

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



DELEGATURA PROPIEDAD INDUSTRIAL

División de Nuevas Creaciones

SOLICITUD

PATENTE DE INVENCION

ENTRADA EN FASE NACIONAL

21. EXPEDIENTE No.

06-68308

54. TITULO

COPOLIMEROS DE INJERTO DE POLIESTER-ALMIDON, BIODEGRADABLES, Y

METODO DE PREPARACION DE LOS MISMOS

51. CLASIFICACION INTERNACIONAL

71. SOLICITANTE

MICHIGAN STATE UNIVERSITY

DOMICILIO

EAST LANSING, MI 48824, ESTADOS UNIDOS DE AMERICA

74. APODERADO

JUAN PABLO CADENA SARMIENTO

22. SANTAFE DE BOGOTA, D.C.

PETITORIO

AS: 101.337



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Fec 2006-07-13 17:41:45 Dep. 2020 NUECREACIONES on
Tra 11 PATENTEIYII
Cve. 378 FASENACIONALI
Act 411 PRESENTACION Folios 142

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)

Nombre. MICHIGAN STATE UNIVERSITY

Dirección 238 Administration Building, East
Lansing, MI 48824, Estados Unidos de América

Lugar de Constitución. Estados Unidos

Teléfono.

Fax:

E-mail:

IDENTIFICACION

C.C. ☐

NIT ☐

C.E. ☐

Otro ☐

Cual _____

Número _____

3

REPRESENTANTE
O APODERADO

Nombre: JUAN PABLO CADENA SARMIENTO

Dirección. Cra 7 No. 16-56 Piso 9

Teléfono: 380-2200

Fax: 380-2700

E-mail:

IDENTIFICACION

C.C. ☒

NIT ☐

C.E. ☐

Otro ☐

Cual _____

Número 80.410.337 TP 57492

4

INVENTOR (ES)
(72)

Nombre: Ramani NARAYAN, Sunder BALAKRISHNAN, Yogaraj NABAR, Jean-Mane RAQUEZ,
Philippe DUBOIS

Dirección: 4275 Conifer Circle, Okemos, MI 48864, US ; 1636 Indian Way, Okemos, MI
48864, US, 1523 Spartan Village, Apt J, East Lansing, MI 48823, US , 701 Cherry Lane, Apt.
104, East Lansing, MI 48823, US, Rue Grande, 1, B-4260 Ciptet, Bélgica (Respectivamente)

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

5 PCT (86)

Solicitud Internacional No. PCT/US2005/041238 Fecha 15-11-2005

Publicación Internacional No WO 2006/055505 A2 Fecha 26-05-2006

Título (54): COPOLÍMEROS DE INJERTO DE POLIÉSTER-ALMIDÓN, BIODEGRADABLES, Y
MÉTODO DE PREPARACIÓN DE LOS MISMOS

7 Clasificación Internacional (51) _____

8 Prioridad

SI ☒

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(33) País de Origen

US

(32) Fecha

19-11-2004

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10/993,186

9 Comprobante de pago No. 06-40,599

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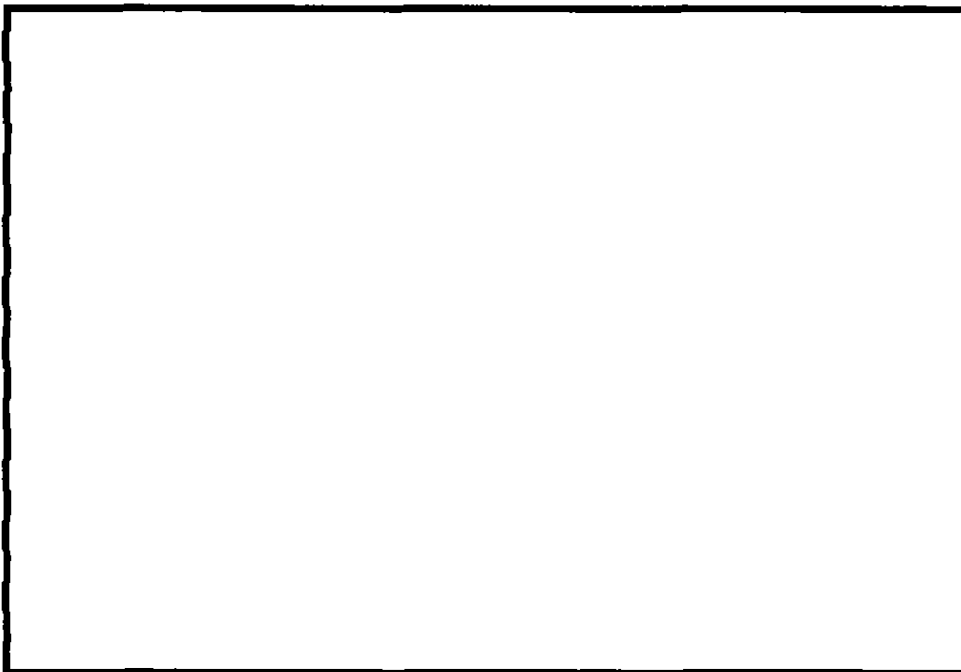
Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página.

10

ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud. \$463'.000
- ☐ Documento que acredite la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☐ Poderes, si fuere el caso
- ☐ 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

11 FIGURA CARACTERÍSTICA:



12 Solicito la concesión de la patente

NOMBRE JUAN PABLO CADENA SARMIENTO

FIRMA

C C 80 410 337 de Usaquén, T.P. 57492 del C.S.U.

