. The composition of any one of Claims 1, 2, 3, or 4 wherein the chemical modifier is the dibasic organic acid.

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13. The composition of any one of Claims 1, 2, 3, or 4 wherein the chemical modifier is the anhydride.
14. The composition of any one of Claims 1, 2, 3, or 4 wherein the chemical modifier is present in an amount between about 0.5% to about 10% by weight of the starch polymer,
15. The composition of Claim 4 wherein the nanoclay is selected from a group consisting of montmorillonite; smectite, hectorite and mixtures thereof.
16. The composition of Claim 4 wherein the nanoclay is present in an amount between about 0.5 to 25 wt% of the mixture.
17. The composition of Claim 3 wherein the free radical initiator is present and is 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane.
18. The composition of Claim 3 wherein the free radical initiator is present in the mixture in an amount between about 0.01 to 2.0 wt% of the mixture.
19. The composition of any one of Claims 1, 2, 3, or 4 wherein the mixture is processed in a twin-screw extruder at a temperature in the range of about 100°C to 200°C.

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20. The composition of any one of Claims 1, 2, 3, or 4 wherein the acids or anhydrides are selected from the group consisting of maleic-, succinic-, itaconic-, phthalic- and mixtures thereof.
21. The composition of any one of Claims 1, 2, 3, or 4 wherein the chemical modifier is about 2% to 5% by weight of the starch polymer of the mixture.
22. A process for preparing a starch based composition which comprises reactively blending a mixture which comprises a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer and, optionally a free radical initiator wherein the mixture is extruded with heating and venting of water from the mixture.
23. The process of Claim 22 wherein the starch polymer and modifier are mixed as powders.
24. The process of Claim 22 wherein the processing is at a temperature between about 130 and 180°C.
25. The composition of any one of Claims 2, 3, or 4 wherein the plasticizer is glycerol.
26. The composition of any one of Claims 2, 3, or 4 wherein the plasticizer is about 15 to 30% by weight of the composition.

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27. The composition of any one of Claims 1, 2, 3, or 4 wherein the acid is maleic acid and the anhydride is maleic anhydride.

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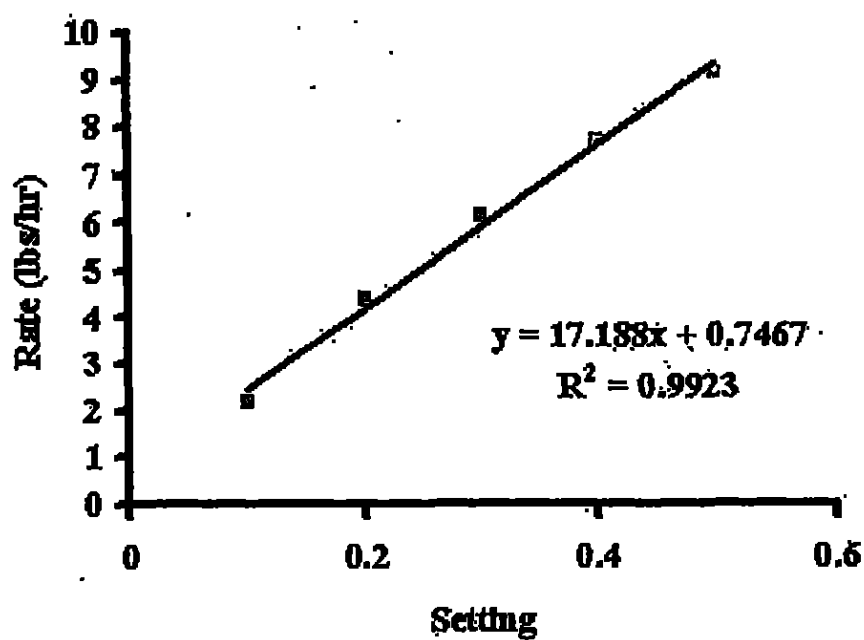


FIGURE 1

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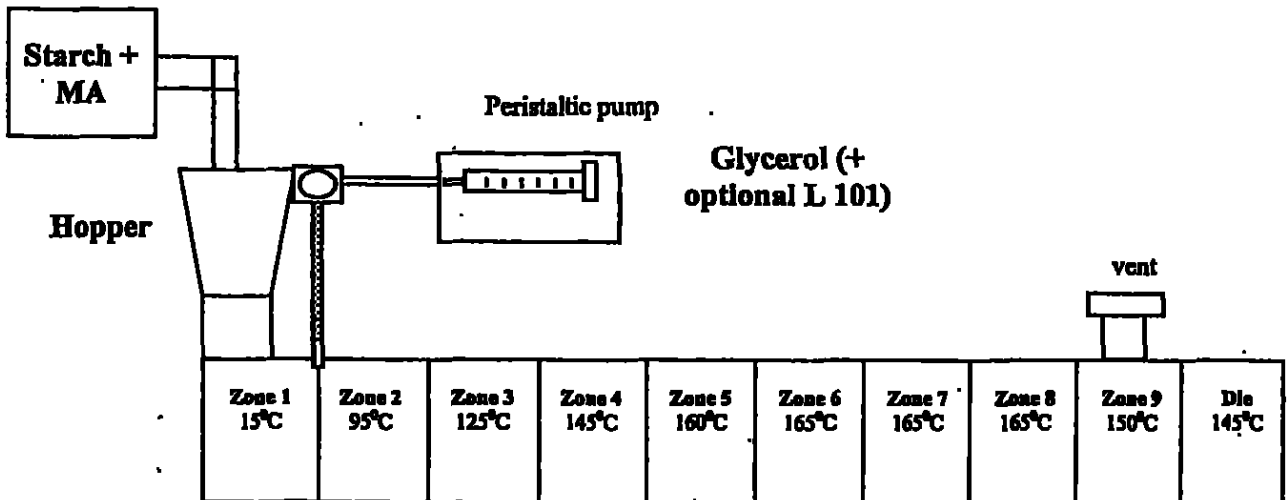


FIGURE 2

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FIG. 3A



FIG. 3B



FIG. 3C

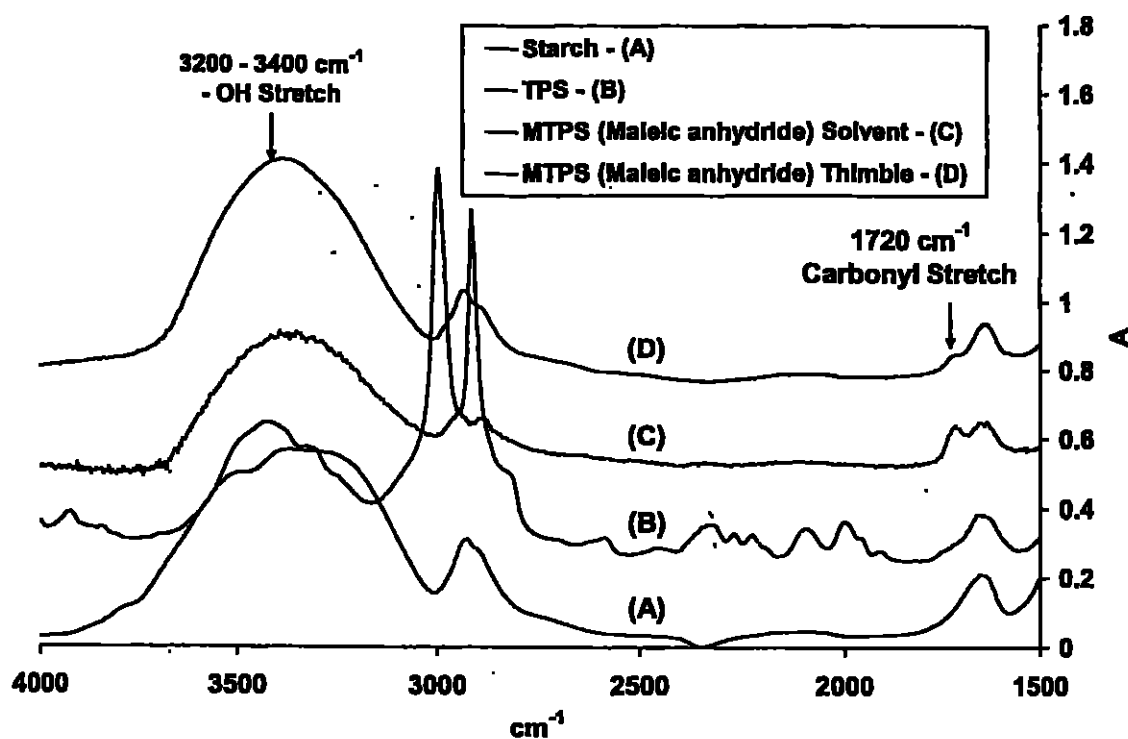


FIGURE 4

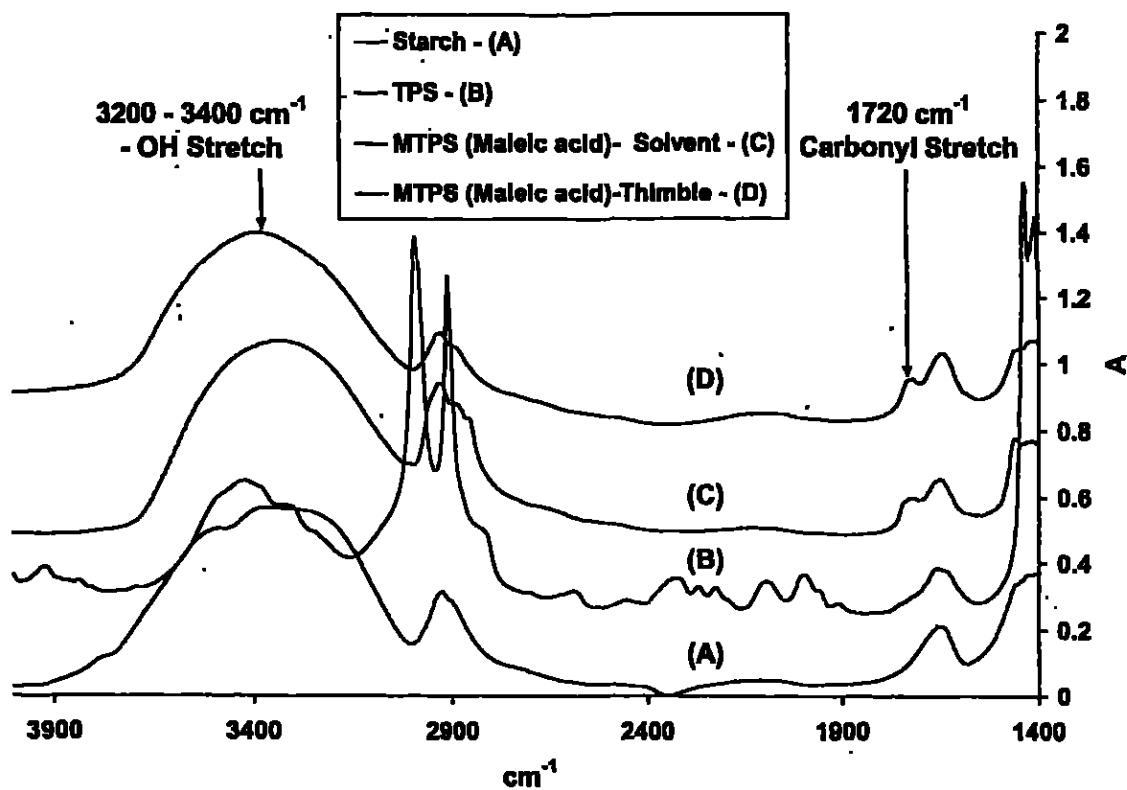


FIGURE 5

(12) SOLICITUD INTERNACIONAL PUBLICADA BAJO EL TRATADO DE COOPERACIÓN INTERNACIONAL EN MATERIA DE PATENTES (PCT)

(19) Organización Mundial de Propiedad Intelectual
Oficina Internacional



(43) Fecha de Publicación Internacional

28 de mayo de 2006 (28.05.2006)

(10) Número de Publicación Internacional

PCT

WO 2006/055504 A2

(51) Clasificación Internacional de Patentes:
C08B 30/12 (2006.01), C08J 103/06 (2006.01)

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(21) No. Solicitud Internacional: PCT/US2005/041237

(22) Fecha de Presentación Internacional:
15 de noviembre de 2005 (15.11.2005)

(25) Idioma de Presentación: Inglés

(26) Idioma de Publicación: Inglés

(30) Datos relativos a la Prioridad:
10/993,309 19 de noviembre de 2004 (19.11.2004) US

(71) Solicitante (para todos los países destinatarios con
excepción de US): MICHIGAN STATE UNIVERSITY
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(51) Países designados (a menos que se indique lo
contrario para cada clase de protección
disponible): AE, AG, AL, AM, AT, AU, AZ, BA, BB,
BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU,
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NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT,
TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(54) Países designados (a menos que se indique lo
contrario para cada clase de protección
disponible): ARIPO (BW, GH, GM, KE, LS, MW,
MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurselática
(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), Europea
(AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR,
GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL,
PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG,
CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,
TG).

Publicado:

— con informe internacional de búsqueda y a
volver a publicar al recibo de dicho informe

Para códigos de dos letras y otras abreviaturas, remítase
a las "Notas Guía sobre Códigos y Abreviaturas" que
aparece al comienzo de cada edición regular del Boletín
Oficial PCT.

(54) Título: COMPOSICIONES DE ALMIDÓN PLASTIFICADO, MODIFICADO QUÍMICAMENTE, POR
PROCESAMIENTO CON EXTRUSIÓN

(57) Extracto: Se prepara un almidón plastificado modificado químicamente (CMPS) haciendo reaccionar almidón con un
ácido dibásico orgánico o un anhídrido del ácido en la presencia de un plastificante, usando iniciadores opcionales de
radicales libres y, opcionalmente, con la incorporación de nanoarcillas en el proceso de extrusión reactiva. El almidón es
termoplástico y tiene una viscosidad más baja que el almidón termoplástico tradicional. El CMPS es útil en preparar
composiciones de polímero de almidón, las cuales son por lo menos parcialmente biodegradables.

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**COMPOSICIONES DE ALMIDÓN PLASTIFICADO, MODIFICADO
QUÍMICAMENTE, POR PROCESAMIENTO CON EXTRUSIÓN**

REFERENCIA CRUZADA A SOLICITUDES RELACIONADAS

[0001] No Aplicable

**DECLARACIÓN CON RESPECTO A INVESTIGACIÓN O
DESARROLLO PATROCINADOS FEDERALMENTE**

[0002] No Aplicable

**DECLARACIÓN CON RESPECTO A DERECHOS
GUBERNAMENTALES**

[0003] No Aplicable

ANTECEDENTES DE LA INVENCION

(1) Campo de la invención

[0004] La presente invención se refiere a una composición de almidón plastificado, modificado químicamente (CMPS - *chemically modified plasticized starch*), biodegradable, y a una composición CMPS de nanoarcilla-almidón modificado químicamente, y a un proceso para su preparación. Preferiblemente, la invención concierne a un proceso de extrusión con doble tornillo para fabricar la composición de almidón modificado químicamente haciendo reaccionar almidón con un ácido dibásico o anhídrido del ácido como modificador, en la presencia de un plastificante y un iniciador opcional de radicales libres para el ácido o anhídrido, con el fin de proporcionar las composiciones de almidón plastificado, las cuales poseen una capacidad de transformación mejorada y viscosidad reducida, y es particularmente útil cuando se combina con otros polímeros termoplásticos.

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(2) Descripción del Arte Relacionado

[0005] En las últimas dos décadas, se han invertido esfuerzos considerables en el desarrollo de polímeros biodegradables y mezclas que utilizan almidón. Las características de procesamiento y las propiedades mecánicas de polímeros de almidón no modificado son muy pobres comparadas con los polímeros sintéticos típicos.

[0006] Los desarrollos previos en el área de materiales biodegradables obtenidos del almidón involucran el uso de un plastificante externo para solvatar los gránulos de almidón e impartir capacidad de transformación por fusión ("*melt processability*") y aumentar la flexibilidad a temperatura ambiente del producto final. Algunos de los esfuerzos pioneros en tales materiales se discutieron en la Patente de los Estados Unidos No. 3,312,641 (A. E. Staley Mfg. Co.) y la Solicitud de Patente Canadiense No. 838,572 (USDA, Lincoln, Nebr.). El tema de estas patentes era la extrusión de amilosa usando principalmente agua como plastificante. Además, se incorporaron igualmente en el sistema alcohol poli(vinílico), glicerol y otros materiales relacionados. En las Patentes de los Estados Unidos No. 3,949,145, 4,133,784, y 4,337,181 (USDA, Peoria, Ill.) se evaluaron películas moldeadas a partir de dispersiones a base de agua de almidón, glicerol y otros polímeros. Más recientemente, en las Solicitudes de Patente Europea EP 282,451, 304,401, 327,505, 404,723, 404,728, y 408,503 (Warner Lambert Co.) se discutieron composiciones extruidas utilizando agua; sistemas libres de agua usando glicerol se discutieron en la Solicitud Internacional PCT WO 90/05,161 (Tomka); y formulaciones usando agua y otros plastificantes como glicerol fueron objeto de la Solicitud Internacional PCT WO 92/19680 (Novamont S.p.a.), la Solicitud de Patente Europea EP 400,531 (Butterfly S.r.l.), y la Solicitud Internacional PCT WO 90/14,388 (Agri-Tech Industries, Inc.).

[0007] WO92/19680 (Novamont) describe el uso de almidón no secado (alrededor de 12% de humedad) en composiciones poliméricas

biodegradables. Estas composiciones producen películas cuyas propiedades son sensibles a la humedad. W093/00116 (P&G) describe composiciones plásticas, que utilizan almidón "desestructurado", una forma en la que la cristalinidad del almidón se ha destruido por calor. El término "almidón desestructurado" se refiere a un almidón en el cual se destruye la estructura cristalina granular, resultando en la formación de un material amorfo homogéneo que se funde y fluye como un termoplástico. El proceso de "desestructuración" se lleva a cabo calentando los gránulos de almidón en la presencia de agua a temperaturas y presiones elevadas en un volumen cerrado como una extrusora. Entre más alta sea la cantidad de agua empleada, menor es la temperatura necesaria para completar la "desestructuración". Composiciones típicas para los procesos de "desestructuración" incluyen extruir almidón con alrededor de 15-20% de agua en peso, junto con otros aditivos. Se ha argumentado que el concepto de "desestructuración" es sólo una nueva denominación asignada a un concepto viejo de la gelatinización y/o plastificación del almidón, que se originó por primera vez en la industria de alimentos. El término gelatinización se refiere al proceso de ruptura de la estructura granular del almidón calentando una suspensión de almidón a temperaturas en el rango de 50°-80°C. El procesamiento tradicional en la industria de alimentos involucra además el calentamiento y mezclado de almidones para resultar en la formación de una masa plastificada homogénea, como se discute por Shogren, R. L., et al., Starch/Stärke 45, 276-280 (1993). La plastificación del almidón usando agua y glicerol se divulgó en épocas tan tempranas como 1947 para aplicaciones farmacéuticas ("The Pharmacopoeia of the United States of America", XIII, p. 513-514, 1947).

[0008] La principal diferencia entre las diferentes aplicaciones tiene que ver con las relaciones de almidón y plastificante (agua, glicerol o ambos), usados en la composición. Esto lleva a diferencias en las características reológicas y finales de cada composición, que es apropiada para la aplicación específica. Una elevada proporción de plastificante (70-

90% en peso) resulta en un material en forma de jalea. Contenidos medios de plastificante (40-70% en peso) son más apropiados para aplicaciones en alimentos, que poseen buena elasticidad combinada con una rigidez razonable, para poder conformar y moldear varios productos. Contenidos bajos de plastificante (10-40% en peso) son apropiados para aplicaciones plásticas que requieren características de mayor rigidez y mejor resistencia mecánica. Más recientemente, se ha informado de la plastificación del almidón en la ausencia de agua, usando alcoholes polihídricos como glicerol y sorbitol. El término plastificación en el sentido clásico, como se emplea en la industria de polímeros, implica la transformación de un material cristalino rígido en un material menos cristalino (si no amorfo), plegable, con una temperatura de transición vítrea disminuida. La Patente Japonesa No. 04-48,851 divulga la fabricación de láminas biodegradables a base de mezclas de almidón y poliésteres biodegradables, derivados de reacciones de dioles y ácidos. El almidón tiene un contenido normal de humedad de alrededor de 10 a 12% en peso.

[0009] En un sistema plastificado típico con almidón, la difusión del plastificante fuera del producto, cuando se expone a condiciones de baja humedad, y la difusión de agua hacia adentro del producto bajo condiciones de alta humedad es un resultado inevitable. Esto ocasiona resquebrajamiento del producto debido a la pérdida de plastificante (baja humedad) y problemas asociados con la conservación de la configuración del producto, la textura y la forma, debido al exceso de agua absorbida (humedad alta). Estos efectos son perjudiciales especialmente cuando se utiliza agua como plastificante, pero son predominantes incluso en formulaciones de almidón sin agua como base, que incorporan plastificantes higroscópicos. En general, debido a la escasa durabilidad del almidón plastificado luego de la exposición a diferentes ambientes (como consecuencia de su naturaleza hidrófila), es probable que, en sí mismo, sea muy escaso el uso comercial del almidón plastificado nativo o no modificado.