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

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 06 - 40,599
FECHA : MAYO 30 DE 2006

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
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Fec 2006-07-13 17 41 45 Dep. 2020 NUECREACIONES
Tra 11 PATENTEIYII
Cve. 378 FASCNACIONALI
Act. 411 PRESENTACION Folios 142

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	050-00110-6	55098364	30/05/2006	20,660,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		1 TRAMITES DE SOL. DE PATENTE DE IN	463,000.00
		TOTAL :	\$ 463,000.00

SON: CUATROCIENTOS SESENTA Y TRES MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES

PATENTE ☒ PCT/US2005/041238 MODELO DE UTILIDAD ☐ DISEÑO INDUSTRIAL ☐

SOLICITANTE/S RAZON SOCIAL O APELLIDOS Y NOMBRES MICHIGAN STATE UNIVERSITY

DOMICILIO EAST LANSING, MI 48824, ESTADOS UNIDOS DE AMERICA

APODERADO JUAN PABLO CADENA SARMIENTO

TITULO COPOLIMEROS DE INJERTO DE POLIESTER-ALMIDON, BIODEGRADABLES, Y METODO DE PRE-
PARACION DE los... -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 BALAKRISHNAN, YOGARAJ NABAR, JEAN-MARIE RAQUEZ,

OTROS PHILIPPE DUBOIS

OFICINA DE COMUNICACIONES

(19) World Intellectual Property Organization
International Bureau



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 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2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 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2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 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**STARCH-POLYESTER BIODEGRADABLE GRAFT
COPOLYMERS AND A METHOD OF PREPARATION THEREOF**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] None

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable.

STATEMENT REGARDING GOVERNMENT RIGHTS

[0003] None

BACKGROUND OF THE INVENTION

(1) Field of the Invention

[0004] The present invention relates to starch-polyester graft copolymers. The present invention particularly relates to a chemically modified starch-polyester graft copolymer and a chemically modified starch-nano clay polyester graft copolymer. A process of making these graft copolymers using reactive processing such as reactive extrusion is disclosed. The starch-polyester graft copolymers have improved processability, surface properties, and an extended range of mechanical properties.

(2) Description of Related Art

[0005] Plastic packaging is subjected to pressure from existing and proposed environmental and disposal regulations, and market based sustainability initiatives. It presents a major disposal problem for companies and municipalities as it is lightweight and bulky and so does not lend itself to a

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viaable economic and environmentally responsible recycling operation due to expensive handling and transportation costs. It is not biodegradable, which makes disposal in soil or composting operations untenable. Further, issues such as sustainability, industrial ecology, biodegradability, and recyclability are becoming major considerations in a company's product packaging design, especially with single use disposable packaging. Natural biopolymers provide biodegradable, sustainable solutions for the manufacture of short-life, single use disposable packaging, consumer goods, and marine plastics. Starch, an anhydroglucose polymer, offers a structural platform to manufacture sustainable, biodegradable packaging. Examples of patents that disclose the manufacture of starch and blends of starch and other polymers include U.S. Patent 4,673,438 to Wittwer et al.; U.S. Patent 4,095,054 to Lay et al.; U.S. Patent 5,256,711 to Tokiwa et al.; U.S. Patent 5,275,774 to Bahr et al.; U.S. Patent 5,382,611 to Stepto et al. and U.S. Patent 5,405,564 to Stepto et al. Lately, there have been business reports of the use of thermoplastic starch (TPS) as a component in multi phase blends (W. Wiedmann, and E. Strobel, Starch, 43, 138 (1991); R.L. Shorgen, G.F. Fanta, and W.M. Doan, Starch, 45, 276 (1993); P. Forssell, J. Mikkila, and T. Sourtti, J.M.S. Pure Appl. Chem., A33, 703 (1996); R. Narayan, Polymers from Agricultural Co products, ACS Symp Ser. (1994); and J.J.G. Van Soest, K. Benes, and D.de. Wit, Polymer, 37, 3543 (1996). Still others have manufactured thermoplastic starch blends in which native starch is initially blended with a small quantity of water and a less volatile plasticizer such as glycerin in order to form starch melts that are subjected to a degassing procedure prior to cooling and solidification in

order to remove substantially all of the water therefrom. Examples of such patents include U.S. Patents 5,412,005, 5,280,055, 5,288,765, 5,262,458, 5,462,980 and 5,512,378 to Bastioli et al.

[0006] Starch granules exhibit hydrophilic properties and strong inter-molecular association via hydrogen bonding due to the hydroxyl groups on the granule surface. The hydrophilicity and thermal sensitivity render the starch polymer unsuitable for thermoplastic applications. In this respect, some authors have emphasized on finding the optimal polymer or mixture of polymers and other admixtures in order to thereby "optimize" the properties of the starch. One drawback is that most of the polymers and other admixtures are themselves significantly more expensive than starch, which tends to increase the cost of such polymer blends compared to starch melts. Another drawback is that such additives will only be able to marginally alter the mechanical properties of the starch/polymer blends when viewed from a materials science perspective.