[0010] Las modificaciones físicas o químicas del almidón son una alternativa viable para resolver algunos de estos problemas. Las modificaciones físicas incluyen recubrir los gránulos de almidón con agentes de encolado hidrófobos y aglutinantes, similares a los utilizados en la industria papelera, como colofonia, proteínas, como proteínas de soya y silanos o recubrir físicamente el producto final con materiales hidrófobos como ceras de bajo peso molecular, y resinas naturales (zeína, colofonia, goma laca y similares) y polímeros no polares de peso molecular más elevado. El reticulado ("*cross-linking*") de los gránulos de almidón o almidón plastificado es otra ruta de modificación física para incrementar la hidrofobicidad de materiales a base de algodón. Las modificaciones químicas incluyen reacciones de injerto y sustitución no degradable de los hidroxilos en el almidón con grupos funcionales como ésteres, éteres, isocianatos y similares. Anhídridos cíclicos de ácido dibásico tales como anhídrido succínico proporcionan ésteres de almidón, que contienen un grupo carboxilato libre el cual aumenta la capacidad de retención de agua del producto (Patente de los Estados Unidos No. 2,461,139; 1949). La misma química puede llevarse a cabo con anhídrido maleico para proporcionar el semiéster de maleato. El tratamiento de una suspensión de almidón con un anhídrido cíclico de ácido dicarboxílico, que contiene un grupo sustituyente hidrófobo, proporciona productos con propiedades estabilizantes de emulsión (Patente de los Estados Unidos No. 2,661,349; 1953). Estos ésteres de almidón son útiles como dispersantes en recubrimientos para reemplazar pintura, obtenible en el comercio, con contenido de dispersantes. La Patente de los Estados Unidos 3,732,207 discute la producción de ésteres de almidón calentando almidón con anhídrido maleico o succínico a 100-155 °C en un proceso por lotes, con tiempos de reacción de 10 horas en la presencia de 0.5-15% de humedad para proporcionar un producto con un grado de sustitución (DS) de 0.02 a 0.04.

[0011] Tomasik et al., Starch 47 96 (1995) hicieron reaccionar en extrusoras almidones de maíz, que contenían cantidades variables de humedad (18, 20 y 30%), con anhídridos succínicos, maleicos y ftálicos para formar ésteres de almidón. Durante la extrusión se agregó amortiguador carbonato, a pH 8 o pH 9, como medio. Está demostrado que la extrusión de almidón con anhídridos cíclicos en medio alcalino presenta un método fácil de preparación de almidones aniónicos de carácter hidrófobo. No obstante, este método tiene varias limitaciones serias, resultantes de la química y el proceso de extrusión. Por ejemplo, es sumamente difícil extruir estas muestras a temperaturas de alrededor de 130°C debido a la alta viscosidad resultante del almidón fundido. Además, el uso de agua es extremadamente problemático en el procesamiento y la calidad del producto final.

[0012] El arte previo relacionado se describe en:

- (1) Ramani Narayan, Steven Bloembergen and Amit Lathia, A Method of Preparing Biodegradable Modified-Starch Moldable Products and Films., Patente de los Estados Unidos 5,869,647, 9 de febrero de 1999, julio de 1993;
- (2) Narayan, R., Biodegradable Multi-Component Polymeric Materials Based on Unmodified Starch-Like Polysaccharides, Patente de los Estados Unidos 5,500,465, 31 de octubre de 1995;
- (3) Narayan, R., Krishnan, M., DuBois, P., Polysaccharides Grafted With Aliphatic Polyesters Derived From Cyclic Esters, Patente de los Estados Unidos 5, 540, 929, 30 de julio de 1996;
- (4) Narayan, R., Krishnan, M., DuBois, P., Polysaccharides Grafted With Aliphatic Polyesters Derived From Cyclic Esters, Patente de los Estados Unidos 5,578,691, 26 de noviembre de 1996;
- (5) Narayan, R., Krishnan, M., DuBois, P., Polysaccharides Grafted With Aliphatic Polyesters Derived From Cyclic Esters, Patente de los Estados Unidos 5, 616,671, 1 de abril de 1997;

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- (6) Solicitud de Patente de los Estados Unidos presentada conjuntamente con la presente solicitud.

OBJETOS

[0013] Constituye un objeto de la presente invención proveer un almidón plastificado, modificado químicamente, y composiciones de plastificantes que tienen propiedades mejoradas. Es también un objeto de esta invención proveer un proceso que es económico y reproducible. Estos y otros objetos serán cada vez más evidentes por referencia a la siguiente descripción.

SUMARIO DE LA INVENCION

[0014] La presente invención se relaciona con composiciones de almidón plastificado, modificado químicamente (CMPS), reactivo, biodegradable con baja viscosidad y excelente capacidad de transformación. Además, la presente invención se refiere a un proceso de extrusión reactiva continua para fabricar las composiciones. Un aspecto importante de esta invención es que el proceso no utiliza adición de agua, y evita problemas tales como viscosidad elevada, obstrucción de la masa fundida de almidón termoplástico en la boquilla o espumación de la masa fundida de almidón termoplástico. Además, la composición resultante del almidón modificado químicamente es altamente reactiva para proporcionar copolímeros de injerto con poliésteres, como se describe en detalle en nuestra solicitud de patente co-pendiente, que se incorpora aquí por referencia. Estos copolímeros de injerto almidón-poliéster son fácilmente transformables en películas y productos moldeados usando equipo de procesamiento de plásticos convencional, y el producto resultante tiene el balance más preferido en propiedades mecánicas, resistencia al agua, capacidad de transformación y la tasa de biodegradación. La invención describe asimismo una novedosa composición de nanoarcilla-almidón modificado químicamente con dispersabilidad mejorada de la nanoarcilla en la matriz,



reactividad y capacidad de transformación para reacción subsiguiente con poliésteres, como se describe en nuestra solicitud de patente co-pendiente.

[0015] De acuerdo con la presente invención, se provee una composición de almidón plastificado, modificado químicamente (CMPS), de baja viscosidad, reactivo, biodegradable, preparada por la combinación reactiva o procesamiento con extrusión de almidón en la presencia de modificadores químicos, un plastificante y un iniciador opcional de radicales libres.

[0016] La presente invención provee asimismo un producto nanoarcilla-almidón modificado químicamente, biodegradable, preparado por procesamiento con extrusión reactiva de almidón en la presencia de modificadores, plastificantes y material nanoarcilla.

[0017] La presente invención concierne asimismo a una composición que comprende una mezcla de ésteres de almidón de un ácido dibásico o un anhídrido de un ácido dibásico, en donde la mezcla tiene la viscosidad reducida de un almidón natural en sulfóxido de dimetilo.

[0018] La presente invención se refiere igualmente a una composición a base de almidón, que comprende una mezcla reaccionada de un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico y anhídrido del ácido orgánico dibásico, o sus mezclas, y un plastificante.

[0019] En particular la presente invención se relaciona con una composición a base de almidón, que contiene una mezcla extruida reactivamente de un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido de un ácido orgánico dibásico y sus mezclas, un plastificante y, opcionalmente, un iniciador de radicales libres para la

reacción, en donde la mezcla se ha extruido con calor y purga de agua de la mezcla.

[0020] Además, la presente invención tiene que ver con una composición a base de almidón modificado químicamente, biodegradable, la cual contiene una mezcla extruida reactivamente que comprende un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido de un ácido orgánico dibásico y sus mezclas, un plastificante y, opcionalmente, un iniciador de radicales libres para la reacción y una nanoarcilla, en donde la mezcla se ha extruido con calor y purga de agua de la mezcla.

[0021] Preferiblemente el polímero de almidón se selecciona del grupo conformado por almidón de maíz, almidón de papa, almidón de yuca, almidón de arroz, almidón de trigo y almidón de casabe. Preferiblemente el polímero de almidón en la mezcla está presente en una cantidad entre alrededor de 5% a 90% en peso de la mezcla. Preferiblemente el polímero de almidón es un almidón no modificado, oxidado o almidón hidrolizado en medio ácido con una viscosidad reducida en caliente ("*thin boiling starch*") de 0 a 95 grados de fluidez. Preferiblemente el polímero de almidón tiene un contenido de humedad de alrededor de 0.5% a 15% en peso. Preferiblemente el polímero de almidón está en forma pulverizada. Preferiblemente el plastificante es un alcohol polihídrico. Preferiblemente el plastificante está presente en una cantidad entre alrededor de 10 a 50% en peso de la mezcla. Preferiblemente el modificador químico está presente en una cantidad entre alrededor de 0.5% a alrededor de 10% en peso del polímero de almidón. Preferiblemente la nanoarcilla se selecciona del grupo conformado por montmorilonita; esmectita, hectorita y sus mezclas. Preferiblemente la nanoarcilla está presente en una cantidad entre alrededor de 0.5 a 25 % en peso de la mezcla. Preferiblemente el iniciador de radicales libres es 2,5-bis (*terc*-butilperoxi)-2,5-dimetilhexano u otro peróxido orgánico. Preferiblemente el iniciador de radicales libres está

presente en la mezcla en una cantidad entre alrededor de 0.01 a 2.0 % en peso de la mezcla. Preferiblemente la mezcla se procesa en una extrusora de doble tornillo a una temperatura en el rango de alrededor de 100°C a 200°C. Preferiblemente los anhídridos se seleccionan del grupo conformado por maleicos, succínicos, itacónicos, ftálicos y sus mezclas. Preferiblemente el modificador químico es alrededor de 2% a 5% en peso del polímero de almidón de la mezcla.

[0022] La presente invención concierne asimismo a un proceso para preparar una composición a base de almidón, que comprende extruir reactivamente una mezcla que contiene un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido de un ácido orgánico dibásico y sus mezclas, un plastificante y, opcionalmente, un iniciador de radicales libres, en donde la mezcla se extruye con calentamiento y purga de agua de la mezcla. Preferiblemente el polímero de almidón y el modificador se mezclan como polvos. El procesamiento se lleva preferiblemente a cabo a 100-250°C.

BREVE DESCRIPCIÓN DE LAS FIGURAS

[0023] Otras ventajas de la presente invención se apreciarán fácilmente en la medida que la misma se entienda mejor por referencia a la siguiente descripción detallada, cuando se considera en conexión con los dibujos acompañantes en donde:

[0024] FIGURA 1 es un gráfico que ilustra la curva de calibración de la bomba de glicerol utilizada en la síntesis de almidón plastificado, modificado químicamente (CMPS); por procesamiento con extrusión reactiva usando modificador de anhídrido maleico o ácido maleico.

[0025] FIGURA 2 es un diagrama de un aparato de flujo de extrusión para la preparación de CMPS.

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[0026] FIGURAS 3A, 3B y 3C muestran las configuraciones del tornillo usado para el procesamiento con extrusión reactiva en la síntesis de CMPS.

[0027] FIGURA 4 es un gráfico que muestra los resultados FTIR de muestras de CMPS producido usando modificador de anhídrido maleico por el procesamiento con extrusión reactiva. Las muestras de CMPS se extrajeron en disolvente THF usando un aparato Soxhlet. El residuo del cartucho del aparato (*"the thimble of the apparatus"*) se secó a peso constante y se condujo un análisis FTIR. Se evaporó el disolvente del extracto y el extracto se secó a peso constante y se condujo un análisis FTIR.

[0028] FIGURA 5 es un gráfico que muestra los resultados FTIR de muestra de CMPS producido usando un modificador de ácido maleico por procesamiento con extrusión reactiva. Las muestras de CMPS se extrajeron en el disolvente THF usando un aparato Soxhlet. El residuo del cartucho se secó a peso constante y se condujo un análisis FTIR. Se evaporó el disolvente del extracto y el extracto se secó a peso constante y se condujo un análisis FTIR.

DESCRIPCIÓN DETALLADA DE LA INVENCION

[0029] La presente invención provee (i) una composición de almidón modificado químicamente, biodegradable, (ii) una composición de nanoarcilla-almidón modificado químicamente, biodegradable, (iii) y un método para su elaboración en donde, generalmente, la composición se prepara por un procesamiento con extrusión reactiva continua. Preferiblemente, la presente invención se relaciona con a) una composición de almidón modificado químicamente, altamente reactivo, biodegradable, con baja viscosidad y alta capacidad de transformación, que proporciona copolímeros de injerto con poliésteres biodegradables, como se describe en nuestra solicitud de patente co-pendiente. Otro objeto de la presente

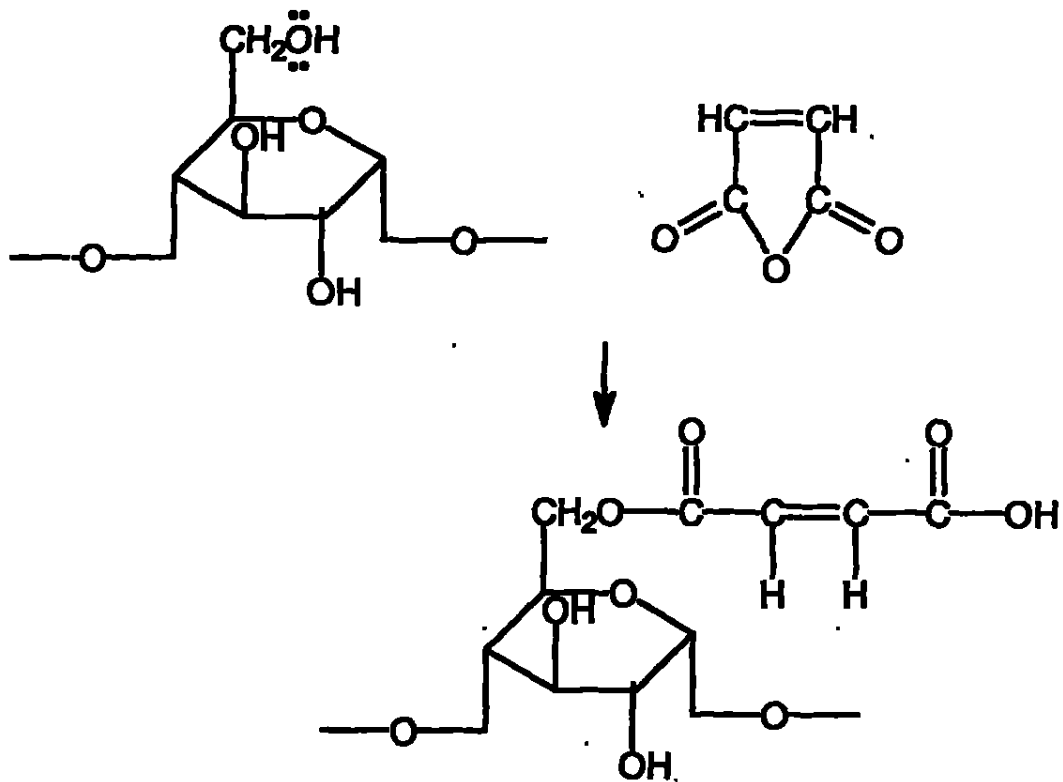
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invención es proporcionar b) una novedosa composición de nanoarcilla-almidón modificado químicamente con dispersabilidad mejorada de la nanoarcilla en la matriz, reactividad y capacidad de transformación para la reacción subsiguiente con poliésteres, como se describe en nuestra solicitud de patente co-pendiente.

[0030] Los componentes de la composición de almidón modificado químicamente, biodegradable, empleados en el proceso, que están dentro del ámbito de esta invención, incluyen preferiblemente los siguientes:

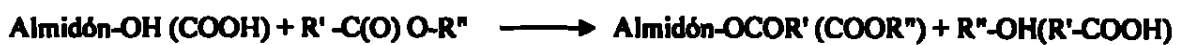
- (I) Almidón preferiblemente seleccionado del grupo de almidón de papa, almidón de maíz, almidón de maíz ceroso, almidón de yuca, almidón de arroz, almidón de trigo y almidón de casabe y similares
- (II) Plastificante preferiblemente seleccionado del grupo de compuestos polihidroxi incluidos glicerol, etilenglicol y similares
- (III) Modificador seleccionado del grupo de ácidos dibásicos y sus compuestos de anhídridos cíclicos; y
- (IV) Opcionalmente, iniciador de radicales libres seleccionado del grupo de peróxidos similares.

Las reacciones propuestas son:



Síntesis Maleica

H^+ (funcionalidad ácida)



Anhídridos



Almidón Modificado

Química de Trans-esterificación

[0031] El almidón $(C_6H_{10}O_5)_n$, es una mezcla de polímeros lineales (amilosa) y ramificados (amilopectina). La amilosa es esencialmente un polímero lineal de unidades de D-glucopiranosilo $\alpha(1 \rightarrow 4)$ enlazadas. La amilopectina es un polímero altamente ramificado de unidades de D-glucopiranosilo que contienen enlaces $\alpha(1 \rightarrow 4)$, con enlaces $\alpha(1 \rightarrow 6)$ en los puntos de las ramas. El proceso de la presente invención puede usar varios tipos de almidones, tales como almidón de maíz ordinario que contiene alrededor de 75% de amilopectina (polímero de almidón ramificado de peso molecular más elevado) y 25% de amilosa (polímero de almidón lineal de peso molecular más bajo), así como productos de maíz híbrido que contienen más de 50% de amilosa, comercializado por Corn Products, Inc. (Chicago, Illinois). Varios otros almidones, tales como almidón de papa,

almidón de yuca, almidón de arroz, almidón de trigo, almidón de casabe y otros almidones familiares a los expertos en el arte pueden utilizarse de acuerdo con la presente invención. Composiciones que tienen niveles cada vez mayores de polímeros de almidón lineal tienen la máxima probabilidad de ser la elección correcta en términos de capacidad de transformación, formación de película, moldeo y propiedades mecánicas. El componente de almidón en la composición de almidón modificado químicamente es 5% a 90% en peso, preferiblemente desde 50% a 80% en peso.

[0032] A las composiciones inventivas se agrega un plastificante para obtener una mayor capacidad de transformación del material y flexibilidad del producto, aunque típicamente los plastificantes ablandan las composiciones en las cuales se incluyen. Los plastificantes preferidos son alcoholes polihídricos. Más preferiblemente, se utiliza glicerol como plastificante apropiado puesto que induce una alta flexibilidad, es virtualmente inodoro, tiene un punto de ebullición relativamente elevado, es biodegradable y se obtienen en el comercio con un costo razonable. La concentración de plastificante en el producto final de almidón modificado químicamente es 15% a 50% en peso y, preferiblemente, desde 20% a 30% en peso.

[0033] Los modificadores preferidos que son útiles en la presente invención tienen que proporcionar un producto éster de almidón modificado químicamente. El producto éster de almidón puede formarse preferiblemente por reacción de los grupos hidroxilo de almidón con un ácido dibásico o anhídrido cíclico para obtener enlaces éster con grupos carboxílicos pendientes, como se muestra en Esquema 1. El grupo carboxílico pendiente derivado pueden catalizar asimismo la reacción ya mencionada entre los grupos hidroxilo en el almidón, y los ácidos dibásicos o sus anhídridos cíclicos. Los ácidos dibásicos más preferidos y sus anhídridos cíclicos incluyen anhídridos maleicos, succínicos, itacónicos, ftálicos y esteáricos y sus combinaciones. El modificador está

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preferiblemente presente en una cantidad de alrededor de 0.5% a alrededor de 10% en peso del polímero de almidón y proporciona asimismo un ambiente ácido para la mezcla.

[0034] Opcionalmente, puede usarse un iniciador de radicales libres para mejorar la resistencia del fundido del producto de almidón modificado químicamente. Se prefiere que el iniciador de radicales libres sea un peróxido orgánico tal como 2,5-dimetil-2,5-bis (*terc*-butilperoxi)hexano, *terc*-butilperoctoato, *terc*-butilperoxipivalato, peróxido de dicumilo, 1,1-bis(*terc*-butilperoxi)-3,3,5-trimetilciclohexano, bis(*terc*-butilperoxi-isopropil)benceno y similares. En igual forma pueden usarse compuestos azo, tales como azobisisobutironitrilo. El iniciador de radicales libres está presente en la cantidad de 0.01 a 2.0 % en peso de la masa total.

[0035] La presente invención se refiere también a un producto de nanoarcilla-almidón modificado químicamente, preparado por procesamiento con extrusión reactiva del almidón en la presencia de modificadores, plastificantes y material de nanoarcilla.

[0036] Las nanoarcillas pueden ser útiles para proporcionar una resistencia mecánica incrementada, retardo a la llama, propiedades de barrera de gas, y barrera mejorada al vapor de agua para el producto de almidón nanoarcilla modificado químicamente (ii). Otra incorporación preferida es que las nanoarcillas útiles para la presente invención se dispersan bien en el producto arcilla-almidón modificado químicamente, biodegradable. Las nanoarcillas preferidas son arcillas de esmectita, hectorita, incluidos filosilicatos tales como minerales de arcilla de esmectita, por ejemplo, montmorilonita, particularmente montmorilonita sódica; bentonita; hectorita; saponita; estevensita; beidelita; y similares. Las arcillas utilizadas son típicamente arcillas de esmectita, particularmente bentonita y hectorita. Las arcillas de esmectita poseen algunas características estructurales similares a los minerales mejor conocidos, talco

y mica. El rango preferido de nanoarcillas varía desde 0.5 a 25 % en peso de la masa total.