[0007] In order to improve on these drawbacks, graft copolymerization of vinyl monomer on the starch backbone was used to modify starch. Fanta and Bagley have reviewed the synthesis and discussed some applications of starch graft copolymers (G.F. Fanta and E.B. Bagley, Encyclopedia of Polymer Science, John Wiley & Sons: New York (1970); and G.F. Fanta, Block and Graft Copolymers- Vol I, John Wiley & Sons: New York (1973). Otey et al. (F.H. Otey, R.P. Westhoff and W.M. Doane, Industrial Engineering Chemistry Products Research Development, 19, 592 (1980); F.H. Otey and R.P. Westhoff, Industrial Engineering Chemistry Products Research Development, 23, 284 (1984); and F.H. Otey, R.P. Westhoff and W.M. Doane, Industrial

Engineering Chemistry Products Research Development, 26, 1659 (1987)) blended starch with poly (ethylene-co-acrylic acid) (EAA). In these papers, the authors suggested the formation of hydrogen bonds between the carboxylic group in EAA and the hydroxyl group in starch. Increasing the level of starch decreased the percentage elongation of the film and increased the diffusion rate of water. Similar complexes like EAA can also be formed with the hydroxyl groups of the polyethylene-vinyl alcohol (EVOH) copolymer. They report a reaction between the anhydride group in the synthetic polymer with the -OH groups of starch. U.S. Patent 5,462,983 to Bloembergen et al. reports on blends and alloys containing lignocelluloses like starch, cellulose acetate etc. U.S. Patent 5,314,934 to Tomka et al. provides a process to produce a polyolefin-starch polymer blend. Ethylene/acrylate/maleic anhydride terpolymer was used as a compatibilizer. These blends were reported to be blown into film with properties comparable to LDPE. U.S. Patent 5,234,977 to Bastioli et al. discloses a material used for the production of biodegradable articles in film, sheet or fiber form, which can be produced by extrusion from a molten mass that includes a synthetic thermoplastic polymer and a destructured starch to which a boron containing compound such as boric acid has been added. U.S. Patent 6,277,899 to Bastioli et al. discloses a polymeric composition comprising filler melt-dispersed in a matrix comprising, a destructured starch component, a synthetic thermoplastic polymeric component and a fluidizing agent. U.S. Patent 5,412,005 to Bastioli et al. discloses biodegradable polymeric compositions containing a starch based component and a polymeric component, preferably polymers of ethylene-vinyl alcohol or polyvinylalcohol.

[0008] U.S. Patent Nos. 6,235,816 and 6,472,497 describe starch polyester blends.

[0009] Other references are:

(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

[0010] It is therefore an object of the present invention to provide novel grafted starch polyester compositions which have

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novel properties. It is further an object of this invention to provide economical and reproducible compositions. These and other objects will become increasingly apparent from the following description.

SUMMARY OF THE INVENTION

[0011] The present invention relates to a starch-polyester graft copolymer composition comprising starch or chemically modified starch with segments of a polyester grafted onto the starch. Preferably the chemically modified starch is a starch which is thermoplastic. Preferably the composition comprises about 0.5 to 10% by weight of the composition of a plasticizer. Preferably the composition contains natural or an organically modified nanoclay. Preferably the starch is selected from the group consisting of corn, potato, wheat, rice, sago, tapioca, waxy maize, sorghum and high amylose starch. Preferably the chemically modified plasticized starch (CMPS) is prepared from a reactively extruded 50% to 80% by weight of the starch, a chemical modifier from 0.5% to about 10% by weight of the starch, a plasticizer from 10 to 50 wt-% of the composition, and optionally a free radical initiator in an amount ranging between 0.01 to 2.0 wt % of the composition. Preferably the chemically modified plasticized starch (CMPS) is prepared from a blend comprising starch polymer, from 50% to 80% by weight, a chemical modifier from 0.5% to about 10% by weight of the starch polymer, more preferably from 2% to 5% by weight of the starch, a plasticizer from 10 to 50 wt-% of the composition, a nanoclay, wherein the nanoclays are added in an amount ranging from 0.5 to 25 wt% of the total composition. Preferably the plasticizer is selected from the group consisting of polyhydric

alcohols like glycerol, sorbitol, and ethylene glycol. Preferably the modifier is selected from the group consisting of dibasic acids or their anhydrides. Preferably the composition contains a free radical initiator. Preferably the free radical initiator is a peroxide. Preferably the composition contains a nanoclay selected from a group consisting of montmorillonite, smectite, hectorite, and mixtures thereof. Preferably the composition is completely biodegradable. Preferably the composition has been grafted in a melt phase in an extruder. Preferably the composition has been grafted in a twin screw extruder at a temperature in the range of 100°C-200°C.

[0012] The present invention also relates to a process for the preparation of a starch polyester graft co-polymer composition which comprises blending a mixture of an organic acid or anhydride of the acid with starch or a chemically modified starch and a polyester polymer at a temperature which grafts the segments of a polyester onto the starch to form the composition.

[0013] Most preferably the present invention relates to a starch based copolymer 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 organic anhydride of a dibasic organic acid and mixtures thereof, a plasticizer, a biodegradable polyester resin, a nanoclay, and optionally a free radical initiator, wherein the mixture has been extruded, with heating and venting of water from the mixture.

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[0014] Most preferably the present invention also relates to a process for preparing a starch based composition which comprises reactively extruding a mixture 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 organic anhydride of a dibasic organic acid and mixtures thereof, a plasticizer, a biodegradable polyester resin, a nanoclay, and optionally a free radical initiator, wherein the mixture has been extruded, with heating and venting of water from the mixture.