[0037] El proceso de modificación reactiva de almidón para formar almidón plastificado, modificado químicamente (CMPS), en una extrusora evita los problemas tradicionalmente observados, tales como atascamiento de la masa fundida de almidón plastificado en la boquilla o espumación de la masa fundida del almidón plastificado en la boquilla, observados durante la termo-plastificación ordinaria del almidón. El aparato utilizado en llevar a cabo el proceso de extrusión puede ser cualquier extrusora tipo tornillo. Aunque puede emplearse una extrusora de un solo tornillo o de doble tornillo, se prefiere utilizar una extrusora de doble tornillo. Tales extrusoras tendrán típicamente tornillos rotativos en un cilindro horizontal ("*a horizontal cylindrical barrel*") con un puerto de entrada montado en un extremo y una boquilla de moldeo montada en el extremo de descarga. Cuando se usan tornillos dobles, éstos pueden ser co-rotativos y con alto grado de ajuste entre roscas o sin él ("*intermeshing or non-intermeshing*"). Cada tornillo comprenderá un aspa helicoidal o secciones roscadas y, típicamente, tendrá una sección de alimentación relativamente profunda, seguida por una sección de transición ahusada y una sección dosificadora de profundidad constante, comparativamente superficial. Los tornillos accionados mecánicamente, se encajan por lo general apretadamente en el cilindro o barril para permitir el mezclado, calentamiento y cizalladura del material, a medida que pasa por la extrusora.

[0038] El control de la temperatura a lo largo del barril de la extrusora es importante y se realiza en zonas en toda la longitud del tornillo. Con frecuencia, se utilizan medios intercambiadores de calor, típicamente un pasaje tal como un canal, una cámara o perforación localizada en la pared del barril, para circular un medio calentado tal como aceite, o un calentador eléctrico tales como los calentadores Calrod o tipo serpentín.

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Adicionalmente, pueden disponerse también medios intercambiadores de calor en el eje del dispositivo de tornillo, o a lo largo de él.

[0039] De acuerdo con las prácticas de diseño convencional pueden introducirse variaciones en cualquiera de los elementos utilizados en la extrusora, según se desee. Una descripción más detallada de variaciones típicas de extrusión y diseño pueden encontrarse en "Encyclopedia of Polymer Science and Engineering", volumen 6, 1986, páginas 571 a 631.

[0040] En la realización del proceso de extrusión, las temperaturas en la extrusora variarán dependiendo del material particular, las propiedades y aplicación deseadas. Aquellas pueden variar desde alrededor de 100° a 250°C y, preferiblemente, variarán desde alrededor de 150° a 200°C.

[0041] Además, el almidón modificado químicamente, biodegradable (i), y las composiciones de nanoarcilla-almidón modificado químicamente, biodegradable (ii) pueden fabricarse en un proceso de paso único, en donde los componentes se mezclaron previamente entre sí y luego se introdujeron en la boca de alimentación de una extrusora de doble tornillo (tal como una extrusora de dos tornillos co-rotativos Century ZSK-30) con una velocidad de alimentación de 500-9.000 g/h mediante dosificación de un sólido. Alternativamente, los componentes pueden introducirse separadamente; en el caso de un componente líquido, por medio de una bomba peristáltica y, en el caso de un componente sólido, por medio de una dosificación de sólido con una velocidad de alimentación de 40-8.000 g/h.

[0042] La composición de almidón modificado químicamente, biodegradable y las composiciones de nanoarcilla-almidón modificado químicamente, biodegradable, son particularmente útiles para fabricar copolímeros de injerto poliéster-almidón, como se describe en nuestra solicitud de patente co-pendiente, mencionada previamente.



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[0043] Los siguientes ejemplos experimentales demuestran la utilidad de la presente invención para formar almidón modificado químicamente, biodegradable (i), y composiciones de nanoarcilla-almidón modificado químicamente, biodegradable (ii).

[0044] Ejemplos de materiales fabricados de acuerdo con la presente invención son biodegradables, como se demuestra por métodos de ensayo ASTM estándar.

EJEMPLOS

Ejemplo 1

[0045] La modificación química de polímero de almidón se llevó a cabo en la siguiente forma:

[0046] Almidón de maíz ordinario color perla plateado ("*regular silver pearl corn-starch*"), obtenido de Cargill Inc. se modificó reactivamente usando anhídrido maleico/ácido maleico en una extrusora CENTURY co-rotativa de doble tornillo con un diámetro de tornillo de 30 mm y una relación L/D de 40. Se molió anhídrido maleico (MA) hasta obtener un polvo fino usando una maja y mortero y se mezcló con el almidón (800 gm de almidón + [20 gm] anhídrido maleico) usando una mezclador de cocina durante 15 minutos antes de cargarse al puerto de alimentación de la extrusora. El glicerol se mezcló con 2,5-bis(*terc*-butilperoxi)-2,5-dimetilhexano (Luperox 101) {200 gm de glicerol + 1.6 gm de Luperox 101} y se bombeó a la extrusora usando una bomba peristáltica. Las tasas relativas de la mezcla almidón/MA a las mezclas glicerol/Luperox 101 se mantuvieron a 80:20. La curva de calibración para la bomba de glicerol se muestra en Figura 1. La configuración del tornillo usada para el tratamiento maleico ("*maleation*") tenía como finalidad transportar y amasar elementos, como se muestra en las FIGURAS 3A a 3C. Se aplicó un vacío de agua al puerto de purga para eliminar la mezcla de ácido maleico sin reaccionar/agua. El almidón plastificado modificado

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químicamente, CMPS, se recogió y molió hasta obtener un polvo fino. El CMPS molido se almacenó en un horno a 50°C. Las condiciones de procesamiento con extrusión para el tratamiento maleico reactivo se ilustran en la Tabla 1.

TABLA 1: Condiciones de Procesamiento con Extrusión en la Síntesis de CMPS

ZONA	AJUSTE	ACTUAL	UNIDADES
ZONA 1	15	39	°C
ZONA 2	95	103	°C
ZONA 3	125	122	°C
ZONA 4	145	146	°C
ZONA 5	160	157	°C
ZONA 6	165	161	°C
ZONA 7	165	167	°C
ZONA 8	165	164	°C
ZONA 9	150	156	°C
BOQUILLA	145	147	°C
TEMPERATURA DE FUSIÓN		148	°C
VELOCIDAD DEL MOTOR		125	RPM
TORQUE		35	%
PRESIÓN		92	Psia
VELOCIDAD DEL ALIMENTADOR, CENTURY		155 (Tasa =12.3 lbs/h)	%
BOMBA DE GLICEROL		0.1 (Tasa = 3.07 lbs/h)	%
VELOCIDAD DEL ALIMENTADOR, EXTRUSORA		—	%

[0047] El CMPS producido se extrajo usando tetrahidrofurano (THF) en un aparato Soxhlet para eliminar el anhídrido maleico y ácido maleico sin reaccionar (formados con el agua presente en el almidón). El análisis FTIR (FIGURA 4) del residuo Soxhlet (luego de secar en un horno a 50°C de un día para otro) confirmó el injerto del anhídrido maleico en la

estructura de sostén del almidón con la presencia del pico éster de carbonilo en 1720 cm^{-1} .

Ejemplo 2

[0048] Se siguió el procedimiento suministrado en el Ejemplo 1 usando modificador ácido maleico en lugar de anhídrido maleico. Se extrajo el CMPS producido usando tetrahidrofurano (THF) en un aparato Soxhlet para retirar el ácido maleico sin reaccionar. El análisis FTIR (FIGURA 5) conducido en el residuo Soxhlet (luego de secar en un horno a 50°C de un día para otro) confirmó el injerto del ácido maleico en la estructura de soporte del almidón con la presencia del pico éster de carbonilo en 1720 cm^{-1} .

Ejemplo 3

[0049] Se siguió el procedimiento en el Ejemplo 1 para producir CMPS modificado usando 2.4 % en peso de anhídrido maleico, con y sin iniciador. Se produjo almidón plastificado modificado químicamente (CMPS) por plastificación de almidón de maíz ordinario (Corn Products, Inc., Brazil) usando 20% en peso de plastificante glicerol en una extrusora de doble tornillo. Se determinaron la viscosidad intrínseca del almidón, PS, CMPS (2.4 % en peso de anhídrido maleico y 0.1 % en peso de Luperox 101) y CMPS (sin Luperox 101) en disolvente DMSO usando un viscosímetro Cannon Ubbelohde (OB). La viscosidad intrínseca del almidón fue de alrededor de 1.6 dl/g mientras que la de PS se redujo a 1.2 dl/g. No obstante, con el tratamiento maleico sin la adición de Luperox 101, la viscosidad intrínseca del CMPS cayó drásticamente a 0.29 dl/g. Esta reducción se atribuye a una disminución en el peso molecular debida a la hidrólisis del almidón en la presencia de ácido maleico. No obstante, con la adición de Luperox 101, la viscosidad intrínseca creció ligeramente a 0.31 dl/g. Este aumento se atribuye a la ocurrencia de reacciones de ramificación o reticulado.

Ejemplo 4

[0050] Modificación química de polímero de almidón para formar productos de nanoarcilla-almidón plastificado modificado químicamente.

[0051] Almidón de maíz ordinario color perla plateado, obtenido de Cargill Inc. se modificó reactivamente usando anhídrido maleico/ácido maleico en una extrusora CENTURY™ co-rotativa de doble tornillo con un diámetro de tornillo de 30 mm y una relación L/D de 40 en la presencia de BENTONE 166™, que es una arcilla de hectorita de alquilarilamonio, obtenida de Elementis Specialties (Highstown, NJ), con características de dispersabilidad enormemente mejoradas. Se molió anhídrido maleico (MA) hasta obtener un polvo fino usando una maja y mortero y se mezcló con el almidón (800 gm de almidón + 20 gm de anhídrido maleico + 150 gm de BENTONE 166) usando un mezclador de cocina durante 15 minutos antes de cargarse al puerto de alimentación de la extrusora. Se bombearon 200 gm de glicerol a la extrusora utilizando una bomba peristáltica. Las tasas relativas de la mezcla almidón/MA/BENTONE 166 al glicerol se mantuvieron a 80:20.

Ejemplo 5

[0052] Se siguió el procedimiento en el Ejemplo 4 para producir CMPS modificado usando 2.5% en peso de anhídrido maleico y BENTONE 111™, que es un derivado orgánico de una arcilla de esmectita especial, obtenida de Elementis Specialties. Se molió anhídrido maleico (MA) hasta obtener un polvo fino usando maja y mortero y se mezcló con el almidón (800 gm de almidón + 20 gm de anhídrido maleico + 150 gm de BENTONE 111) usando un mezclador de cocina durante 15 minutos, antes de cargarse al puerto de alimentación de la extrusora. Se bombearon 200 gm de glicerol a la extrusora utilizando una bomba peristáltica. Las tasas relativas de la mezcla almidón/ MA/BENTONE 111 al glicerol se mantuvieron a 80:20.

Ejemplo 6

[0053] Se siguió el procedimiento en el Ejemplo 4 para producir un producto arcilla-CMPS usando 2.5% en peso de anhídrido maleico y Cloisite 30B™, que es una arcilla de montmorilonita modificada con sal de amonio dihidroxicuaternario, obtenida de Southern Clay Products.

[0054] Preferiblemente los ésteres de almidón con el plastificante (glicerol) tienen una viscosidad en el rango de alrededor de 0.15 a 0.3 dl/gm en DMSO. El almidón natural tienen una viscosidad de 1.51 dl/gm y el almidón plastificado tiene una viscosidad de 1.20 dl/gm. En consecuencia, hay una viscosidad significativamente reducida.

[0055] Se pretende que la descripción precedente sea únicamente ilustrativa de la presente invención y que la presente invención se limite sólo por las reivindicaciones expuestas a continuación.



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REIVINDICAMOS:

1. Una composición que contiene una mezcla de ésteres de almidón de un ácido dibásico o un anhídrido de un ácido dibásico, en donde la mezcla tiene una viscosidad reducida de un almidón natural en sulfóxido de dimetilo.
2. Una composición a base de almidón que contiene un mezcla reaccionada de un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido del ácido orgánico dibásico, o sus mezclas, y un plastificante.
3. Una composición a base de almidón que contiene una mezcla extruida reactivamente de un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido de un ácido orgánico dibásico y sus mezclas, un plastificante y, opcionalmente, un iniciador de radicales libres para la reacción, en donde la mezcla se ha extruido con calentamiento y purga de agua de la mezcla.
4. Una composición a base de almidón modificado químicamente, biodegradable, que contiene una mezcla extruida reactivamente que comprende un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido de un ácido orgánico dibásico y sus mezclas, un plastificante y, opcionalmente, un iniciador de radicales libres para la reacción y una nanoarcilla, en donde la mezcla se ha extruido con calentamiento y purga de agua de la mezcla.

5. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde dicho polímero de almidón se selecciona del grupo conformado por almidón de maíz, almidón de papa, almidón de yuca, almidón de arroz, almidón de trigo y almidón de casabe.
6. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde el polímero de almidón en la mezcla está presente en una cantidad entre alrededor de 5% a 90% en peso de la mezcla.
7. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde polímero de almidón es un almidón no modificado, oxidado o almidón hidrolizado en medio ácido con una viscosidad reducida en caliente ("*thin boiling starch*") de 0 a 95 grados de fluidez.
8. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde el polímero de almidón tiene un contenido de humedad de alrededor de 0.5% a 15% en peso.
9. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde dicho polímero de almidón está en forma pulverizada.
10. La composición de una cualquiera de las Reivindicaciones 2, 3, ó 4 en donde el plastificante es un alcohol polihídrico.
11. La composición de una cualquiera de las Reivindicaciones 2, 3, ó 4 en donde el plastificante está presente en una cantidad entre alrededor de 10 a 50 % en peso de la mezcla.

12. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde el modificador químico es el ácido orgánico dibásico.
13. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde el modificador químico es el anhídrido.
14. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde el modificador químico está presente en una cantidad entre alrededor de 0.5% a alrededor de 10% en peso del polímero de almidón.
15. La composición de la Reivindicación 4 en donde la nanoarcilla se selecciona del grupo conformado por montmorilonita; esmectita, hectorita y sus mezclas.
16. La composición de la Reivindicación 4 en donde la nanoarcilla está presente en una cantidad entre alrededor de 0.5 a 25 % en peso de la mezcla.
17. La composición de la Reivindicación 3 en donde el iniciador de radicales libres está presente y es 2,5-bis(*terc*-butilperoxi)-2,5-dimetilhexano.
18. La composición de la Reivindicación 3 en donde el iniciador de radicales libres está presente en la mezcla en una cantidad entre alrededor de 0.01 a 2.0 % en peso de la mezcla.
19. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde la mezcla se procesa en una extrusora de doble tornillo a una temperatura en el rango de alrededor de 100°C a 200°C.

20. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde los ácidos o anhídridos se seleccionan del grupo conformado por maleicos, succínicos, itacónicos, ftálicos y sus mezclas.
21. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde el modificador químico es alrededor de 2% a 5% en peso del polímero de almidón de la mezcla.
22. Un proceso para preparar una composición a base de almidón que comprende combinar reactivamente una mezcla que contiene un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido de un ácido orgánico dibásico y sus mezclas, un plastificante y, opcionalmente, un iniciador de radicales libres, en donde la mezcla se extruye con calentamiento y purga de agua de la mezcla.
23. El proceso de la Reivindicación 22 en donde el polímero de almidón y el modificador se mezclan como polvos.
24. El proceso de la Reivindicación 22 en donde el procesamiento tiene lugar a una temperatura entre alrededor de 130 y 180°C.
25. La composición de una cualquiera de las Reivindicaciones 2, 3, ó 4 en donde el plastificante es glicerol.
26. La composición de una cualquiera de las Reivindicaciones 2, 3, ó 4 en donde el plastificante es alrededor de 15 a 30% en peso de la composición.

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27. La composición de una cualquiera de las Reivindicaciones 1, 2, 3, ó 4 en donde el ácido es ácido maleico y el anhídrido es anhídrido maleico.

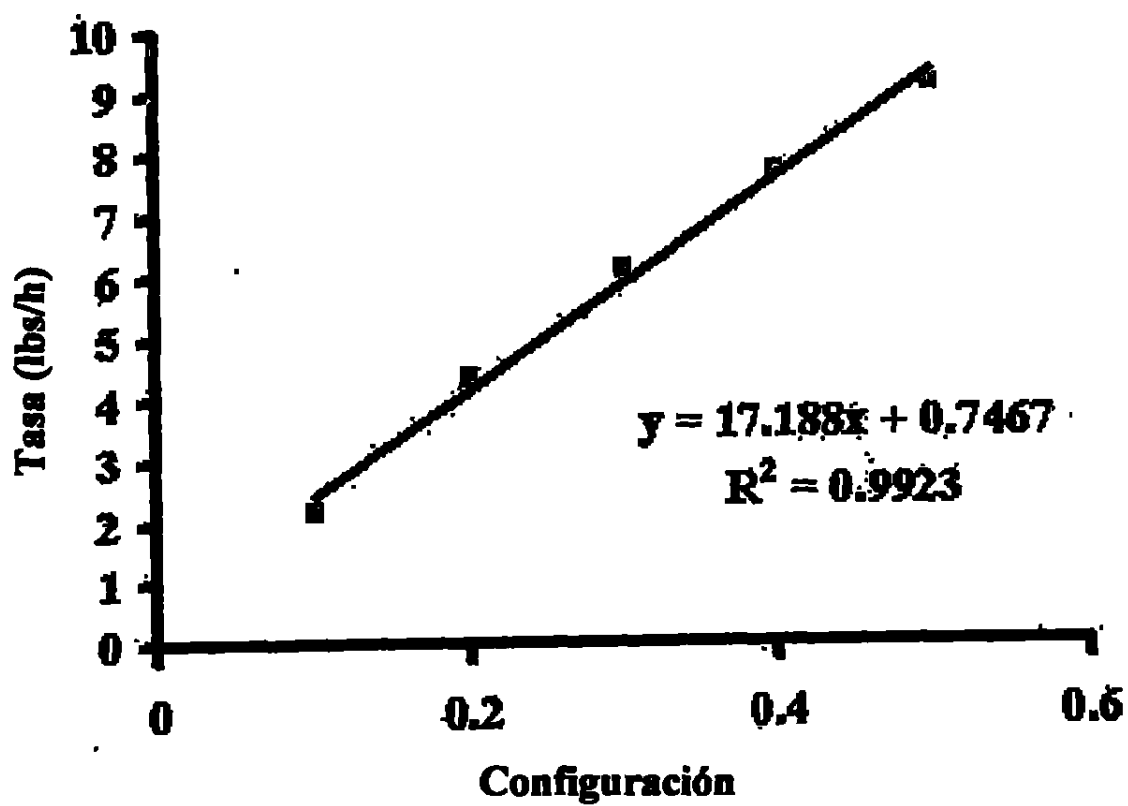


FIGURA 1

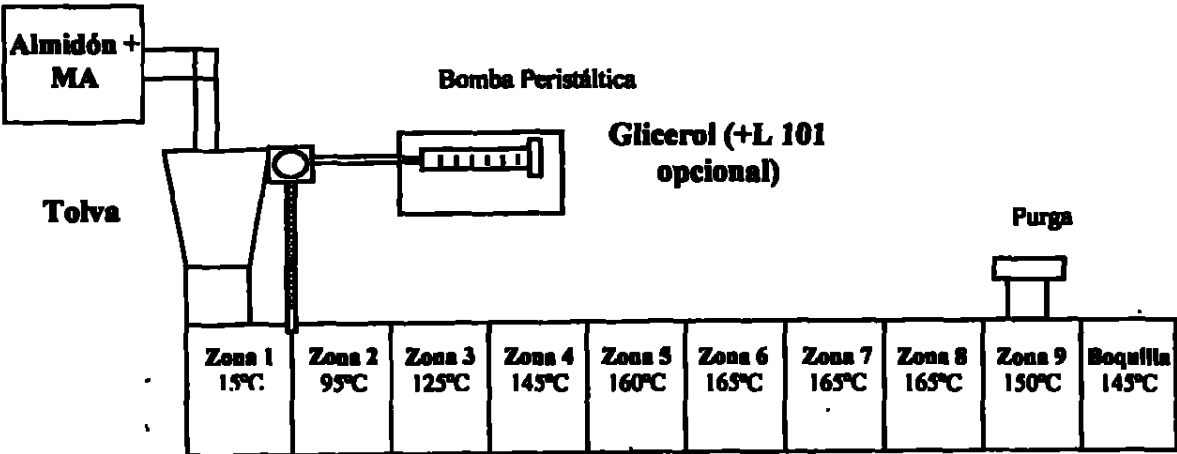
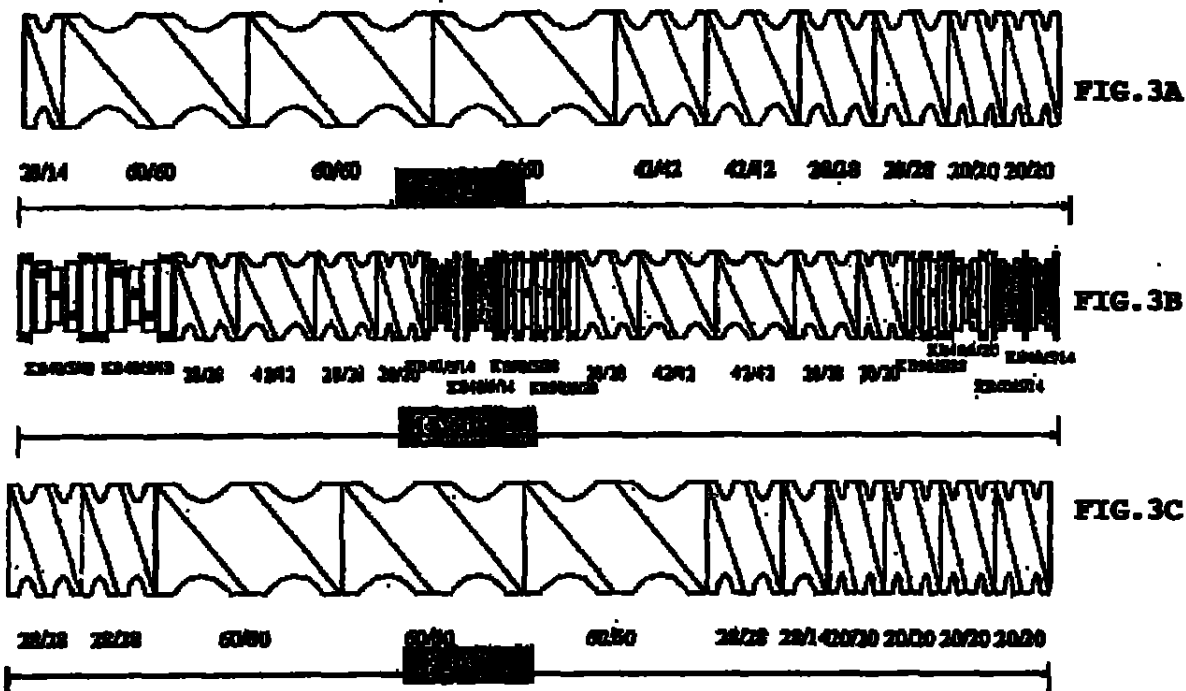