[0015] In the present invention the mechanism of reaction is that the fragments of a polyester resin from the processing react with hydroxyl groups of the starch. The acid or anhydride reacts with the polyester polymer to produce the reactive fragments. Thus the present invention provides a unique composition with the fragments of the polyester polymer bonded to the starch.

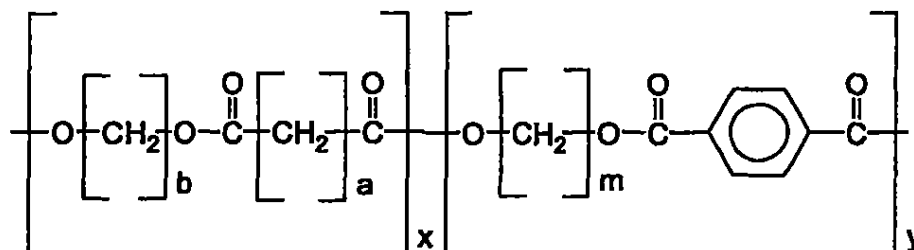
[0016] The present invention particularly provides new amphiphilic, starch-polyester graft copolymer and chemically modified starch-polyester graft copolymer compositions comprising a chemically modified starch or chemically modified starch-nanoclay product produced continuously in a twin-screw co-rotating extruder. The chemically modified plasticized starch product with lower viscosity and good processability and the chemically modified plasticized starch-nano clay product is described in the copending patent application. The starch-polyester graft copolymers of the present invention can be readily blown, extrusion cast into film, and molded. Examples of biodegradable polyesters include poly(caprolactone) (PCL),

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poly(vinylacetate-co-vinylalcohol) (PVAc/VA), poly(lactic acid) or polylactide (PLA), poly(glycolic acid) or polyglycolide (PGA), and related copolyesters including the various combinations of stereoisomers, bacterial and synthetic poly(.beta.-hydroxybutyrate) (PHB), Poly(.beta.-hydroxybutyrate-co-.beta.-hydroxyvalerate) (PHB/V), and other poly(.beta.-hydroxyalkanoates) (PHA), biodegradable aliphatic polyesters, and aliphatic-aromatic copolyesters. Preferably the polyester is selected from the group consisting of the composition in which the polyester is selected from the group consisting of:



where R is lower alkyl and aromatic groups containing 1 to 12 carbon atoms; n is 0 to 10; and x is 200 to 2000; and



, where a, b and m are 2 to 8; and x/y is between 3/2 and 10/1.

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[0017] The present invention provides new polymeric materials, which are environmentally responsible and fully biodegradable as per ASTM standards.

[0018] In accordance with the present invention, there is provided a biodegradable moldable product or film prepared from a graft copolymer containing starch or chemically modified starch or chemically modified starch-nano clay composition and a polyester, which is preferably biodegradable. It has been found that new starch-polyester graft copolymers with good elongation, compressibility and surface properties.

[0019] In one embodiment of this invention, starch is extruded with aliphatic-aromatic co-polyester and particularly poly butylenes (adipate-co-terephthalate) in the presence of maleic acid as a trans-esterification catalyst to form starch-polyester graft copolymers compositions with good elongation, compressibility and surface properties. In another embodiment chemically modified starch or a chemically modified starch-nano clay product has been reacted with aliphatic and aliphatic-aromatic copolyesters to provide new graft copolymer products with enhanced properties and processability.

BRIEF DESCRIPTION OF THE FIGURES

[0020] Figure 1 is a diagram of an extrusion apparatus for the production of polyester grafted starch.

[0021] Figures 2A, 2B and 2C are drawings depicting the screw configuration used for the reactive extrusion production of the novel graft copolymers. The screw configuration is divided into three sections (Figure 2A) followed by (Figure 2B)

and further followed by (Figure 2C).

[0022] Figure 3 is a graph showing the FTIR results of graft copolymers of ECOFLEX™, (poly (butylene adipate-co-terephthalate)), obtained from BASF (Germany), with plasticized starch (PS). To validate the reactivity, FTIR scans of pure ECOFLEX™, PS and ECOFLEX™/PS blend (without the catalyst) are also shown.

[0023] Figure 4 is a graph showing the FTIR results of graft copolymers of ECOFLEX™ with CMPS (made using both maleic anhydride and maleic acid modifiers). To validate the reactivity, FTIR scans of pure ECOFLEX™ and regular cornstarch are also shown.

[0024] Figure 5 shows bar graphs depicting tensile strength values of ECOFLEX™, graft copolymer of ECOFLEX™ with CMPS, graft copolymer of cross-linked ECOFLEX™ with CMPS, graft copolymer of ECOFLEX™ with PS and LDPE.

[0025] Figure 6 shows bar graphs depicting modulus of elasticity values of ECOFLEX™, graft copolymer of ECOFLEX™ with CMPS, graft copolymer of cross-linked ECOFLEX™ with CMPS, graft copolymer of ECOFLEX™ with PS and LDPE.