FIGURA 2



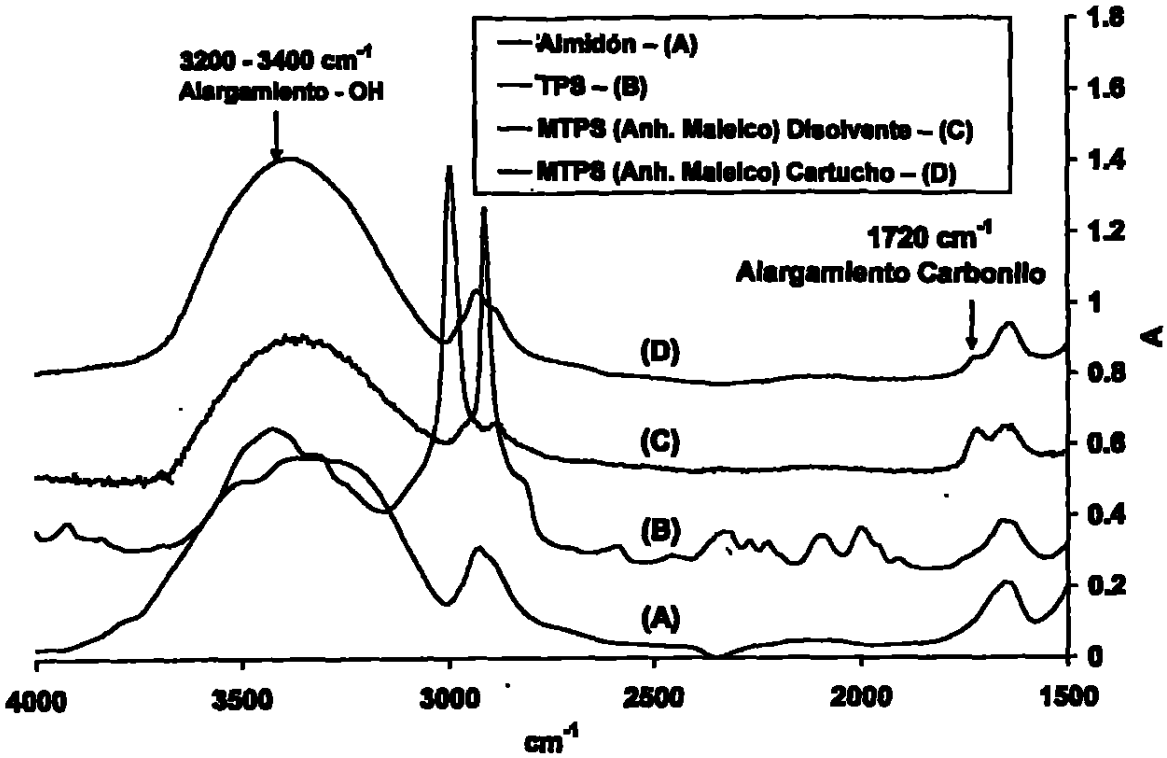


FIGURA 4

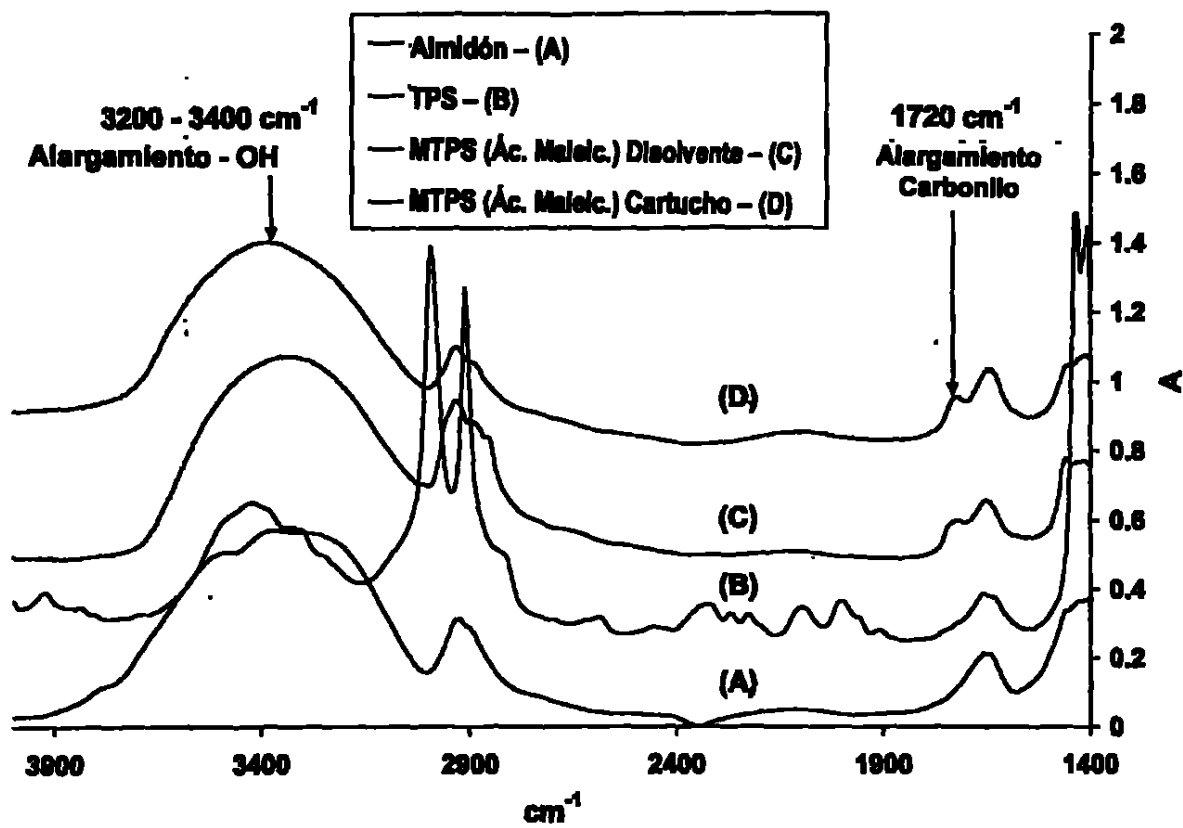


FIGURA 5

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To:
IAN C. MCLBOD
MCLBOD & MOYNE, P.C.
2190 COMMONS PARKWAY
OKREMOS, MI 48864

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT AND
THE WRITTEN OPINION OF THE INTERNATIONAL
SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Date of mailing
(day/month/year) **31 OCT 2006**

Applicant's or agent's file reference
MSU 4.2-724

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.
PCT/US05/41237

International filing date
(day/month/year) 15 November 2005 (15.11.2005)

Applicant
MICHIGAN STATE UNIVERSITY

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

When? The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.

Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes
1211 Geneva 20, Switzerland, Facsimile No.: (41-22) 338.82.70.

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

Shortly after the expiration of 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90b/s.1 and 90b/s.3, respectively, before the completion of the technical preparations for international publication.

The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

Within 19 months from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later); otherwise, the applicant must, within 30 months from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

In respect of other designated Offices, the time limit of 30 months (or later) will apply even if no demand is filed within 19 months.

See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the ISA/ US

Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
Facsimile No. (571) 273-3201

Authorized officer

Kryncki William

Telephone No. 571-272-1024

Jean Proctor
Paralegal Specialist

Form PCT/ISA/220 (January 2004)

(See notes on accompanying sheet)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference MSU 4.2-724	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. PCT/US05/41237	International filing date (day/month/year) 15 November 2005 (15.11.2005)	(Earliest) Priority Date (day/month/year) 19 November 2004 (19.11.2004)
Applicant MICHIGAN STATE UNIVERSITY		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the Report

a. With regard to the language, the international search was carried out on the basis of:



the international application in the language in which it was filed.



a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, see Box No. I

2. ☐ Certain claims were found unsearchable (See Box No. II)

3. ☐ Unity of invention is lacking (See Box No. III)

4. With regard to the title,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the abstract,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the drawings,

a. the figure of the drawings to be published with the abstract is Figure No. _____



as suggested by the applicant.



as selected by this Authority, because the applicant failed to suggest a figure.



as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US05/41237

A. CLASSIFICATION OF SUBJECT MATTER

IPC: C08B 30/12(2006.01);C09J 103/06(2006.01)

USPC: 536/48;106/207.1,207.5

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)

U.S. : 536/48; 106/207.1,207.5

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,011,392 A (RUDOLPH et al) 08 March 1977, see entire document.	1,2 5-14,20,21,27
Y	US 2003/0141637 A1 (KESSELMANS et al) 31 July 2003, see entire document.	3, 5-14,17-21,26-27
Y	US 4,231,803 A (BOVIER et al) 04 November 1980, see entire document.	25+2, 25+3



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
"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"A" 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

14 September 2006 (14.09.2006)

Date of mailing of the international search report

31 OCT 2006

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US

Commissioner for Patents

P.O. Box 1450

Alexandria, Virginia 22313-1450

Facsimile No. (571) 273-3201

Authorized officer

Krynaski William

Telephone No. 571-272-1024

Jean Proctor

Paralegal Specialist

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:
IAN C. MCLEOD
MCLEOD & MOYNE, P.C.
2190 COMMONS PARKWAY
OKEMOS, MI 48864

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

Applicant's or agent's file reference MSU 4.2-724		Date of mailing (day/month/year) 31 OCT 2006
International application No. PCT/US05/41237		International filing date (day/month/year) 15 November 2005 (15.11.2005)
International Patent Classification (IPC) or both national classification and IPC IPC: C08B 30/12 (2006.01); C09J 103/06 (2006.01) USPC: 536/48; 106/207.1, 106/207.5		Priority date (day/month/year) 19 November 2004 (19.11.2004)
Applicant MICHIGAN STATE UNIVERSITY		

1. This opinion contains indications relating to the following items:

- | | | |
|-------------------------------------|--------------|--|
| ☒ | Box No. I | Basis of the opinion |
| ☐ | Box No. II | Priority |
| ☐ | Box No. III | Non-establishment of opinion with regard to novelty, inventive step and industrial applicability |
| ☐ | Box No. IV | Lack of unity of invention |
| ☒ | Box No. V | Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability, citations and explanations supporting such statement |
| ☐ | Box No. VI | Certain documents cited |
| ☐ | Box No. VII | Certain defects in the international application |
| ☐ | Box No. VIII | Certain observations on the international application |

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bb(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA/ US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (571) 273-3201	Date of completion of this opinion 14 September 2006 (14.09.2006)	Authorized officer Krynaki William Jean Proctor Paralegal Specialist Telephone No. 571-272-1024
--	---	---

Form PCT/ISA/237 (cover sheet) (April 2005)

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No. 76

PCT/US05/41237

Box No. I Basis of this opinion

1. With regard to the language, this opinion has been established on the basis of:

- ☒ the international application in the language in which it was filed
☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. With regard to any nucleotide and/or amino acid sequence disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:

a. type of material

- ☐ a sequence listing
☐ table(s) related to the sequence listing

b. format of material

- ☐ on paper
☐ in electronic form

c. time of filing/furnishing

- ☐ contained in the international application as filed.
☐ filed together with the international application in electronic form.
☐ furnished subsequently to this Authority for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table(s) relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US05/41237

Box No. V Reasoned statement under Rule 43 *bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims <u>3-4, 15-19, 22-26</u>	YES
	Claims <u>1, 2, 5-14, 20-21, 27</u>	NO
Inventive step (IS)	Claims <u>15-16, 22-24</u>	YES
	Claims <u>1-14, 17-21, 25+2, 25+3</u>	NO
Industrial applicability (IA)	Claims <u>1-27</u>	YES
	Claims <u>NONE</u>	NO

2. Citations and explanations:

Claims 3-4, 15-19, 22-26 meet the criteria set out in PCT Article 33(2), because the prior art does not teach or fairly suggest the claim limitations.

Claims 15-16, 22-24 meet the criteria set out in PCT Article 33(3), because the prior art does not teach or fairly suggest the claim limitations.

Claims 1-27 meet the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

Claims 1, 2, each of claims 5-14, 20, 21 and 27 depending from claims 1 and 2 and claim 26+2 lack novelty under PCT Article 33(2), as being anticipated by US 4011392.

The examples of the reference teach the formation of starch ester by treating cornstarch with agent including succinic, maleic and phthalic acids and the corresponding anhydrides. Example 2 discloses a composition comprising 60% starch ester and 20% butyl cellosolve - a polyhydric alcohol plasticizer. The similar starting materials and process conditions would be expected to produce products exhibiting similar properties.

Claims 3 and 5-14, 17-21, 26 and 27 as dependent from claim 3 and claims 22-24 lack an inventive step under PCT Article 33(3), as being obvious over US 4011392, as applied above, in view of US 2003/014637.

The difference between these claims and the primary reference is the composition is reactively extruded. US 2003/014637, paragraph [0035] teaches starches can be esterified using any conventional reagent by mixing the starch and reagent, such as anhydride, in an extruder operated at 125-160 C. It would have been obvious to one of ordinary skill in the art to carry out the reaction in an extruder because the secondary reference teaches it would be expected to work for any conventional esterification agent.

Claims 25+2 and 25+3, lack an inventive step under PCT Article 33(3), as being obvious over US 4011392, as applied above, in view of US 2003/014637 in further view of US 4231803.

The limitation added by claim 25 is that the plasticizer is glycerol. Claim 2 teaches one of ordinary skill in the art that glycerol is a useful plasticizer for starch esters. It would have been obvious to one of ordinary skill in the art to use glycerol as the plasticizer in the prior art combination for that reason.

Claims 15, 16 and 5-14, 19-21 and 25-27 as dependent upon claim 4 are allowable over the prior art of record. The prior art fails to teach or suggest the improvements obtained by adding a nanoclay to a reactively extruded mixture of starch and a chemical modifier of a dibasic organic acid or anhydride thereof and a plasticizer.

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under Article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the *PCT Applicant's Guide*, a publication of WIPO.

In these Notes, "Article," "Rule" and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report and the written opinion of the International Searching Authority, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only (see *PCT Applicant's Guide*, Volume I/A, Annexes B1 and B2).

The attention of the applicant is drawn to the fact that amendments to the claims under Article 19 are not allowed where the International Searching Authority has declared, under Article 17(2), that no international search report would be established (see *PCT Applicant's Guide*, Volume I/A, paragraph 296).

What parts of the international application may be amended ?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Preliminary Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When ? Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments ?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How ? Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments ?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

PATENT COOPERATION TREATY

PCT/US2005/041237

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PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF RECEIPT OF RECORD COPY

(PCT Rule 24.2(a))

To:

RECEIVED

MCLEOD, Ian, C. MAK 02 2006
McLeod & Moyne, P.C.
2190 Commons Parkway
Okemos, MI 48864
United States of America

IAN C. McLEOD

Date of mailing (day/month/year) 12 February 2006 (12.02.2006)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference MSU 4.2-724 PCT	International application No. PCT/US2005/041237

The applicant is hereby notified that the International Bureau has received the record copy of the International application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

MICHIGAN STATE UNIVERSITY (for all designated States except US)
NARAYAN, Ramani et al (for US)

International filing date : 15 November 2005 (15.11.2005)
Priority date(s) claimed : 19 November 2004 (19.11.2004)
Date of receipt of the record copy
by the International Bureau : 19 January 2006 (19.01.2006)
List of designated Offices :

AP : BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW
EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
EP : AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO,
SE, SI, SK, TR
OA : BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
National : AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK,
LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 338.89.85	Authorized officer: Hélène CAMPIN (Fax 338 8965) Telephone No. (41-22) 338 9716
--	---

Continuation of Form PCT/IB/301

NOTIFICATION OF RECEIPT OF RECORD COPY

Date of mailing (day/month/year) 12 February 2006 (12.02.2006)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference MSU 4.2-724 PCT	International application No. PCT/US2005/041237

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- time limits for entry into the national phase - see updated Important Information (as of April 2002)
- requirements regarding priority documents (if applicable)

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

INFORMATION ON TIME LIMITS FOR ENTERING THE NATIONAL PHASE

The applicant is reminded that the "national phase" must be entered before each of the designated Offices indicated on the cover sheet of this Notification by paying national fees and furnishing translations, as prescribed by Articles 22 and 39 and the applicable national laws. In addition, the applicant may also have to comply with other special requirements applicable in certain Offices. It is the applicant's responsibility to ensure the necessary steps to enter the national phase are taken in a timely fashion. Most Offices do not issue reminders to applicants in connection with the entry into the national phase.

The applicable time limit for entering the national phase will, subject to what is said in the following paragraph, be 30 MONTHS from the priority date, not only in respect of any elected Office if a demand for international preliminary examination is filed before the expiration of 19 months from the priority date (see Article 39(1)), but also in respect of any designated Office, in the absence of filing of such demand, where Article 22(1) as modified with effect from 1 April 2002 applies in respect of that designated Office. For further details, see PCT Gazette No. 44/2001 of 1 November 2001, pages 18926, 18932 and 18934, as well as the PCT Newsletter, October and November 2001 and February 2002 issues.

In practice, time limits other than the 30-month time limit will continue to apply, for various periods of time, in respect of certain designated or elected Offices. For regular updates on the applicable time limits (20, 21, 30 or 31 months, or other time limit), Office by Office, refer to the PCT Gazette ("Section IV" part published on a weekly basis), to the PCT Newsletter (on a monthly basis) and to the relevant National Chapters in Volume II of the PCT Applicant's Guide (the paper version of which is updated usually twice a year and the internet version of which is updated usually on a weekly basis). Finally, a cumulative table of all applicable time limits for entering the national phase is available from WIPO's Internet site, via links from various pages the site including those of the Gazette, Newsletter and Guide, at <http://www.wipo.int/pct/en/index.html>.

Information about the requirements for filing a demand for international preliminary examination is set out in the PCT Applicant's Guide, Volume I/A, Chapter IX. Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 18 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before that date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 18-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 18-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau or if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within the time limit which is reasonable under the circumstances (Rule 17.1(a)).

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 18-month time limit (and all other PCT time limits) is the filing date of the earliest application whose priority is claimed (Article 2(xi)(b)).

From the INTERNATIONAL BUREAU

PCTNOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

Date of mailing (day/month/year) 28 March 2006 (28.03.2006)	RECEIVED APR 06 2006 IAN C. McLEOD MCLEOD, Ian, C. McLeod & Moyne, P.C. 2190 Commons Parkway Okemos, MI 48864 ETATS-UNIS D'AMERIQUE	
Applicant's or agent's file reference MSU 4.2-724 PCT		IMPORTANT NOTIFICATION
International application No. PCT/US2005/041237		International filing date (day/month/year) 15 November 2005 (15.11.2005)
International publication date (day/month/year) Not yet published		Priority date (day/month/year) 19 November 2004 (19.11.2004)
Applicant MICHIGAN STATE UNIVERSITY et al		

1. By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).

2. (If applicable) The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

3. (If applicable) An asterisk (*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b) (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
19 November 2004 (19.11.2004)	10/893,309	US	26 January 2006 (26.01.2006)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Form PCT/IB/304 (October 2005)

Authorized officer

Gijsbertus Beijer

Facsimile No. +41 22 740 14 35

Telephone No. +41 22 338 95 61

CSPV58DK

READ

PATENT COOPERATION TREATY

WO 2006/055504
PCT/US2005/041237

FEB 05 2007

From the INTERNATIONAL BUREAU

83

Ian C. McLeod

PCTNOTIFICATION CONCERNING
AVAILABILITY OF THE PUBLICATION
OF THE INTERNATIONAL APPLICATION

To:

MCLEOD, Ian, C.
McLeod & Moynie, P.C.
2190 Commons Parkway
Okemos, MI 48864
ETATS-UNIS D'AMERIQUE**RECEIVED**

FEB 2 2007

IAN C. MCLEOD

Date of mailing (day/month/year)
11 January 2007 (11.01.2007)Applicant's or agent's file reference
MSU 4.2-724 PCT**IMPORTANT NOTICE**International application No.
PCT/US2005/041237International filing date (day/month/year)
15 November 2005 (15.11.2005)Priority date (day/month/year)
19 November 2004 (19.11.2004)

Applicant

MICHIGAN STATE UNIVERSITY et al

The applicant is hereby notified that the International Bureau:

☐ has published the above-indicated international application on under
No. WO☒ has republished the above-indicated international application on 11 January 2007 (11.01.2007) under
No. WO 2006/055504For an explanation as to the reason for this republication of the international application, reference is made to INID codes (15), (48)
or (88) (as the case may be) on the front page of the published international application.A copy of the international application is available for viewing and downloading on WIPO's website at the following address:
<http://www.wipo.int/pctdb> (under "Query" enter the PCT or WO number).The applicant may also request a paper copy of the published international application from the International Bureau by submitting a written
request to PatentScope@wipo.int or to the address provided below.The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Nora Lindner

Facsimile No. +41 22 338 82 70

e-mail: pt02@wipo.int

Form PCT/IB/311 (April 2006)

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference (if desired) (12 characters maximum) MSU 4.2-724 PCT

Box No. I TITLE OF INVENTION
CHEMICALLY MODIFIED PLASTICIZED STARCH COMPOSITIONS BY EXTRUSION PROCESSING

Box No. II APPLICANT ☐ This person is also inventor

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)

MICHIGAN STATE UNIVERSITY
238 Administration Building
East Lansing, Michigan 48824
United States of America

Telephone No.

(517) 355-2186

Facsimile No.

(517) 432-3880

Teleprinter No.

Applicant's registration No. with the Office

State (that is, country) of nationality:
US

State (that is, country) of residence:
US

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)

NARAYAN, Ramani
4275 Conifer Circle
Okemos, Michigan 48864
United States of America

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
US

State (that is, country) of residence:
US

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

McLEOD, Ian C.
McLeod & Moyne, P.C.
2190 Commons Parkway
Okemos, Michigan 48864
United States of America

Telephone No.

(517) 347-4100

Facsimile No.

(517) 347-4103

Teleprinter No.

Agent's registration No. with the Office

20,931

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) BALAKEISHNAN, Sunder 1636 Indian Way Okemos, Michigan 48864 United States of America		This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: IN	State (that is, country) of residence: US	
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental		
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) NABAR, Yogaraj 1523 Spartan Village Apt. J East Lansing, Michigan 48823 United States of America		This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: IN	State (that is, country) of residence: US	
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental		
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) SHIN, Boo-Young Kyoungsean 712-748 KOREA		This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: KR	State (that is, country) of residence: KR	
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental		
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) DUBOIS, Philippe Rue, Grande, 1 4260 Ciplat BELGIUM		This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: BE	State (that is, country) of residence: BE	
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental		
☒ Further applicants and/or (further) inventors are indicated on another continuation sheet.		

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Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) RAQUEZ, Jean-Marie 701 Cherry Lane, Apt. 104 East Lansing, Michigan 48823 United States of America	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
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State (that is, country) of nationality: BE	State (that is, country) of residence: US
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This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental
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Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
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State (that is, country) of nationality:	State (that is, country) of residence:
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This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
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State (that is, country) of nationality:	State (that is, country) of residence:
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This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
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State (that is, country) of nationality:	State (that is, country) of residence:
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This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No. V DESIGNATIONS

The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.

However,

- ☐ DE Germany is not designated for any kind of national protection
- ☐ KR Republic of Korea is not designated for any kind of national protection
- ☐ RU Russian Federation is not designated for any kind of national protection

(The check-boxes above may be used to exclude (irrevocably) the designations concerned in order to avoid the ceasing of the effect, under the national law, of an earlier national application from which priority is claimed. See the Notes to Box No. V as to the consequences of such national law provisions in these and certain other States.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member	regional application: regional Office	international application: receiving Office
item (1) 19 NOVEMBER 2004 (19.11.2004)	10/993,309	US		
item (2)				
item (3)				

- ☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

- ☐ all items ☒ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organisation for which that earlier application was filed (Rule 4.10(b)(ii)):

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA/ US

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) 19 NOVEMBER 2004 Number 10/993,309 Country (or regional Office) US

Box No. VIII DÉCLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of declarations

- ☐ Box No. VIII (i) Declaration as to the identity of the inventor :
- ☐ Box No. VIII (ii) Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent :
- ☐ Box No. VIII (iii) Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application :
- ☐ Box No. VIII (iv) Declaration of inventorship (only for the purposes of the designation of the United States of America) :
- ☐ Box No. VIII (v) Declaration as to non-prejudicial disclosures or exceptions to lack of novelty :

Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains: (a) on paper, the following number of sheets:	This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):	Number of items
request (including declaration sheets) : 5	1. ☒ fee calculation sheet	:
description (excluding sequence listing and/or tables related thereto) : 22	2. ☐ original separate power of attorney	:
claims : 5	3. ☐ original general power of attorney	:
abstract : 1	4. ☐ copy of general power of attorney; reference number, if any:	:
drawings : 5	5. ☐ statement explaining lack of signature	:
Sub-total number of sheets 38	6. ☐ priority document(s) identified in Box No. VI as item(s):	:
sequence listing :	7. ☐ translation of international application into (language):	:
tables related thereto :	8. ☐ separate indications concerning deposited microorganism or other biological material	:
(for both, actual number of sheets if filed on paper, whether or not also filed in electronic form; see (c) below)	9. ☐ sequence listing in electronic form (indicate type and number of carriers)	:
Total number of sheets : 38	(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) :	:
(b) ☐ only in electronic form (Section 801(a)(i))	(ii) ☐ (only where check-box (b)(i) or (c)(i) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter	:
(i) ☐ sequence listing	(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column	:
(ii) ☐ tables related thereto	10. ☐ tables in electronic form related to sequence listing (indicate type and number of carriers)	:
(c) ☐ also in electronic form (Section 801(a)(ii))	(i) ☐ copy submitted for the purposes of international search under Section 802(b-quater) only (and not as part of the international application)	:
(i) ☐ sequence listing	(ii) ☐ (only where check-box (b)(ii) or (c)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-quater)	:
(ii) ☐ tables related thereto	(iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column	:
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the	11. ☐ other (specify):	:
☐ sequence listing:		
☐ tables related thereto:		
(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)		

Figure of the drawings which should accompany the abstract:

Language of filing of the international application: English

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).


 (Ian C. McLeod, Agent)

For receiving Office use only		2. Drawings: ☐ received: ☐ not received:
1. Date of actual receipt of the purported international application:		
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA/	6. ☐ Transmittal of search copy delayed until search fee is paid	

For International Bureau use only
Date of receipt of the record copy by the International Bureau:

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International Application No.

Date stamp of the receiving Office

Applicant's or agent's
file reference

MSU 4.2-724 PCT

Applicant

MICHIGAN STATE UNIVERSITY et al

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE 300.00 **T**

2. SEARCH FEE 300.00 **S**

International search to be carried out by US
(If two or more International Searching Authorities are competent to carry out the international search, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FILING FEE

Where item (b) and/or (c) of Box No. IX apply, enter Sub-total number of sheets } 38
Where item (b) and (c) of Box No. IX do not apply, enter Total number of sheets }

i1 first 30 sheets 1,124.00 **i1**

i2 8 x 13.00 = 104.00 **i2**
number of sheets in excess of 30 fee per sheet

i3 additional component (only if sequence listing and/or tables related thereto are filed in electronic form under Section 801(a)(i), or both in that form and on paper, under Section 801(a)(ii)):

400 x = **i3**
fee per sheet

Add amounts entered at i1, i2 and i3 and enter total at **I** 1,228.00 **I**

(Applicants from certain States are entitled to a reduction of 75% of the international filing fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at **I** is 25% of the international filing fee.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) **P**

5. TOTAL FEES PAYABLE 1,828.00

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

MODE OF PAYMENT

- ☒ authorization to charge deposit account (see below) ☐ postal money order ☐ cash ☐ coupons
☒ cheque ☐ bank draft ☐ revenue stamps ☐ other (specify):

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT (This mode of payment may not be available at all receiving Offices)

- ☐ Authorization to charge the total fees indicated above.
☒ (This check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.
☒ Authorization to charge the fee for priority document.

Receiving Office: RO/ US

Deposit Account No.: 13-0810

Date: 15 NOVEMBER 2005

Name: Ian C. McLeod

Signature: Ian C. McLeod

**TRANSMITTAL LETTER TO THE
UNITED STATES RECEIVING OFFICE**

Date	15 NOV 2005
International Application No.	
Attorney Docket No.	MSU 4.2-724 PCT

L. Certification under 37 CFR 1.10 (if applicable)

EQ 124511117 US	15 NOVEMBER 2005
Express Mail mailing number	Date of Deposit

I hereby certify that the application/correspondence attached hereto is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Mail Stop PCT, Commissioner for Patents, PO Box 1450, Alexandria, VA 22313-1450.

<i>Tammi L. Taylor</i>	Tammi L. Taylor
Signature of person mailing correspondence	Typed or printed name of person mailing correspondence

II. ☒ New International Application

TITLE	CHEMICALLY MODIFIED PLASTICIZED STARCH COMPOSITIONS BY EXTRUSION PROCESSING	Earliest priority date (Day/Month/Year)
		19 NOV 2004

SCREENING DISCLOSURE INFORMATION: In order to assist in screening the accompanying international application for purposes of determining whether a license for foreign transmittal should and could be granted and for other purposes, the following information is supplied. (Note: check as many boxes as apply):

A. ☐ The invention disclosed was not made in the United States.

B. ☐ There is no prior U.S. application relating to this invention.

C. ☒ The following prior U.S. application(s) contain subject matter which is related to the invention disclosed in the attached international application. (NOTE: priority to these applications may or may not be claimed on form PCT/RO/101 (Request) and this listing does not constitute a claim for priority.)

application no.	10/993,309	Filed on	19 NOV 2004
application no.		Filed on	

D. ☐ The present international application contains additional subject matter not found in the prior U.S. application(s) identified in paragraph C. above. The additional subject matter is found on pages _____ and ☐ DOES NOT ALTER ☐ MIGHT BE CONSIDERED TO ALTER the general nature of the invention in a manner which would require the U.S. application to have been made available for inspection by the appropriate defense agencies under 35 U.S.C. 181 and 37 CFR 5.1. See 37 CFR 5.15.

III. ☐ A Response to an invitation from the ROUS. The following document(s) is (are) enclosed:

A. ☐ A Request for An Extension of Time to File a Response

B. ☐ A Power of Attorney (General or Regular)

C. ☐ Replacement pages:

pages		of the request (PCT/RO/101)	pages		of the figures
pages		of the description	pages		of the abstract
pages		of the claims			

D. ☐ Submission of Priority Documents

Priority document		Priority document	
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E. ☐ Fee is specified on attached Fee Calculation sheet form PCT/RO/101 annex

IV. ☒ A Request for Rectification under PCT 81 ☐ A Petition ☐ A Sequence Listing Diskette

V. ☐ Other (please specify):

The person signing this form is this:	☐ Applicant	Ian C. McLeod
	☒ Attorney/Agent (Reg. No.) 20,931	Typed name of signer
	☐ Common Representative	<i>Tammi L. Taylor</i> Signature

PTO-1382 (Rev. 04-2003)

U.S. Department of Commerce: Patent and Trademark Office

(Transmittal Letter to the United States Receiving Office PTO-1382 [13-1])

**CHEMICALLY MODIFIED PLASTICIZED STARCH
COMPOSITIONS BY EXTRUSION PROCESSING**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not Applicable

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable

STATEMENT REGARDING GOVERNMENT RIGHTS

[0003] Not Applicable

BACKGROUND OF THE INVENTION

(1) Field of the Invention

[0004] The present invention relates to a biodegradable chemically modified plasticized starch (CMPS) composition, and a chemically modified starch-nanoclay CMPS composition, and to a process for the preparation thereof. The invention preferably relates to a twin screw extrusion process for manufacturing the chemically modified starch composition by reacting starch with a dibasic acid or anhydride of the acid as a modifier in the presence of plasticizer and an optional free radical initiator for the acid or anhydride to provide the plasticized starch compositions which have improved processability and reduced viscosity, and is particularly useful when combined with other thermoplastic polymers.

(2) Description of Related Art

[0005] In the last two decades, considerable effort has gone into the development of biodegradable polymers and blends using starch. The processing characteristics and mechanical

properties of unmodified starch polymers are very poor compared to typical synthetic polymers.

[0006] The prior developments in the area of biodegradable materials from starch involve the use of an external plasticizer to solvate the starch granules and impart melt processability and enhance the room-temperature flexibility of the final product. Some of the earliest efforts on such materials were discussed in U.S. Pat. No. 3,312,641 (A. E. Staley Mfg. Co.) and Canadian Patent Appl. No. 838,572 (USDA, Lincoln, Nebr.). The subject of these patents was the extrusion of amylose primarily using water as a plasticizer. In addition, poly (vinyl alcohol), glycerol and other related materials were also incorporated in the system. Cast films from water-based dispersions of starch, glycerol and other polymers were evaluated in U.S. Pat. Nos. 3,949,145, 4,133,784, and 4,337,181 (USDA, Peoria, Ill.). More recently, extruded compositions using water were discussed in Eur. Pat. Appl. EP 282,451, 304,401, 327,505, 404,723, 404,728, and 408,503 (Warner Lambert Co.); water-free systems using glycerol were discussed in PCT Int. Appl. WO 90/05,161 (Tomka); and formulations using both water and other plasticizers like glycerol were the subject of PCT Int. Appl. WO 92/19680 (Novamont S.p.a.), Eur. Pat. Appl. EP 400,531 (Butterfly S.r.l.), and PCT Int. Appl. WO 90/14,388 (Agri-Tech Industries, Inc.).

[0007] WO92/19680 (Novamont) describes the use of undried starch (about 12% moisture) in biodegradable polymeric compositions. These compositions produce films whose properties are sensitive to moisture. WO93/00116 (P&G) describes plastic compositions, which use "destructurized" starch, a form where the crystallinity of the starch has been destroyed by heating. The term "destructurized starch" refers to starch in which the granular, crystalline structure is destroyed resulting in the

formation of a homogeneous, amorphous material that melts and flows like a thermoplastic. The "destructurization" process is accomplished by heating starch granules in the presence of water at elevated temperatures and pressures in a closed volume like an extruder. The higher the amount of water used, the lower the temperature needed for "destructurization" to be completed. Typical compositions for the "destructurization" processes include extruding starch with about 15-20% water by weight along with other additives. It has been argued that the concept of "destructurization" is just a new name ascribed to an old concept of gelatinization and/or plasticization of starch that first originated in the food industry. The term gelatinization refers to the process of disruption of the granular structure of starch by heating a starch suspension at temperatures in the range of 50°-80°C. Traditional processing in the food industry involves further heating and mixing of starches to result in the formation of a homogeneous plasticized mass as discussed by Shogren, R. L., et al., Starch/Starke 45, 276-280 (1993). The plasticization of starch using water and glycerol has been reported as early as 1947 for pharmaceutical applications ("The Pharmacopoeia of the United States of America", XIII, p. 513-514, 1947).

[0008] The principal difference between the various applications has to do with the ratios of starch and plasticizer (water, glycerol or both) used in the composition. This leads to differences in the rheological and final characteristics of each composition that is suited to the specific application. A high proportion of plasticizer (70-90% by weight) results in a jelly-like material. Medium plasticizer contents (40-70% by weight) are more suited for food applications that have good elasticity combined with reasonable rigidity to be able to form and shape various products. Low

plasticizer contents (10-40% by weight) are appropriate for plastics applications that require greater rigidity and better mechanical strength characteristics. More recently, plasticization of starch in the absence of water, using polyhydric alcohols like glycerol and sorbitol has been reported. The term plasticization in the classical sense as used in the polymer industry involves transformation of a rigid, crystalline material into a pliable, less crystalline (if not amorphous) material with a lowered glass transition temperature. Japanese Patent No. 04-48,851 discloses the manufacture of biodegradable sheets based upon mixtures of starch and biodegradable polyesters derived from reactions of diols and acids. The starch has normal moisture content of about 10 to 12% by weight.

[0009] In a typical plasticized system with starch, the diffusion of plasticizer out of the product when exposed to low humidity conditions and diffusion of water into the product under high humidity conditions is an inevitable result. This causes embrittlement of the product due to loss of plasticizer (low humidity) and problems associated with retention of product shape, texture, and form due to excess absorbed water (high humidity). These effects are detrimental especially when water is used as a plasticizer, but are prevalent even in non-water based starch formulations that incorporate hygroscopic plasticizers. In general, due to the poor durability of plasticized starch upon exposure to different environments (due to its hydrophilic nature) there is likely to be very little commercial use of plasticized native or unmodified starch by itself.

[0010] Physical or chemical modifications of the starch are a viable alternative to solving some of these problems. Physical modifications include coating the starch granules with

hydrophobic sizing agents and binders similar to those used in the paper industry, like rosin, proteins, like soy proteins and silanes or physically coating the end product with hydrophobic materials like low molecular weight waxes, and natural resins (zein, rosin, shellac and the like) and higher molecular weight non-polar polymers. Cross-linking of the starch granules or plasticized starch is another physical modification route to improving the hydrophobicity of starch-based materials. Chemical modifications include grafting reactions and non-degradative substitution of the hydroxyls on the starch with functional groups like esters, ethers, isocyanates and the like. Cyclic dibasic acid anhydrides such as succinic anhydride yield starch esters containing a free carboxylate group that increases the water-holding capacity of the product (U.S. Patent No. 2,461,139; 1949). The same chemistry can be carried out with maleic anhydride to yield the maleate half ester. Treatment of a starch suspension with a cyclic dicarboxylic acid anhydride containing a hydrophobic substituent group yields products with emulsion stabilizing properties (U.S. Patent No. 2,661,349; 1953). These starch esters have value as dispersants in coatings replacing commercially available paint containing dispersants. U.S. Patent 3,732,207 discusses the production of starch esters by heating starch with maleic or succinic anhydride at 100-155 °C in a batch process with reaction times of 10 hours in the presence of 0.5-15% moisture to give a product with degree of substitution (DS) 0.02 to 0.04.

[0011] Tomasik et al., Starch 47 96 (1995) reacted corn starches in extruders containing varying amounts of moisture (18, 20 and 30%) with succinic, maleic and phthalic anhydrides to form starch esters. Carbonate buffer, either pH 8 or pH 9 was added as a medium during extrusion. It is demonstrated that

extrusion of starch with cyclic anhydrides in alkaline medium presents a facile method of preparation of anionic starches of hydrophobic character based. However, this method has several serious limitations resulting from the chemistry and the extrusion process. For example, it is extremely difficult to extrude these samples at temperatures of around 130°C due to the resultant high viscosity of the starch melt. Also, the use of water is extremely problematic in processing and quality of the final product.

[0012] Related prior art is described in:

- (1) Ramani Narayan, Steven Bloembergen and Amit Lathia, A Method of Preparing Biodegradable Modified-Starch Moldable Products and Films, U.S. Patent 5,869,647, February 9, 1999 , July 1993;
- (2) Narayan, R., Biodegradable Multi-Component Polymeric Materials Based on Unmodified Starch-Like Polysaccharides, U.S. Patent 5,500,465, October 31, 1995;
- (3) Narayan, R., Krishnan, M., DuBois, P., Polysaccharides Grafted With Aliphatic Polyesters Derived From Cyclic Esters, U.S. Patent 5, 540, 929, July 30, 1996;
- (4) Narayan, R., Krishnan, M., DuBois, P., Polysaccharides Grafted With Aliphatic Polyesters Derived From Cyclic Esters, U.S. Patent 5,578,691, November 26, 1996;
- (5) Narayan, R., Krishnan, M., DuBois, P., Polysaccharides Grafted With Aliphatic Polyesters Derived From Cyclic Esters, U.S. Patent 5, 616,671, April 1, 1997;
- (6) U.S. patent application co-filed with the present application.

OBJECTS

[0013] It is an object of the present invention to provide a chemically modified plasticized starch and plasticizer compositions which have improved properties. It is further an object of this invention to provide a process which is economical and reproducible. These and other objects will become increasingly apparent by reference to the following description.