[0026] Figure 7 shows bar graphs depicting break elongation values of ECOFLEX™, graft copolymer of ECOFLEX™ with CMPS, graft copolymer of cross-linked ECOFLEX™ with CMPS, graft copolymer of ECOFLEX™ with PS and LDPE.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The starting starch material useful in this invention

can be any of several starches, native or modified. Such starches include those derived from any plant source including corn, potato, wheat, rice, sago, tapioca, waxy maize, sorghum and high amylose starch, i.e., starch having at least 40% and more particularly at least 65% by weight of amylose content, such as high amylose corn, etc. Starch flours can also be used as a starch source. Also included are the conversion products derived from any of the former bases including, for example, dextrin prepared by hydrolytic actions of acid and/or heat; oxidized starches prepared by treatment with oxidants such as sodium hypochlorite; fluidity or thin boiling starches prepared by enzyme conversion or mild acid hydrolysis; and derivatized and crosslinked starches. The starch percentage in the final blend is 5% to 45% by weight and preferably from 10% to 30% by weight.

[0028] The plasticizers are polyhydric alcohols, preferably glycerol sorbitol, ethylene glycol and mixtures thereof. Plasticizer concentration in the final blend is 5% to 50% by weight and preferably from 5% to 20% by weight is preferred.

[0029] Modified starches could also be used in this invention. By modified it is meant that the starch can be derivatized or modified by typical processes known in the art, e.g., esterification, etherification, oxidation, acid hydrolysis, crosslinking and enzyme conversion. Typically, modified starches include esters, such as the acetate and half-esters of dicarboxylic acids, particularly the alkenylsuccinic acids; ethers, such as the hydroxyethyl and hydroxypropyl starches and cationic starches such as starch modified with 2-diethylaminoethyl chloride (DEC) and starch modified with

quaternary ammonium reagents such as 3-chloro-2-hydroxypropyltrimethylammonium chloride; starches oxidized with hypochlorite; starches reacted with crosslinking agents such as phosphorus oxychloride, epichlorohydrin, and phosphate derivatives prepared by reaction with sodium or potassium orthophosphate or tripolyphosphate and combinations thereof. These and other conventional modifications of starch are described in publications such as "Starch: Chemistry and Technology", Second Edition, Edited by Roy L. Whistler, et al., chapter X; Starch Derivations: Production and Uses by M. W. Rutenberg, et al., Academic Press, Inc. 1984.

[0030] Examples of biodegradable polyester polymers include poly(caprolactone) (PCL), poly(vinylacetate-co-vinylalcohol) (PVAc/VA), poly(lactic acid) or polylactide (PLA), poly(glycolic acid) or polyglycolide (PGA), and related copolyesters including the various combinations of stereoisomers, bacterial and synthetic poly(-hydroxybutyrate) poly(.beta.-hydroxybutyrate-co-.beta.-hydroxyvalerate) (PHB/V), and other poly(.beta.-hydroxyalkanoates) (PHA), and aliphatic-aromatic biodegradable polyesters such as ECOFLEX™.

[0031] In forming starch-polyester graft copolymers of this invention, the selected starch starting material is preferably reacted with biodegradable polyester polymers in the presence of maleic anhydride or maleic acid or mixtures thereof, which functions as a trans-esterification catalyst.

[0032] The maleic anhydride and/or its hydrolyzed acid counterpart is combined with the starch or the plasticized starch in an amount of from about 0.1 to 10% by weight of

anhydride (or acid) and preferably about 0.5 to 4% anhydride (or acid) based on the dry weight of starch. The anhydride or hydrolyzed acid is usually added in the form of a fine powder and is co-extruded with the biodegradable polyester by adding it directly to the extruder. In the case of using maleated starches, maleic anhydride already present in the system functions as a catalyst and hence there is no need to add again. Other organic diacids or anhydrides can be used as described in our copending application, which is incorporated herein by reference.

[0033] While any starch may be used in this invention as noted previously, the starch materials that are particularly useful in this invention are corn, potato, tapioca and high amylose starch; i.e., starch containing at least 40% by weight and preferably at least 65% by weight of amylose. Further preferred are the starches that are modified by maleation, especially using maleic anhydride or maleic acid. Blends of two or more of the starch starting materials may be used as well as additive or synthetic compounds to improve properties such as water resistance, strength, flexibility, color, etc.

[0034] The apparatus used in carrying out the extrusion process can be any screw type extruder. While the use of a single or twin screw extruder can 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

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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.

[0035] 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.

[0036] Variations in any of the elements used in the extruder can 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.

[0037] In carrying out the extrusion process, temperatures in the extruder vary depending on the particular material, desired properties and application. They generally range from about 100°C to 250°C, and preferably will range from about 150°C to 210°C. The total moisture content of the starch in the extruder, i.e., moisture present in the inlet feed starch as well as water in the aqueous anhydride and/or acid, is about 25% or less by weight, based on the weight of starch. More

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particularly, the total moisture content of the starch ranges from about 8 to 25% preferably about 10 to 21% and more preferably from about 15 to 21 % by weight, based on the weight of starch.

[0038] Further, the starch-polyester graft copolymers can be manufactured in a one-step process; wherein the starch is first plasticized in a first section of the extruder followed by addition of the polyester along-with a trans-esterification catalyst to form the starch-polyester graft copolymer. Further, starch can be maleated using maleic anhydride or maleic acid in the presence of glycerol plasticizer in the first section of the extruder, followed by addition of the polyester downstream to form the starch-polyester graft copolymer.

[0039] By utilizing the starch-polyester graft copolymer, the overall processing temperature can be reduced to well below the processing temperature of the pure polyester component. This is particularly important for manufacturing with high-melting polyesters such as PHB and PHB/V, which thermally degrade at higher processing temperatures and therefore have a narrower processing window. This improvement is attributed to the compatibility achieved by the reactive blending process, resulting in changes in the crystalline microstructure of the polyester component and/or the morphology of the multi-phase material thereby rendering it processable at lower processing temperatures. It is important that the compounds be compatible.