SUMMARY OF THE INVENTION

[0014] The present invention relates to biodegradable, reactive, chemically modified plasticized starch (CMPS) compositions with low viscosity and good processability. Further, the present invention relates to a continuous reactive extrusion process for manufacturing the compositions. An important aspect of this invention is that the process uses no added water, and prevents problems such as high viscosity, clogging of the thermoplastic starch melt at the die or foaming of the thermoplastic starch melt. Furthermore, the resulting chemically modified starch composition is highly reactive to yield graft copolymers with polyesters as described in detail in our co-pending patent application, which is incorporated herein by reference. These starch-polyester graft copolymers are readily processable into films, and molded products using conventional plastics processing equipment, and the resultant product has the most preferred balance in mechanical properties, water resistance, processability and the rate of biodegradation. The invention also describes a new chemically modified starch-nano clay composition with improved dispersability of the nano clay in the matrix, reactivity and processability for subsequent reaction with polyesters as described in our co-pending patent application.

af 98

[0015] In accordance with the present invention, there is provided a biodegradable, reactive low viscosity chemically modified plasticized starch composition (CMPS) prepared by the reactive blending or extrusion processing of starch in the presence of chemical modifiers, a plasticizer and an optional free-radical initiator.

[0016] The present invention also provides a biodegradable chemically modified starch-nano clay product prepared by reactive extrusion processing of starch in the presence of modifiers, plasticizers and nanoclay material.

[0017] The present invention also relates to a composition which comprises a mixture of starch esters of a dibasic acid or an anhydride of a dibasic acid, wherein the mixture has reduced viscosity from a natural starch in dimethyl sulfoxide.

[0018] The present invention also relates to a starch based composition which comprises a reacted mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, and anhydride of the dibasic organic acid, or mixtures thereof, and a plasticizer.

[0019] In particular the present invention relates to a starch based composition which comprises a reactively extruded mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer and, optionally a free radical initiator for the reaction, wherein the mixture has been extruded with heating and venting of water from the mixture.

[0020] Further, the present invention relates to a biodegradable, chemically modified starch based composition which comprises a reactively extruded mixture comprising a biodegradable starch polymer, a chemical modifier selected from

the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer optionally a free radical initiator for the reaction and a nanoclay, wherein the mixture has been extruded with heating and venting of water from the mixture.

[0021] Preferably the starch polymer is selected from the group consisting of cornstarch, potato starch, tapioca starch, rice starch, wheat starch, and cassava starch. Preferably the starch polymer in the mixture is present in an amount between about 5% to 90% by weight of the mixture. Preferably the starch polymer is an unmodified, oxidized or thin boiling starch of 0 to 95 degree fluidity. Preferably the starch polymer has moisture content of about 0.5% to 15% by weight. Preferably the starch polymer is in a pulverized form. Preferably the plasticizer is a polyhydric alcohol. Preferably the plasticizer is present in an amount between about 10 to 50 wt% of the mixture. Preferably the chemical modifier is present in an amount between about 0.5% to about 10% by weight of the starch polymer. Preferably the nanoclay is selected from a group consisting of montmorillonite; smectite, hectorite and mixtures thereof. Preferably the nanoclay is present in an amount between about 0.5 to 25 wt% of the mixture. Preferably the free radical initiator is 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane or other organic peroxide. Preferably the free radical initiator is present in the mixture in an amount between about 0.01 to 2.0 wt% of the mixture. Preferably the mixture is processed in a twin-screw extruder at a temperature in the range of about 100°C to 200°C.

Preferably the anhydrides are selected from the group consisting of maleic-, succinic-, itaconic-, phthalic- and mixtures thereof. Preferably the chemical modifier is about 2% to 5% by weight of the starch polymer of the mixture.

97 100

[0022] The present invention also relates to a process for preparing a starch based composition which comprises reactively extruding a mixture which comprises a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer and, optionally a free radical initiator wherein the mixture is extruded with heating and venting of water from the mixture. Preferably the starch polymer and modifier are mixed as powders. The processing is preferably at 100-250°C.

BRIEF DESCRIPTION OF THE FIGURES

[0023] Other advantages of the present invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

[0024] FIGURE 1 is a graph which depicts the calibration curve of the glycerol pump used in the synthesis of chemically modified plasticized starch (CMPS); by reactive extrusion processing using maleic anhydride or maleic acid modifier.

[0025] Figure 2 is an extrusion flow apparatus diagram for the preparation of CMPS.

[0026] FIGURES 3A, 3B and 3C show the screw configurations used for reactive extrusion processing in the synthesis of CMPS.

[0027] FIGURE 4 is a graph showing FTIR results of CMPS samples produced using maleic anhydride modifier by the reactive extrusion processing. CMPS samples were extracted in THF solvent using a Soxhlet apparatus. Residue from the thimble of the apparatus was dried to constant weight and FTIR analysis conducted. Solvent was evaporated from the extract and the extract dried to constant weight and FTIR analysis conducted.

94 101

[0028] FIGURE 5 is a graph showing the FTIR results of CMPS samples produced using maleic acid modifier by reactive extrusion processing. CMPS samples were extracted in THF solvent using a Soxhlet apparatus. Residue from the thimble was dried to constant weight and FTIR analysis conducted. Solvent was evaporated from the extract and the extract dried to constant weight and FTIR analysis conducted.

DETAILED DESCRIPTION OF THE INVENTION

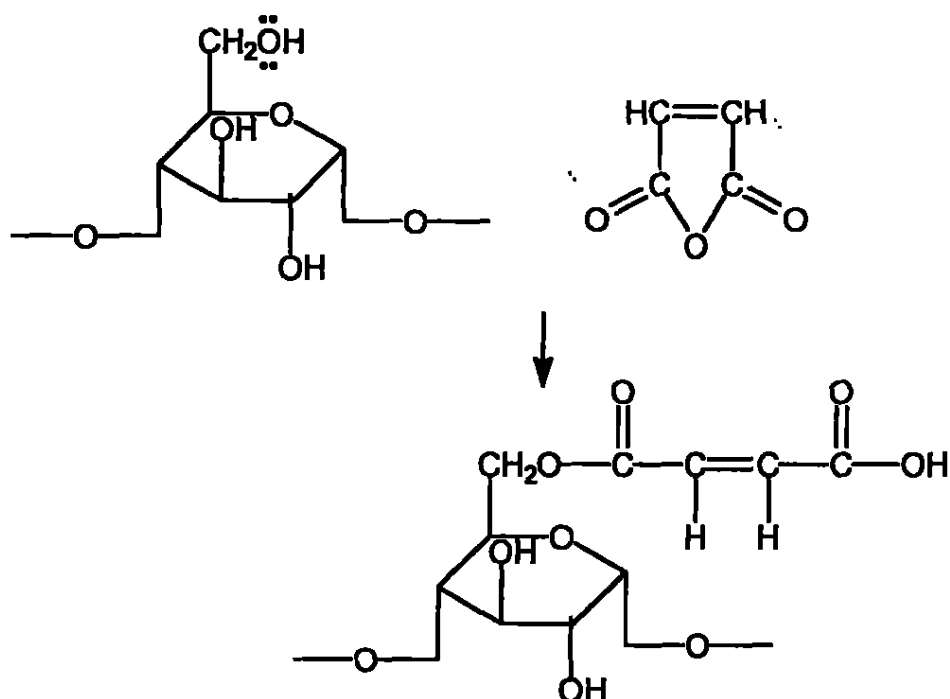
[0029] The present invention provides (i) a biodegradable chemically modified starch composition, (ii) a biodegradable chemically modified starch-nanoclay composition, (iii) and a method for making thereof wherein, generally, the composition is prepared by continuous reactive extrusion processing. Preferably, the present invention concerns a) biodegradable, highly reactive, chemically modified starch composition with low viscosity and high processability, that yields graft copolymers with biodegradable polyesters as described in our co-pending patent application. Another object of the present invention is to provide b) a new chemically modified starch-nanoclay composition with improved dispersability of the nanoclay in the matrix, reactivity and processability for subsequent reaction with polyesters as described in our co-pending patent application.

[0030] The components of the biodegradable chemically modified starch composition that are employed in the process that is within the scope of this invention preferably include the following:

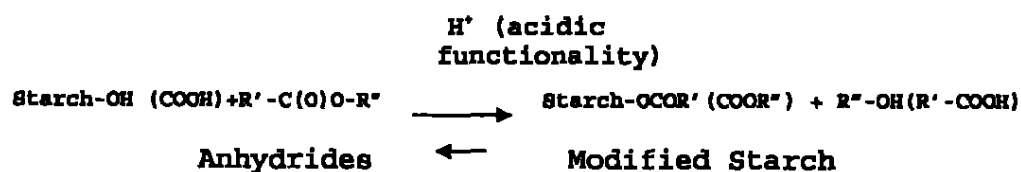
- (I) Starch preferably selected from the group of potato starch, corn starch, waxy starch, tapioca starch, rice starch, wheat starch, and cassava starch and the like

- (II) Plasticizer preferably selected from the group of polyhydroxy compounds including glycerol, ethylene glycol, and the like
- (III) Modifier selected from the group of dibasic acids and their cyclic anhydride compounds; and
- (IV) Optionally, free radical initiator selected from the group of peroxides, and the like.

The proposed reactions are:



Maleation Chemistry



Transesterification Chemistry

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[0031] Starch ($C_6H_{10}O_5$)_n, is a mixture of linear (amylose) and branched (amylopectin) polymers. Amylose is essentially a linear polymer of .alpha.(1.fwdarw.4) linked D-glucopyranosyl units. Amylopectin is a highly-branched polymer of D-glucopyranosyl units containing .alpha.(1.fwdarw.4) linkages, with .alpha.(1.fwdarw.6) linkages at the branch points. The process of the present invention can use various types of starches, such as regular corn starch which contains about 75% amylopectin (higher molecular weight branched starch polymer) and 25% amylose (lower molecular weight linear starch polymer), as well as hybrid corn starch products containing more than 50% amylose, sold by Corn Products, Inc. (Chicago, Illinois). Various other starches, such as potato starch, tapioca starch, rice starch, wheat starch, cassava starch, and other starches familiar to those skilled in the art can be utilized in accordance with the present invention. Compositions having increased levels of linear starch polymers are most likely to be the correct choice in terms of processability, film forming, molding and mechanical properties. The starch component in the chemically modified starch composition is 5% to 90% by weight, preferably from 50% to 80% by weight.

[0032] A plasticizer is added to the inventive compositions to achieve greater material processability and product flexibility, although plasticizers typically soften the compositions in which they are included. The preferred plasticizers are polyhydric alcohols. More preferably, glycerol is used as a suitable plasticizer since it induces high flexibility, is virtually odorless, has a relatively high boiling point, is biodegradable, and is commercially available at a reasonable cost. Plasticizer concentration in the final chemically modified starch product is 15% to 50% by weight and

preferably from 20% to 30% by weight.

[0033] The preferred modifiers that are useful in the present invention are to provide a chemically modified starch ester product. The starch ester product may preferentially be formed by reaction of the starch hydroxyl groups with a dibasic acid or cyclic anhydride to obtain ester linkages with pendant carboxylic groups as shown in Scheme I. The derived pendant carboxylic group can also catalyze the aforementioned reaction between the hydroxyl groups on the starch, and the dibasic acids or their cyclic anhydrides. The more preferred dibasic acids and their cyclic anhydrides include maleic-, succinic-, itaconic-, phthalic- and stearic anhydrides and combinations thereof. The modifier is preferably present in amount of about 0.5% to about 10% by weight of the starch polymer and also provides an acidic environment for the mixture.

[0034] Optionally, a free radical initiator may be used for improving the melt-strength of chemically modified starch product. It is preferred that the free radical initiator be an organic peroxide such as 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane, tert-butylperoctoate, tert-butylperoxypivalate, dicumylperoxide, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, bis(tert-butylperoxyisopropyl)benzene and the like. Azo compounds, such as azobisisobutyronitrile can be also used. The free radical initiator is present in the amount of 0.01 to 2.0 wt percent of the total mass.

[0035] The present invention also relates to a biodegradable chemically modified starch-nano clay product, prepared by reactive extrusion processing of starch in the presence of modifiers, plasticizers, and nanoclay material.

[0036] Nanoclays can be useful to provide an increased mechanical strength, flame retardancy, gas barrier properties,

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and improved barrier to water vapor for chemically modified nanoclay starch product (ii). Another preferred embodiment is that the nanoclays useful for the present invention are well-dispersed in the biodegradable chemically modified starch-clay product. The preferred nanoclays are smectite, hectorite clays including phyllosilicates such as smectite clay minerals, e.g., montmorillonite, particularly sodium montmorillonite; bentonite; hectorite; saponite; stevensite; beidellite; and the like. The clays used are typically smectite clays, particularly bentonite and hectorite. Smectite clays possess some structural characteristics similar to the better-known minerals talc and mica. The preferred range of nanoclays is ranging from 0.5 to 25 wt % of the total mass.

[0037] The reactive modification process of starch to form chemically modified plasticized starch (CMPS) in an extruder prevents the traditionally seen problems, such as clogging of the plasticized starch melt at the die or foaming of the plasticized starch melt at the die, observed during the regular thermo-plasticization of starch. The apparatus used in carrying out the extrusion process may be any screw type extruder. While the use of a single or twin screw extruder may be used, it is preferred to use a twin-screw extruder. Such extruders will typically have rotating screws in a horizontal cylindrical barrel with an entry port mounted over one end and a shaping die mounted at the discharge end. When twin screws are used, they may be co-rotating and intermeshing or non-intermeshing. Each screw will comprise a helical flight or threaded sections and typically will have a relatively deep feed section followed by a tapered transition section and a comparatively shallow constant-depth meter section. The motor driven screws, generally fit snugly into the cylinder or barrel to allow mixing, heating and shearing of the material as it passes

through the extruder.

[0038] Control of the temperature along the length of the extruder barrel is important and is accomplished in zones along the length of the screw. Heat exchange means, typically a passage such as a channel, chamber or bore located in the barrel wall, for circulating a heated media such as oil, or an electrical heater such as calrod or coil type heaters, are often used. Additionally, heat exchange means may also be placed in or along the shaft of the screw device.

[0039] Variations in any of the elements used in the extruder may be made as desired in accordance with conventional design practices. A further description of extrusion and typical design variations can be found in "Encyclopedia of Polymer Science and Engineering", Volume 6, 1986, pp. 571 to 631.

[0040] In carrying out the extrusion process, temperatures in the extruder will vary depending on the particular material, desired properties and application. They can generally range from about 100.degree. to 250 degree. C. and preferably will range from about 150.degree. to 200.degree. C.

[0041] Further, the biodegradable chemically modified starch (i), and biodegradable chemically modified starch-nanoclay compositions (ii) can be manufactured in a one-step process; wherein the components were previously mixed together, and were then introduced into the feed throat of a twin-screw extruder (such as a Century ZSK-30 co-rotating twin screw extruder) at a feed rate of 500-9000 g/hr by means of a solid metering. Alternatively, the components may be separately introduced in the case of liquid component by means of a peristaltic pump, and in the case of solid component by means of a solid metering

at a feed rate of 40-8000 g/hr.

[0042] The biodegradable, chemically modified starch composition and the biodegradable, chemically modified starch-nanoclay compositions are particularly useful for manufacturing starch-polyester graft copolymers as described in our co pending patent application referred to previously.

[0043] The following experimental examples demonstrate the utility of the present invention for forming biodegradable chemically modified starch (i), and biodegradable chemically modified starch-nanoclay (ii) compositions.

[0044] Examples of materials made in accordance with the present invention are biodegradable as demonstrated by standard ASTM test methods.

EXAMPLES

Example 1

[0045] Chemical modification of starch polymer was carried out as follows:

[0046] Regular silver pearl corn-starch, obtained from Cargill Inc. was reactively modified using maleic anhydride/maleic acid in a twin-screw co-rotating CENTURY extruder with a screw diameter of 30 mm and a L/D ratio of 40. Maleic anhydride (MA) was ground to a fine powder using a mortar and pestle and mixed with the starch (800 gm starch + [20 gm] maleic anhydride) using a kitchen blender for 15 minutes before being fed to the feed port of the extruder. Glycerol was mixed with 2, 5-Bis (tert-butylperoxy)-2, 5-dimethylhexane (Luperox 101) {200 gm glycerol + 1.6 gm Luperox 101} and pumped to the extruder using a peristaltic pump. The relative rates of the starch/MA mixture to the glycerol/Luperox 101 mixtures were maintained at 80:20. The calibration curve for the glycerol pump is shown in Figure 1. The screw configuration used for the maleation consisted of conveying and kneading elements as shown in Figures 3A to 3C. A water vacuum was applied at the vent port to remove the unreacted maleic acid/water mixture. The chemically modified plasticized starch, CMPS, was collected and ground to a fine powder. Ground CMPS was stored in an oven at 50°C. The extrusion processing conditions for the reactive maleation is outlined in Table 1.

TABLE 1: Extrusion Processing conditions in the synthesis of CMPS

ZONE	SET	ACTUAL	UNITS
ZONE1	15	39	°C
ZONE2	95	103	°C
ZONE3	125	122	°C
ZONE4	145	146	°C
ZONE5	160	157	°C
ZONE6	165	161	°C
ZONE7	165	167	°C
ZONE8	165	164	°C
ZONE9	150	156	°C
DIE	145	147	°C
MELT TEMP.		148	°C
MOTOR SPEED		125	RPM
TORQUE		35	%
PRESSURE		92	Psia
FEEDER SPEED, CENTURY		155 (Rate = 12.3 lbs/hr)	%
GLYCEROL PUMP		0.1 (Rate = 3.07 lbs/hr)	%
FEEDER SPEED, EXT		-	%

107 110

[0047] CMPS produced was extracted using tetrahydrofuran (THF) in a Soxhlet apparatus to remove the unreacted maleic anhydride and maleic acid (formed by reaction with water present in starch). FTIR analysis (Figure 4) of the Soxhlet residue (after drying in an oven at 50°C overnight) confirmed grafting of the maleic anhydride onto the starch backbone with the presence of the ester carbonyl peak at 1720 cm^{-1} .

Example 2

[0048] The procedure given in Example 1 was followed using maleic acid modifier instead of maleic anhydride. CMPS produced was extracted using tetrahydrofuran (THF) in a Soxhlet apparatus to remove the unreacted maleic acid. FTIR analysis (Figure 5) conducted on the Soxhlet residue (after drying in an oven at 50°C overnight) confirmed grafting of the maleic acid onto the starch backbone with the presence of the ester carbonyl peak at 1720 cm^{-1} .

Example 3

[0049] The procedure in Example 1 was followed to produce CMPS modified using 2.4-wt%, maleic anhydride, both with and without the initiator. Chemically modified plasticized starch (CMPS) was produced by plasticization of regular corn starch (Corn Products, Inc-Brazil) using 20-wt% glycerol plasticizer in a twin-screw extruder. The intrinsic viscosity of starch, PS, CMPS (2.4-wt% maleic anhydride and 0.1-wt% Luperox 101) and CMPS (no Luperox 101) were determined in DMSO solvent using Cannon Ubbelohde viscometer (0B). The intrinsic viscosity of starch was around 1.6 dl/g while that of PS reduced to 1.2 dl/g. However, on maleation without addition of Luperox 101, the intrinsic viscosity of CMPS drastically dropped to 0.29 dl/g. This reduction is attributed to a decrease in molecular

weight due to the hydrolysis of starch in the presence of maleic acid. However, on addition of Luperox 101, the intrinsic viscosity increased slightly to 0.31 dl/g. This increase is attributed to branching or cross-linking reactions occurring.

Example 4

[0050] Chemical modification of starch polymer to form chemically modified plasticized starch-nano clay products.

[0051] Regular silver pearl corn-starch, obtained from Cargill Inc. was reactively modified using maleic anhydride/maleic acid in a twin-screw co-rotating CENTURY[™] extruder with a screw diameter of 30 mm and a L/D ratio of 40 in the presence of BENTONE 166[™], which is an alkylaryl ammonium hectorite clay, obtained from Elementis Specialties (Highstown, NJ), with greatly improved dispersability characteristics. Maleic anhydride (MA) was ground to a fine powder using a mortar and pestle and mixed with the starch (800 gm starch + 20 gm maleic anhydride + 150 gm BENTONE 166) using a kitchen blender for 15 minutes before being fed to the feed port of the extruder. 200 gm glycerol was pumped to the extruder using a peristaltic pump. The relative rates of the starch/MA/BENTONE 166 mixture to the glycerol were maintained at 80:20.

Example 5

[0052] The procedure in Example 4 was followed to produce CMPS modified using 2.5-wt%, maleic anhydride and BENTONE 111[™], which is an organic derivative of a special smectite clay, obtained from Elementis Specialties. Maleic anhydride (MA) was ground to a fine powder using a mortar and pestle and mixed with the starch (800 gm starch + 20 gm maleic anhydride + 150 gm BENTONE 111) using a kitchen blender for 15 minutes before being fed to the feed port of the extruder. 200 gm glycerol was

pumped to the extruder using a peristaltic pump. The relative rates of the starch/MA/BENTONE 111 mixture to the glycerol were maintained at 80:20.

Example 6

[0053] The procedure in Example 4 was followed to produce CMPS-clay product using 2.5-wt%, maleic anhydride and Cloisite 30B[™], which is a montmorillonite clay modified with dihydroxy quaternary ammonium salt obtained from Southern Clay Products.

[0054] Preferably the starch esters with the plasticizer (glycerol) have a viscosity in the range of about 0.15 to 0.3 dl/gram in DMSO. Natural starch has a viscosity of 1.51 dl/gm and plasticized starch has a viscosity of 1.20 dl/gm. Thus there is a significantly reduced viscosity.

[0055] It is intended that the foregoing description be only illustrative of the present invention and that the present invention be limited only by the hereinafter appended claims.

WE CLAIM:

1. A composition which comprises a mixture of starch esters of a dibasic acid or an anhydride of a dibasic acid, wherein the mixture has reduced viscosity from a natural starch in dimethyl sulfoxide.
2. A starch based composition which comprises a reacted mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of the dibasic organic acid or mixtures thereof and a plasticizer.
3. A starch based composition which comprises a reactively extruded mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer and, optionally a free radical initiator for the reaction, wherein the mixture has been extruded with heating and venting of water from the mixture.
4. A biodegradable, chemically modified starch based composition which comprises a reactively extruded mixture comprising a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer optionally a free radical initiator for the reaction and a nanoclay, wherein the mixture has been extruded with heating and venting of water from the mixture.

- 117 114
5. The composition of any one of Claims 1, 2, 3, or 4 wherein said starch polymer is selected from the group consisting of cornstarch, potato starch, tapioca starch, rice starch, wheat starch, and cassava starch.
 6. The composition of any one of Claims 1, 2, 3, or 4 wherein the starch polymer in the mixture is present in an amount between about 5% to 90% by weight of the mixture.
 7. The composition of any one of Claims 1, 2, 3, or 4 wherein starch polymer is an unmodified, oxidized or thin boiling starch of 0 to 95 degree fluidity.
 8. The composition of any one of Claims 1, 2, 3, or 4 wherein the starch polymer has moisture content of about 0.5% to 15% by weight.
 9. The composition of any one of Claims 1, 2, 3, or 4 wherein said starch polymer is in a pulverized form.
 10. The composition of any one of Claims 2, 3, or 4 wherein the plasticizer is a polyhydric alcohol.
 11. The composition of any one of Claims 2, 3, or 4 wherein the plasticizer is present in an amount between about 10 to 50 wt% of the mixture.
 12. The composition of any one of Claims 1, 2, 3, or 4 wherein the chemical modifier is the dibasic organic acid.

13. The composition of any one of Claims 1, 2, 3, or 4 wherein the chemical modifier is the anhydride.
14. The composition of any one of Claims 1, 2, 3, or 4 wherein the chemical modifier is present in an amount between about 0.5% to about 10% by weight of the starch polymer.
15. The composition of Claim 4 wherein the nanoclay is selected from a group consisting of montmorillonite; smectite, hectorite and mixtures thereof.
16. The composition of Claim 4 wherein the nanoclay is present in an amount between about 0.5 to 25 wt% of the mixture.
17. The composition of Claim 3 wherein the free radical initiator is present and is 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane.
18. The composition of Claim 3 wherein the free radical initiator is present in the mixture in an amount between about 0.01 to 2.0 wt% of the mixture.
19. The composition of any one of Claims 1, 2, 3, or 4 wherein the mixture is processed in a twin-screw extruder at a temperature in the range of about 100°C to 200°C.

20. The composition of any one of Claims 1, 2, 3, or 4 wherein the acids or anhydrides are selected from the group consisting of maleic-, succinic-, itaconic-, phthalic- and mixtures thereof.
21. The composition of any one of Claims 1, 2, 3, or 4 wherein the chemical modifier is about 2% to 5% by weight of the starch polymer of the mixture.
22. A process for preparing a starch based composition which comprises reactively blending a mixture which comprises a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an anhydride of a dibasic organic acid and mixtures thereof, a plasticizer and, optionally a free radical initiator wherein the mixture is extruded with heating and venting of water from the mixture.
23. The process of Claim 22 wherein the starch polymer and modifier are mixed as powders.
24. The process of Claim 22 wherein the processing is at a temperature between about 130 and 180°C.
25. The composition of any one of Claims 2, 3, or 4 wherein the plasticizer is glycerol.
26. The composition of any one of Claims 2, 3, or 4 wherein the plasticizer is about 15 to 30% by weight of the composition.

27. The composition of any one of Claims 1, 2, 3, or 4 wherein the acid is maleic acid and the anhydride is maleic anhydride.

ABSTRACT OF THE DISCLOSURE

A chemically modified plasticized starch (CMPS) is prepared by reacting starch with an organic dibasic acid or an anhydride of the acid in the presence of a plasticizer using optional free radical initiators, and optionally with the incorporation of nano clays in the reactive extrusion process. The starch is thermoplastic and has a lower viscosity than the traditional thermoplastic starch. The CMPS is useful in preparing starch polymer compositions which are at least partially biodegradable.

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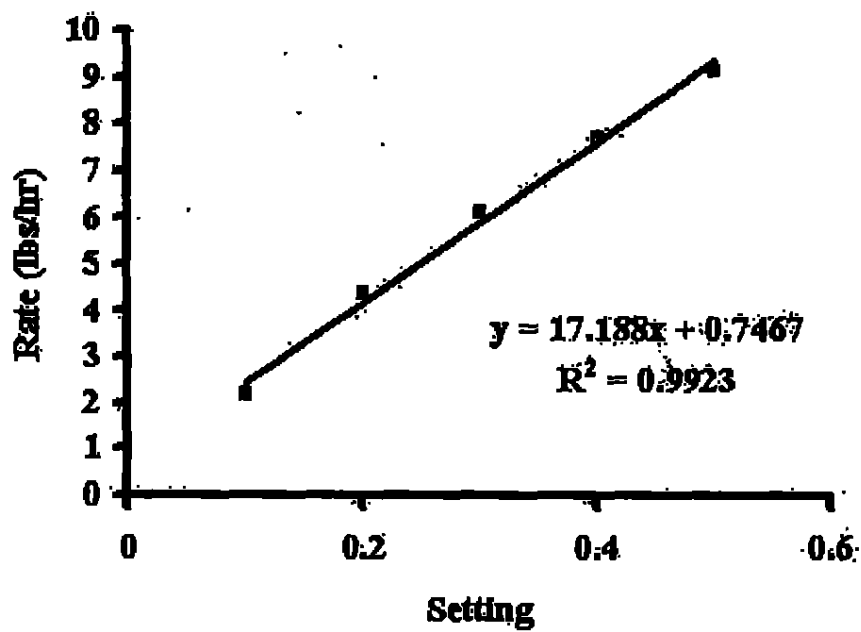


FIGURE 1

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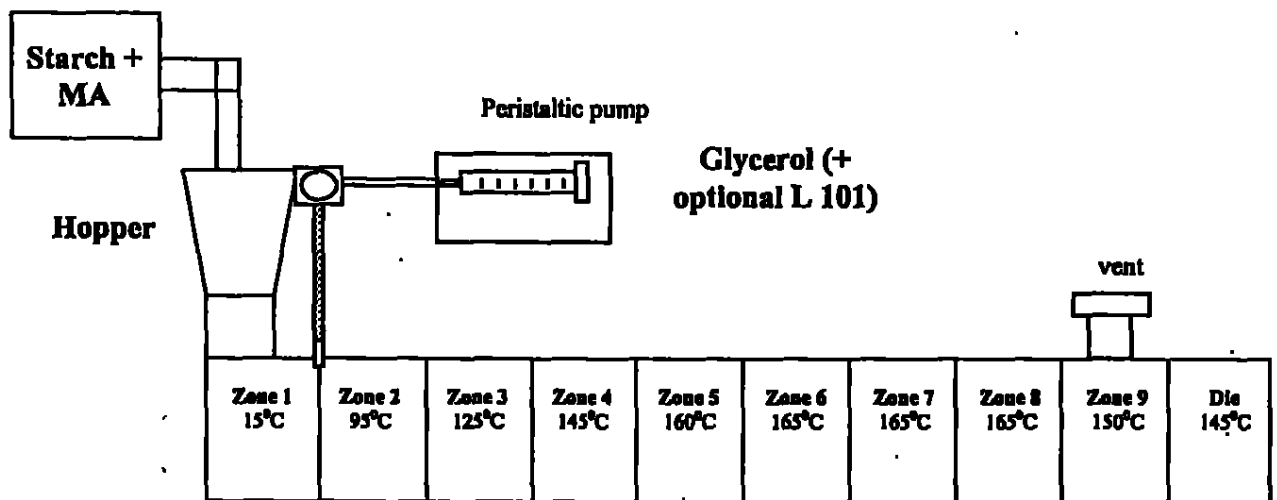
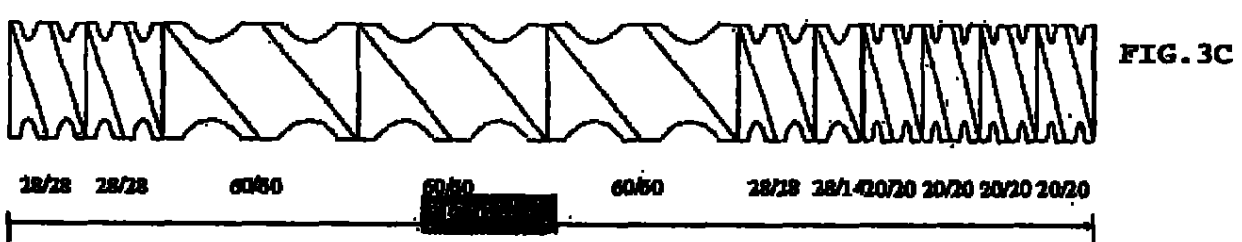
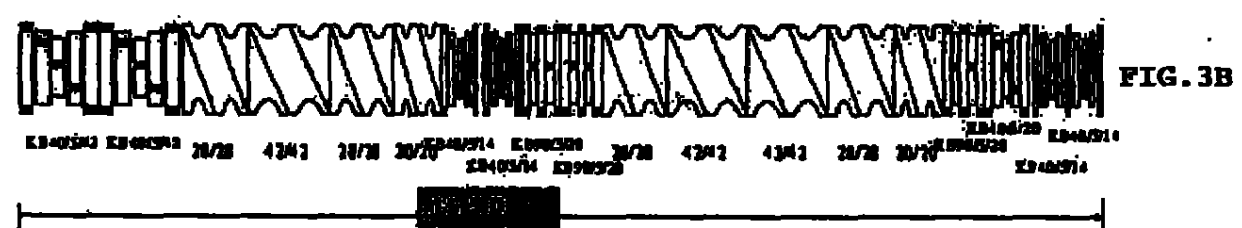
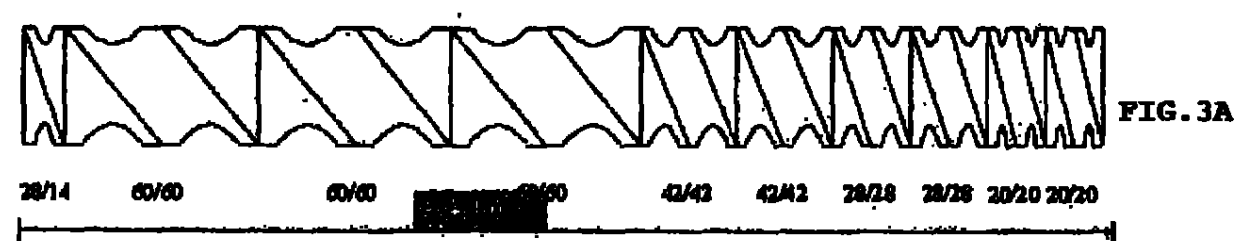


FIGURE 2

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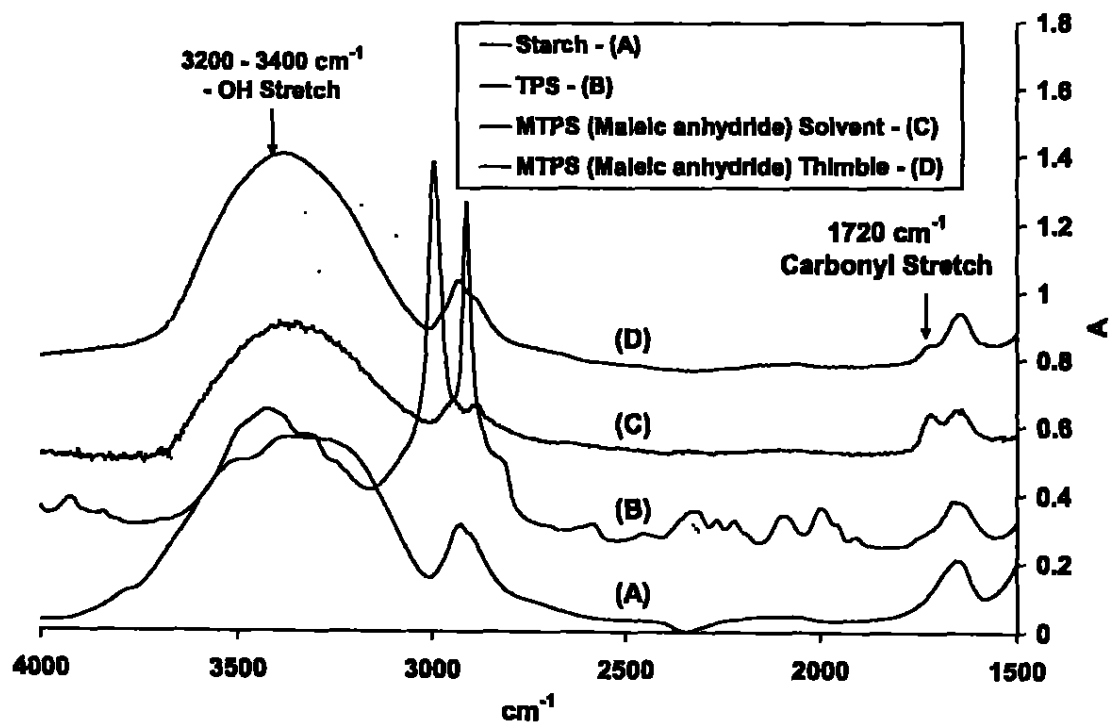


FIGURE - 4

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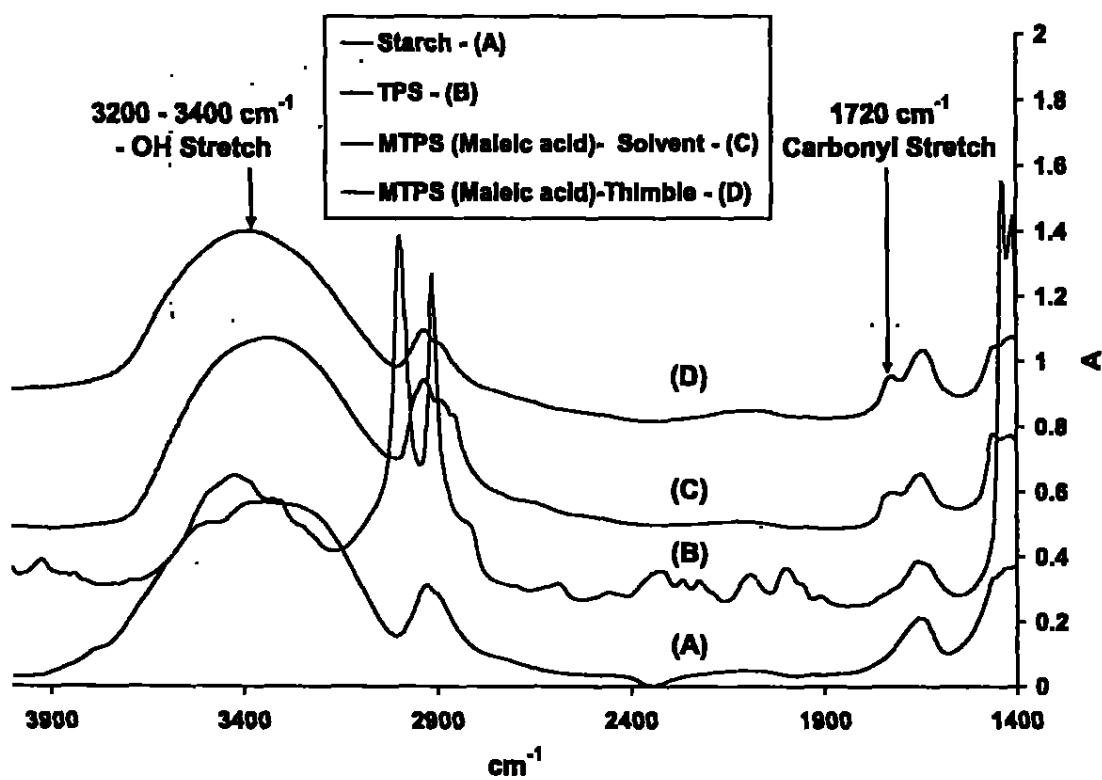


FIGURE 5

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT 12/124

To:
IAN C. MCLEOD
MCLEOD & MOYNE, P.C.
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OKEMOS, MICHIGAN 48864

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NOTIFICATION OF RECEIPT
OF DEMAND BY COMPETENT INTERNATIONAL
PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

Applicant's or agent's file reference MSU 4.2-724		Date of mailing (day/month/year) 27 Jul 2006	
International application No. PCT/US2005/041237		International filing date (day/month/year) 15 Nov 2005	
Applicant MICHIGAN STATE UNIVERSITY		Priority date (day/month/year) 19 Nov 2004	

1. The applicant is hereby notified that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

16 Jun 2006

2. That date of receipt is:

- ☒ the actual date of receipt of the demand by this Authority (Rule 61.1(b)).
- ☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).
- ☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☐ **ATTENTION:** That date of receipt is after the expiration of 19 months from the priority date. Consequently, in respect of some Offices, the demand does not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)) and the acts for entry into the national phase must therefore be performed within 20 months from the priority date (or later in some Offices). However, in respect of some other Offices, the time limit of 30 months (or later) may nevertheless apply. See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/ Mail Stop PCT, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-3201	Authorized officer Latrice Russell Telephone No. 703-308-9290 EX 117
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Form PCT/IPEA/402 (April 2002; reprint January 2004)

Practitioner's Docket No. MSU 4.2-724 PCT
IN THE UNITED STATES DESIGNATED OFFICE (DO/US)

72/125

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/US2005/041237	15 NOVEMBER 2005	19 NOVEMBER 2004

TITLE OF INVENTION

CHEMICALLY MODIFIED PLASTICIZED STARCH COMPOSITIONS BY EXTRUSION PROCESSING

APPLICANT(S)

MICHIGAN STATE UNIVERSITY et al

Mail Stop PGT
Commissioner for Patents
P.O. Box 1460
Alexandria, VA 22313-1460

CHAPTER II DEMAND and
FEE in the amount of \$773

NOTE (FACSIMILE): For Correspondence subsequent to filing in an international application before the U.S. Receiving Office, the U.S. International Searching Authority, or the U.S. International Examining Authority:

Papers in international applications: 571 273 3201 facsimile number

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See "Updated Lists of Exceptions to the Centralized Delivery and Facsimile Transmission Policy for Patent Related Correspondence," September 19, 2005; 1289 OG 98, October 18, 2005, Exceptions for Certain Facsimile Transmitted Correspondence, Item 1.

(Text continued on page 13-87)

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I hereby certify that this paper, along with any document referred to, is being deposited with the United States Postal Service on this date 16 JUNE 2006, in an envelope addressed to the Commissioner for Patents, P.O. Box 1460, Alexandria, VA 22313-1460 as "Express Mail Post Office to Addressee" Mailing Label No. EQ 496329043 US.

Tammi L. Taylor

(Type or print name of person mailing paper)

Tammi L. Taylor

Signature of person certifying

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

***WARNING:** Each paper or fee filed by "Express Mail" must have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b).

"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will not be granted on petition." Notice of Oct. 24, 1998, 60 Fed. Reg. 56,438, at 56,442.

(First Page of Letter—United States Designated Office (DO/US) [13-4])

127 126

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below.

IPEA/ US

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty.

The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty.

For International Preliminary Examining Authority use only		
Identification of IPEA		Date of receipt of DEMAND
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference MSU 4.2-724 PCT
International application No. PCT/US2005/041237	International filing date (day/month/year) 15 November 2005 (15.11.2005)	(Earliest) Priority date (day/month/year) 19 November 2004 (19.11.2004)
Title of invention CHEMICALLY MODIFIED PLASTICIZED STARCH COMPOSITIONS BY EXTRUSION PROCESSING		
Box No. II APPLICANT(S)		
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) MICHIGAN STATE UNIVERSITY 238 Administration Building East Lansing, Michigan 48824 United States of America		Telephone No. (517) 356-2188
		Facsimile No. (517) 432-3880
		Teleprinter No.
		Applicant's registration No. with the Office
State (that is, country) of nationality: US		State (that is, country) of residence: US
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) NARAYAN, Ramani 4275 Conifer Circle Okemos, Michigan 48864 United States of America		
State (that is, country) of nationality: US		State (that is, country) of residence: US
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) BALAKRISHNAN, Sunder 1636 Indian Way Okemos, Michigan 48864 United States of America		
State (that is, country) of nationality: IN		State (that is, country) of residence: US
☒ Further applicants are indicated on a continuation sheet.		

Continuation of Box No. II APPLICANT(S)

If none of the following sub-boxes is used, this sheet should not be included in the demand.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

NABAR, Yogaraj
1523 Spartan Village, Apt. J
East Lansing, Michigan 48823
United States of America

State (that is, country) of nationality:
INState (that is, country) of residence:
US

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

SHIN, Boo-Young
Kyoungsan 712-749
KOREA

State (that is, country) of nationality:
KRState (that is, country) of residence:
KR

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

DUBOIS, Philippe
Rue, Grande, 1
4280 Cliplet
BELGIUM

State (that is, country) of nationality:
BEState (that is, country) of residence:
BE

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

RAQUEZ, Jean-Marie
701 Cherry Lane, Apt. 104
East Lansing, Michigan 48823
United States of America

State (that is, country) of nationality:
BEState (that is, country) of residence:
US☐ Further applicants are indicated on another continuation sheet.