[0040] The compositions of the present invention can retain their biodegradability if a degradable polyester polymer is used. The water resistance of the starch and modified starches

is improved by graft copolymerization with high molecular weight biodegradable polyesters, especially with semi-crystalline polyesters such as PCL or PHB/V, and similar biodegradable polyesters. This is further achieved by engineering the appropriate blend composition, through the choice of polyester, starch and plasticizer.

[0041] The present invention can be processed by various methods known in the art, such as extrusion pelletizing, injection molding, and film forming. For example, the starch-polyester graft copolymer compositions made in accordance with the present invention can be injection molded to give a variety of molded products, and extrusion cast or even solution cast to give translucent flexible films, as well as transparent films.

[0042] The following experimental examples demonstrate the utility of the present invention for forming biodegradable products containing a biodegradable starch or plasticized starch and biodegradable polyester in the presence of a transesterification catalyst.

[0043] Examples of materials made in accordance with the present invention in compost experiments confirm biodegradability.

Example 1

[0044] The synthesis of ECOFLEX™(PBAT)- plasticized starch (PS) graft copolymers was accomplished in a twin-screw co-rotating CENTURY extruder using maleic acid as a transesterification catalyst. PS was produced by plasticization of regular corn-starch, obtained from Corn Products, Inc. (Chicago, IL) (moisture content of 12%) using glycerol (20-wt

%) as a plasticizer in the same extruder. Maleic acid, obtained from Aldrich, was ground to a fine powder using a mortar and pestle and pre-blended with the ECOFLEX™ polyester (poly (butylene adipate-co-terephthalate)), obtained from BASF (Germany)) before being fed to the feed port of the extruder. The concentration of maleic acid used was 1-wt% with respect to the total concentration. Meanwhile, PS, previously oven dried overnight at 50°C, was ground to a fine powder and fed using an external feeder to the feed port of the extruder. The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (ECOFLEX™ + Maleic acid): PS. The temperature profile is shown in Figure 1 and Table 1, and the screw configuration used is shown in Figure 2, respectively. In Figures 2A, 2B and 2C, the entire screw configuration is divided into 3 sections; section 1 of 12.5D distance followed by section 2 of 15.5D distance and finally section 3 with 12D distance. The vent port was kept open to remove unreacted maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line.

[0045] Table 1: Extrusion Processing Conditions in the synthesis of ECOFLEX-(PS/CMPS) graft copolymers

ZONE	SET	ACTUAL	UNITS
ZONE1	15	70	C
ZONE2	95	99	C
ZONE3	125	122	C
ZONE4	145	149	C
ZONE5	160	170	C
ZONE6	165	192	C
ZONE7	165	196	C
ZONE8	165	193	C
ZONE9	150	185	C
DIE	145	153	C
MELT TEMP.		153	C
MOTOR SPEED		254	RPM
TORQUE		67	%
PRESSURE		92	Psia
FEEDER SPEED, CENTURY (Ecoflex + Maleic acid)		135 (~8 lb/hr)	%
FEEDER SPEED, MINI			%
FEEDER SPEED, EXT (TPS)		0.80 (3.4 lb/hr)	%

[0046] The resulting pellets were dried in an oven overnight at 75°C. The pellets were totally extracted in Dichloro methane using a Soxhlet extraction unit. The extracted graft copolymer solution was cast to form transparent films. FTIR analysis (Figure 3) of the films confirmed reactivity and the true existence of a graft copolymer.

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Example 2

[0047] The procedure of Example 1 was followed using PCL™ (Poly (epsilon-caprolactone), obtained from Dow Chemical (Midland, MI); Molecular weight of 70,000 g/mol) polyester instead of ECOFLEX™. The resulting pellets were also dried in an oven overnight at 75°C. The pellets were totally extracted in Dichloro methane using a Soxhlet extraction unit. The extracted graft copolymer solution was cast to form transparent films. FTIR analysis of the films confirmed reactivity and the true existence of a graft copolymer.

Example 3

[0048] The synthesis of starch-polyester graft copolymers was carried out as follows: Chemically modified plasticized starch (CMPS), produced by reactive extrusion processing of regular corn-starch, obtained from Corn Products (Chicago, IL), using maleic acid modifier, and glycerol (20-wt%) plasticizer as explained in the co-pending patent application was oven dried overnight at 75°C and ground to a fine powder and fed using an external feeder to the feed port of the extruder. This composition is described in Applicants' co-pending application which is incorporated herein by reference. ECOFLEX™ was also fed to the feed port of the extruder using CENTURY™ feeder (Traverse City, MI). The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (ECOFLEX: CMPS). The temperature profile and the screw configuration used are similar to Example 1. The vent port was kept open to remove unreacted maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at 75°C, to remove surface moisture. The pellets were

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totally extracted in Dichloro methane using a Soxhlet extraction unit. The extracted graft copolymer solution was cast to form transparent films. FTIR analysis of the films (Figure 4) confirmed reactivity and the true existence of a graft copolymer.