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is ☒ agent ☐ common representative
 and ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.
☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.
☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

McLEOD, Ian C.
 MOYNE, Mary M.
 McLEOD & MOYNE, P.C.
 2180 Commons Parkway
 Okemos, Michigan 48864
 United States of America

Telephone No.

(517) 347-4100

Facsimile No.

(517) 347-4103

Teleprinter No.

Agent's registration No. with the Office
 20,831

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION

Statement concerning amendments:*

1. The applicant wishes the international preliminary examination to start on the basis of:

- ☒ the international application as originally filed
 the description ☒ as originally filed
☐ as amended under Article 34
 the claims ☒ as originally filed
☐ as amended under Article 19 (together with any accompanying statement)
☐ as amended under Article 34
 the drawings ☒ as originally filed
☐ as amended under Article 34

2. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.3. ☐ Where the IPEA wishes to start the international preliminary examination at the same time as the international search in accordance with Rule 69.1(b), the applicant requests the IPEA to postpone the start of the international preliminary examination until the expiration of the applicable time limit under Rule 69.1(d).4. ☐ The applicant expressly wishes the international preliminary examination to start earlier than at the expiration of the applicable time limit under Rule 34bis.1(a).

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English

- ☒ which is the language in which the international application was filed
☐ which is the language of a translation furnished for the purposes of international search
☐ which is the language of publication of the international application
☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination

Box No. V ELECTION OF STATES

The filing of this demand constitutes the election of all Contracting States which are designated and are bound by Chapter II of the PCT.

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- | | | |
|--|---|--------|
| 1. translation of international application | : | sheets |
| 2. amendments under Article 34 | : | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | sheets |
| 5. letter | : | sheets |
| 6. other (specify) | : | sheets |

For International Preliminary Examining Authority use only

received	not received
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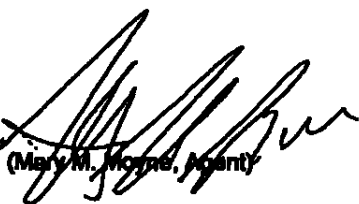
- | | |
|--------------------------|--------------------------|
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |

The demand is also accompanied by the item(s) marked below:

- | | |
|--|---|
| 1. ☒ fee calculation sheet | 5. ☐ statement explaining lack of signature |
| 2. ☐ original separate power of attorney | 6. ☐ sequence listing in electronic form |
| 3. ☐ original general power of attorney | 7. ☐ tables in electronic form related to a sequence listing |
| 4. ☐ copy of general power of attorney, reference number, if any: | 8. ☐ other (specify): |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).


(Mary M. Moyné, Agent)

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply.

☐ The applicant has been informed accordingly.

4. ☐ The date of receipt of the demand is WITHIN the time limit of 19 months from the priority date as extended by virtue of Rule 80.5.

5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

6. ☐ The date of receipt of the demand is AFTER the expiration of the time limit under Rule 54bis.1(a) and item 7 or 8, below, does not apply.

7. ☐ The date of receipt of the demand is WITHIN the time limit under Rule 54bis.1(a) as extended by virtue of Rule 80.5.

8. ☐ Although the date of receipt of the demand is after the expiration of the time limit under Rule 54bis.1(a), the delay in arrival is EXCUSED pursuant to Rule 82.

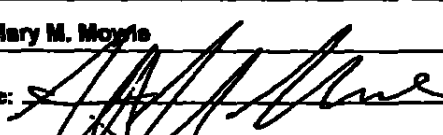
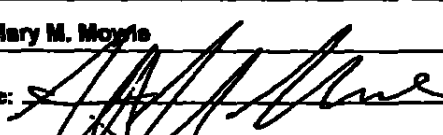
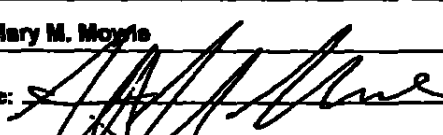
For International Bureau use only

Demand received from IPEA on:

PCT

FEE CALCULATION SHEET

Annex to the Demand

<table border="1" style="width: 100%; border-collapse: collapse;"><tr><td style="width: 50%;">International application No. PCT/US2005/041237</td><td style="width: 50%;"></td></tr><tr><td>Applicant's or agent's file reference MSU 4.2-724 PCT</td><td></td></tr></table>	International application No. PCT/US2005/041237		Applicant's or agent's file reference MSU 4.2-724 PCT		<table border="1" style="width: 100%; border-collapse: collapse;"><tr><td style="height: 40px; vertical-align: top;">For International Preliminary Examining Authority use only</td></tr><tr><td style="height: 40px; vertical-align: top;">Date stamp of the IPEA</td></tr></table>	For International Preliminary Examining Authority use only	Date stamp of the IPEA																		
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Applicant's or agent's file reference MSU 4.2-724 PCT																									
For International Preliminary Examining Authority use only																									
Date stamp of the IPEA																									
Applicant MICHIGAN STATE UNIVERSITY et al																									
CALCULATION OF PRESCRIBED FEES <table style="width: 100%;"><tr><td style="width: 50%;">1. Preliminary examination fee</td><td style="width: 10%; text-align: right;">800.00</td><td style="width: 10%; text-align: center;">P</td><td style="width: 30%;"></td></tr><tr><td colspan="4"> </td></tr><tr><td>2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>)</td><td style="text-align: right;">173.00</td><td style="text-align: center;">H</td><td></td></tr><tr><td colspan="4"> </td></tr><tr><td>3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box</td><td style="text-align: right;">773.00</td><td></td><td></td></tr><tr><td></td><td style="text-align: right;">TOTAL</td><td></td><td></td></tr></table>		1. Preliminary examination fee	800.00	P						2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>)	173.00	H						3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	773.00				TOTAL		
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	TOTAL																								
MODE OF PAYMENT <table style="width: 100%;"><tr><td>☒ authorization to charge deposit account with the IPEA (see below)</td><td>☐ cash</td></tr><tr><td>☒ cheque</td><td>☐ revenue stamps</td></tr><tr><td>☐ postal money order</td><td>☐ coupons</td></tr><tr><td>☐ bank draft</td><td>☐ other (specify):</td></tr></table>		☒ authorization to charge deposit account with the IPEA (see below)	☐ cash	☒ cheque	☐ revenue stamps	☐ postal money order	☐ coupons	☐ bank draft	☐ other (specify):																
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☐ postal money order	☐ coupons																								
☐ bank draft	☐ other (specify):																								
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT (This mode of payment may not be available at all IPEAs) <table style="width: 100%;"><tr><td style="width: 50%; vertical-align: top;">☐ Authorization to charge the total fees indicated above. ☒ (This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.</td><td style="width: 50%; vertical-align: top;">IPEA/ US Deposit Account No.: 13-0510 Date: 16 JUNE 2006 Name: Mary M. Moyle Signature: </td></tr></table>		☐ Authorization to charge the total fees indicated above. ☒ (This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.	IPEA/ US Deposit Account No.: 13-0510 Date: 16 JUNE 2006 Name: Mary M. Moyle Signature: 																						
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Brigard & Castro
BOGOTA - COLOMBIA

AP: 101100
128 131

PODER

POWER OF ATTORNEY

Yo (nosotros) MICHIGAN STATE UNIVERSITY

I (We) MICHIGAN STATE UNIVERSITY

domiciliado(s) en 238 Administration Building, East Lansing, Michigan 48824, Estados Unidos de América

domiciled in 238 Administration Building, East Lansing, Michigan 48824, United States of America

Nombro(amos) a: JUAN PABLO CADENA SARMIENTO y/o CARLOS H. PALACIO EASTMAN y/o MARTIN E. TORRES CARDOZO, de Bogotá, Colombia, apoderados verdaderos y legales con poder especial, amplio y suficiente, para recabar de las oficinas y autoridades colombianas administrativas, judiciales y de policía, en cualquier instancia o recurso, la obtención de patentes de invención, registros de marcas, diseños industriales, modelos de utilidad, depósitos de nombres comerciales, lemas comerciales y enseñanzas, registros de derechos de autor y contratos sobre los mismos, obtención de certificados de obtentor de variedades vegetales, así como sus prórrogas, renovaciones, anotaciones de traspaso, cambios de nombre y/o domicilio; elaborar, tramitar y registrar contratos de licencia y licencias de cualesquiera clases; intervenir como demandante o como demandado en cualquier instancia y recurso ante cualquier juez, corporación, funcionario público o autoridad en acciones judiciales, administrativas y de policía tales como: oposiciones al registro de marcas; acciones de caducidad, cancelación y nulidad; acciones reivindicatorias, acciones derivadas de la obtención o explotación de licencias; acciones de competencia desleal; demandas penales; acciones de indemnización de perjuicios, reclamos y observaciones a solicitudes de patentes, diseños industriales, modelos de utilidad, en el ejercicio de medidas cautelares y en otras acciones o medidas similares.

Hereby appoints JUAN PABLO CADENA SARMIENTO and/or CARLOS H. PALACIO EASTMAN and/or MARTIN E. TORRES CARDOZO, of Bogotá, Colombia, my (our) true and lawful attorneys with special, ample and sufficient power to obtain from the Colombian administrative, judicial and police offices and authorities, in any instance, privileges of patents of invention, registration of trademarks, industrial designs and utility models; registration of commercial names, slogans and emblems, registration of copyright and contracts related thereto, certificates of obtainers of vegetables varieties, as well as extensions, renewals and recordal of assignments and changes of name and domicile related to the above; to prepare, prosecute and register licenses of any kind; to act as plaintiff or defendant in any instance or recourse, and before any judge, corporation, public official or authority in judicial, administrative and police actions, such as: oppositions to the registration of trademarks; caducity, cancellation and nullity actions; claim actions derived from the obtaining or exploitation of licenses, action of unfair competition; criminal proceedings, actions for payment of damages: claims or observations on patent applications, models, industrial designs and utility models; in the exercise of preventive measures and in other actions or similar proceedings.

A este efecto, lo(s) faculto(amos) para elevar solicitudes, formular descripciones, enmiendas, protestas, declaraciones, oposiciones, cancelaciones, nulidades, apelaciones y reclamos; pagar impuestos, cuotas y gravámenes prescritos por la ley; renunciar o desistir a derechos concedidos o en curso de concesión; recibir toda clase de documentos y valores, dando el descargo respectivo, y, en general, para dar ante dichas autoridades todos los pasos necesarios al efecto indicado y tomar todas las medidas que creyeran conducentes al resguardo de mis (nuestros intereses), con todas las demás facultades legales necesarias.

To that effect they hereby empowered to file applications, formulate descriptions, amendments, protests, declarations, oppositions, cancellations, nullities, appeals and claims; to pay taxes, quotas and assessments prescribed by law, renounce or waive the rights granted or in the process of granting; to receive all kinds of documents and valuables, giving the respective release of receipt, and, in general, to take before said authorities the necessary steps to such effect, and any measures that they may deem pertinent to the safeguard of my (our) interest(s) with all the other necessary legal powers.

Este poder comprende la facultad de ratificar o confirmar en mi (nuestro) nombre lo actuado así como la facultad de desistir, transigir, comprometer, y la de sustituirlo en todo o en parte y revocar sustituciones. Asimismo nombro(amos) a: JUAN PABLO CADENA SARMIENTO y/o CARLOS H. PALACIO EASTMAN y/o MARTIN E. TORRES CARDOZO, domiciliado(s) en la Carrera 7 No. 16-56 Piso 9, mis (nuestros) apoderados en Colombia, con facultades para recibir notificaciones y designar apoderados judiciales o extrajudiciales.

This power includes the faculty to ratify or confirm desist, settle and compromise on my (our) behalf, and to substitute this power in whole or in part and to revoke substitutions. At the same time I (We) hereby appoint JUAN PABLO CADENA SARMIENTO and/or CARLOS H. PALACIO EASTMAN and/or MARTIN E. TORRES CARDOZO, domiciled in Carrera 7 No. 16-56, Piso 9, my (our) attorney(s) in fact, with powers to receive notifications and to designate judicial and extrajudicial attorneys.

Otorgado y firmado en

hoy de de 200_

Firma

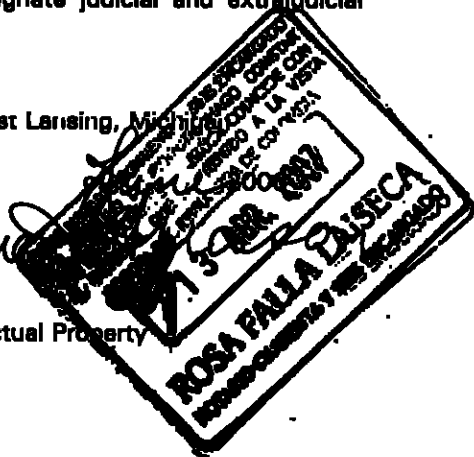
Nombre
Cargo

Granted and signed in East Lansing, Michigan

this 21st day

Signature

Name Loraine J. Hudson
Title Director of Intellectual Property



State of Michigan

12
132



DEPARTMENT OF STATE

AROSTILLE

(Convention de La Haye du 5 Octobre 1961)

1. Country: **UNITED STATES OF AMERICA**

This public document

2. has been signed by: **Doris J. Blanken**

3. acting in the capacity of: **Michigan Notary Public**

4. bears the seal of: **Doris J. Blanken
Eaton County, Michigan**

CERTIFIED

5. at Lansing, Michigan

6. the 6th of July, 2006

7. by Secretary of State, State of Michigan

8. NO. 20588W-06

9. Seal/Stamp:

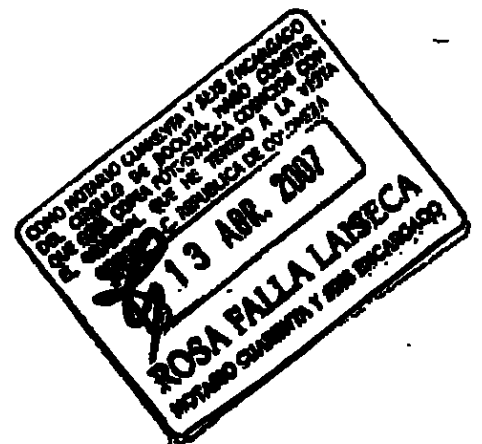
10. Signature:



Terri Lynn Land

Terri Lynn Land

This certification attests only to the authenticity of the signature of the official who signed the official document, the capacity in which that official acted, and where appropriate, the identity of the seal or stamp which the document bears. This certification is not intended to imply that the contents of the document are correct, nor that they have the approval of the State of Michigan.



CERTIFICADO NOTARIAL (SOCIEDAD)

Hoy de
personalmente compareció ante mí

a quien conozco, y de quien me consta que firmó el anterior documento, debidamente juramentado declaró y dijo que él (ella) es

de MICHIGAN STATE UNIVERSITY

Sociedad legalmente constituida para un período de duración que aún no ha terminado; que el declarante está autorizado por dicha compañía para conferir este poder; que el sello estampado por él al pie de tal poder, en nombre y representación de la expresada compañía, es el sello oficial de ella; y que el objeto para el cual se confiere este instrumento está comprendido dentro del objeto social de la sociedad.

El suscrito Notario hace constar que tuvo a la vista las pruebas de la existencia de la sociedad.

Estado de
con fecha

y que quien confiere el presente poder es su representante.

Notario Público (sello)

**CERTIFICADO NOTARIAL
PERSONA NATURAL**

Hoy de de , compareció(eron)
ante mí

a quien (es) conozco y me consta que es(aon) la(s) persona(s) firmante(s) del documento que precede y quien(es) declara(n) que otorgan el mismo para los fines y propósitos que en él se expresan.

Notario Público (sello)

LEGALIZACION POR APOSTILLA ES REQUERIDA.

NOTARIAL CERTIFICATE (CORPORATION)

On this 21 day of June, 2006 of
personally appeared before me

LORAIN J. HUDSON

to me known, and known to me to be the person who signed the foregoing instrument who being by me duly sworn did depose and say that he (she) is the

DIRECTOR OF INTELLECTUAL PROPERTY

of MICHIGAN STATE UNIVERSITY

Which is legally constituted for a term not yet expired, that deponent is authorized by said Company to confer this Power of Attorney: that the seal affixed hereunto by the deponent in the name and on behalf of said Corporation is the corporate seal thereof; and that the purpose for which this instrument is granted is included within the corporate purpose of company.

The undersigned Notary Public attests that he has seen the documents that prove the existence of the company.

State of
under date of

and that he (she) who grants the present power of attorney is its Representative.

Public Notary (Seal)

**NOTARIAL CERTIFICATE
NATURAL PERSON**

On this 21st day of June of 2006
personally appeared before me

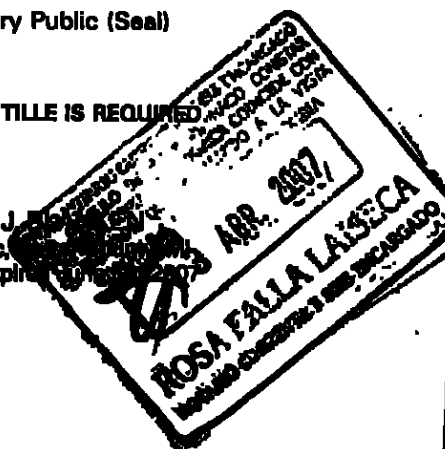
who is(are) known to me and who I attest executed the foregoing document and he (they) declared he (they) grant(a) the document for the uses and purposes therein expressed. -

Doris J. Blanton

Notary Public (Seal)

LEGALIZATION BY APOSTILLE IS REQUIRED

DORIS J. BLANTON
Notary Public
My Comm. Expires



19/134

TRADUCCION AL ESPAÑOL del Documento de Poder otorgado por
MICHIGAN STATE UNIVERSITY domiciliada en 238 Administration
Building, East Lansing, Michigan 48824, Estados Unidos de América..

ESTADO DE MICHIGAN

DEPARTAMENTO DE ESTADO

APOSTILLA

(Convención de La Haya del 5 de octubre de 1961)

1. País: ESTADOS UNIDOS DE AMÉRICA

Este documento público

- | | | |
|----|--------------------------|--|
| 2. | ha sido firmado por | Doris J. Blanken |
| 3. | actuando en capacidad de | Notario público de Michigan |
| 4. | lleva el sello de | Doris J. Blanken
Condado de Eaton, Michigan |

CERTIFICADO

- | | | | |
|----|---|-----|-----------------------|
| 5. | en Lansing, Michigan | 6. | el 6 de julio de 2006 |
| 7. | por el Secretario de Estado, Estado de Michigan | | |
| 8. | NO. 20588W-06 | | |
| 9. | Sello/timbre | 10. | Firma: |
| | | | (Firma) |
| | | | Terri Lynn Land |

La certificación da testimonio de la autenticidad de la firma del funcionario que firmó el documento anexo, la capacidad en la cual actuó ese funcionario, y donde sea apropiado, la identidad del sello o timbre que lleva el documento. Esta certificación no tiene intención de implicar que los contenidos del documento son correctos, ni que tienen la aprobación del Estado de Michigan





No. 07-045888-00000-0000

Fecha 2007-05-08 15:58:42 Dep. 2020 NUECREACION
Tra. 11 PATENTE IYII Eve: 379 FASENACIONAL II
Act 411 PRESENTACION Folios 131

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A

REQUISITOS MINIMOS PARA ADMISION A TRAMITE PCT

PATENTE DE INVENCION

[]

MODELO DE UTILIDAD

[]

- ◆ Indicación de que se solicita la concesión de una patente []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Descripción de la invención []
- ◆ Dibujos de ser estos pertinentes []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

DISEÑO INDUSTRIAL []

- ◆ Indicación de que se solicita el registro de Diseño Industrial []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Representación gráfica y fotográfica del Diseño Industrial o muestra del material que incorpora el diseño []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

ESQUEMA DE TRAZADO []

- ◆ Indicación de que se solicita el registro de un Esquema de Trazado []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Representación gráfica del esquema trazado []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

Edgar Novales

Firma Responsable

Fecha 08-05-02

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REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
CADENA SARMIENTO JUAN PABLO
Apoderado(a) y/o Representante de
MICHIGAN STATE UNIVERSITY

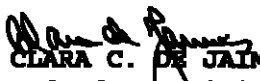
REFERENCIA	Radicación No.	07 45686
	Solicitud internacional	PCT/US2005/041237
	Fecha inicio fase nacional	19/06/2007
	Trámite	11
	Evento	379
	Actuación	430
	Oficio No.	07953

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

1. La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante. (Art. 26-k) Decisión 486. Cuando se trate de documentos otorgados en el extranjero, deben legalizarse de conformidad con lo dispuesto por los artículos 259 y 260 del Código de Procedimiento Civil.

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Unica No.10 de 2001.


CLARA C. DE JAIMES
Jefe de la División de Nuevas Creaciones (E)

El anterior requerimiento fue notificado por fijación en lista de
fecha 6 JUL 2007
adpa11