Example 4

[0049] The synthesis of starch-polyester graft copolymers was carried out as follows: Chemically modified plasticized starch (CMPS), produced by reactive extrusion processing of regular corn-starch, obtained from Corn Products, using maleic acid modifier, BENTONE 166™ (BENTONE 166™ is an alkylaryl ammonium hectorite clay, obtained from Elementis Specialties, with greatly improved dispersibility characteristics. It provides excellent mechanical strength, flame retardancy and highly improved gas barrier properties) and glycerol (20-wt%) plasticizer as explained in the co-pending patent application was oven dried overnight at 75°C and ground to a fine powder and fed using an external feeder to the feed port of the extruder. ECOFLEX™ was also fed to the feed port of the extruder using the CENTURY™ feeder. The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (ECOFLEX: CMPS). The temperature profile and the screw configuration used are similar to Example 1. The vent port was kept open to remove maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at 75°C, to remove surface moisture.

Example 5

[0050] The synthesis of starch-polyester graft copolymers was

carried out as follows: Chemically Modified plasticized starch (CMPS), produced by reactive extrusion processing of regular corn-starch, obtained from Corn Products, using maleic acid modifier, BENTONE 111™ (BENTONE 111™ is an organic derivative of a special smectite clay, obtained from Elementis Specialties. It provides excellent mechanical strength, flame retardancy and highly improved gas barrier properties) and glycerol (20-wt%) plasticizer as explained in the co-pending patent application was oven dried overnight at 75°C and ground to a fine powder and fed using an external feeder to the feed port of the extruder. ECOFLEX™ was also fed to the feed port of the extruder using CENTURY™ feeder. The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (ECOFLEX: CMPS). The temperature profile and the screw configuration used are similar to Example 1. The vent port was kept open to remove maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at 75°C, to remove surface moisture.

Example 6

[0051] The procedure given in Example 3 was followed using polycaprolactone (PCL) polyester instead of ECOFLEX™. The resulting pellets were also dried in an oven overnight at 75°C. The pellets were totally extracted in dichloromethane using a Soxhlet extraction unit. The extracted graft copolymer solution was cast to form transparent films. FTIR analysis of the films confirmed reactivity and the true existence of a graft copolymer.

Example 7

[0052] ECOFLEX™ and cross-linked ECOFLEX™ (Cross-linked using a free radical initiator) were melt extruded with PS and CMPS in different proportions according to the procedure as explained in Example 3. All the samples were extracted in dichloromethane using a Soxhlet apparatus. The results of the extraction are shown in Table 2.

[0053] Table 2: Soxhlet Extraction results of ECOFLEX-CMPS graft copolymers

System	Polyester (Ecoflex or LEcoflex) initially present (gm)	Starch component (PS or CMPS) initially present (gm)	Material extracted (gm)	% Extracted
Ecoflex/CMPS (70/30;w/w)	1.3510	0.579	1.8878	98
Ecoflex/CMPS (60/40;w/w)	1.0682	0.7122	1.7010	96
Ecoflex/CMPS (50/50;w/w)	0.7998	0.7998	0.7503	47
Ecoflex/CMPS (40/60;w/w)	0.8639	0.5759	0.5513	38.2
Ecoflex/CMPS (70/30;w/w) No Initiator used in the preparation of CMPS.	1.9018	0.8150	2.6530	98
Ecoflex/PS (70/30;w/w)	1.2075	0.5175	1.2595	71
LEcoflex/CMPS (65/35;w/w)	3.25	1.748	4.1272	83
LEcoflex/PS (70/30;w/w)	1.0225	0.4382	1.0602	73

[0054] As seen from Table 2, almost complete extraction is achieved for ECOFLEX™/CMPS (70/30 w/w and 60/40 w/w) graft copolymers. When this solution was cast, a transparent film was obtained. This proves that ECOFLEX™ and CMPS are covalently linked making the graft copolymer extractable in Dichloromethane (solvent wherein ECOFLEX™ is soluble, but PS is not). However, due to the insolubility of PS in the solvent, the graft copolymer forms a colloidal dispersion and not a clear transparent solution.

[0055] This result is applicable even to blends containing CMPS made with no peroxide (see row 6 in Table 2). However, for the 50/50 and 40/60 blends, only 47% and 38% respectively (close to the respective ECOFLEX™ amount) were extracted out. This confirms the fact that ECOFLEX™ has not reacted with CMPS. Thus, the reaction is also dependent on the relative amounts of the polyester and CMPS phases present. Also, from Table 2 (rows 7 and 9), it is clearly seen that when PS is used instead of CMPS, there is very minimal or no reaction taking place. This suggests that the reaction between the hydroxyl groups in starch and the ester functionalities in ECOFLEX™ occurs only in the presence of a trans-esterification catalyst such as maleic acid. When ECOFLEX™ polyester was cross-linked and reactively blended with CMPS, around 83% of the polyester was extracted out. This could be due to the fact that certain gel (network) portions of the cross-linked polyester are impermeable to chemical reaction.

Example 8

[0056] Several graft copolymer samples, prepared using both

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PS and CMPS according to procedures explained in Examples 1, 3, 4 and 5 were extruded into films. Films were made using a Killion[™] (Pawcatuck, CT) single-screw blown film unit. The screw diameter was 25.4 mm with L: D ratio of 25:1. The die inner diameter was 50.8 mm with a die gap size of 1.5 mm. The blown film processing conditions are shown in Table 3.

[0057] Table 3: Blown Film Processing Conditions for ECOFLEX-(PS/CMPS) graft copolymers

Set (°F)	70	350	355	360	360	395	395	300
Actual (°F)	73	351	358	357	360	380	395	300

Melt (°F)	364
Screw Speed (RPM)	12.4
FPM (ft/min)	5-6
Pressure (psi)	500-1000

[0058] Tensile properties of the films were determined using INSTRON[™] Mechanical Testing Equipment fitted with a 100 lbs load cell. The crosshead speed was 1 inch per minute. Rectangular film samples, 4'x1' dimension were conditioned at 23°C and 50% Relative Humidity for 40 hours before being tested according to ASTM D-882 testing. The results of the testing are shown in Figures 4, 5 and 6. It is observed that the tensile strength and modulus of elasticity values of ECOFLEX[™]-PS graft copolymer, containing around 30% PS, exhibit almost a six fold decrease as compared to pure ECOFLEX[™] polyester values. However, ECOFLEX[™]/CMPS graft copolymers and cross-linked

ECOFLEX™ (ECOFLEX)/CMPS graft copolymers exhibit tensile values comparable to LDPE. Also, on incorporation of clay in the production of Ecoflex™/CMPS, the film tensile strength further improves to about 2800 - 3000 psi (twice as much as ECOFLEX™/CMPS). Break elongation values of the graft copolymer are higher than ECOFLEX™ and LDPE. Tear and Puncture properties, determined according to ASTM D1922 and ASTM F1306 respectively, were found to be comparable to LDPE. (Table 4)

Table 4: Tear and Puncture properties of ECOFLEX-CMPS (70/30) graft copolymer

Material	Thickness (in)	Tear (g) MD ASTM D 1922	Tear (g) CMD ASTM D 1922	Puncture Max. (lbf) ASTM F 1306	Puncture Ext. (in) ASTM F 1306
LDPE	0.0010- 0.0015	100- 300	-	1.5-3.0	-
Ecoflex-MTPS (70/30) graft copolymer	0.0010- 0.0015	767.7	802.7	1.515	0.6219

[0059] The above examples demonstrate that the present invention provides new starch-based graft copolymers which utilize agricultural resources that can be returned back to nature in an environmentally sound manner. The polymeric materials made in accordance with the present invention are environmentally compatible, this being achieved by designing and engineering fully biodegradable materials that are

thermoplastic, yet breakdown under appropriate environmental conditions in a manner similar to their lignocellulosic counterparts.

[0060] 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 starch-polyester graft copolymer composition comprising starch or chemically modified starch with segments of a polyester grafted onto the starch.
2. The composition of Claim 1 wherein the chemically modified starch is a starch which is thermoplastic.
3. The composition of Claim 1 further comprising about 0.5 to 25% by weight of the composition of a plasticizer.
4. The composition of Claim 1 containing natural or an organically modified nanoclay.
5. The composition of Claim 1 or 2 wherein the starch is selected from the group consisting of corn, potato, wheat, rice, sago, tapioca, waxy maize, sorghum and high amylose starch.
6. The composition of Claim 1 or 2 wherein the starch is chemically modified starch and is prepared from a reactively extruded 50% to 80% by weight of the starch, a chemical modifier from 0.5% to about 10% by weight of the starch, a plasticizer from 10 to 50 wt-% of the

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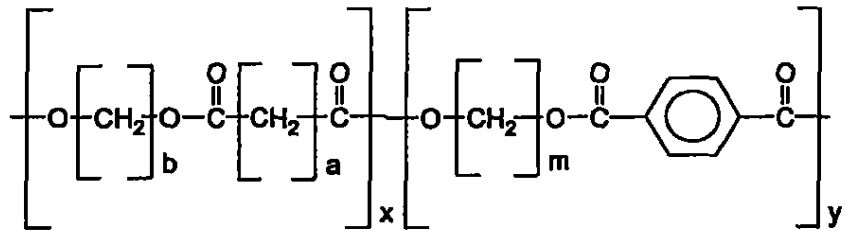
composition, and optionally a free radical initiator in an amount ranging between 0.01 to 2.0 wt % of the composition.

7. The composition of Claim 1 or 2 which is prepared from a blend comprising starch polymer, from 50% to 80% by weight, a chemical modifier from 0.5% to about 10% by weight of the starch polymer, more preferably from 2% to 5% by weight of the starch, a plasticizer from 10 to 50 wt-% of the composition, a nanoclay, wherein the nanoclays are added in an amount ranging from 0.5 to 25 wt % of the total composition.

8. The composition of Claim 1 wherein the polyester is selected from the group consisting of



where R is lower alkyl and aromatic groups containing 1 to 12 carbon atoms; n is 0 to 10; and x is 200 to 2000; and



, where a, b and m are 2 to 8; and x/y is between 3/2 and 10/1.

9. The composition of Claim 1 in which the polyester is 50 to 90 wt-% of the composition.

10. The composition as set forth in Claim 1 or 2 wherein the plasticizer is polyhydric alcohol.

11. The composition as set forth in Claim 1 or 2 wherein a modifier for the chemically modified starch is selected from the group consisting of dibasic acids and their anhydrides.

12. The composition of Claim 1 or 2 further comprising a free radical initiator.

13. The composition of Claim 1 or 2 further comprising a free radical initiator which is a peroxide.

14. The composition of Claim 1 or 2 further comprising a nanoclay selected from a group consisting of montmorillonite, smectite, hectorite, and mixtures thereof.
15. The composition of Claim 1 or 2 which is completely biodegradable.
16. The composition of Claim 1 or 2 which has been grafted in a melt phase in an extruder.
17. The composition of Claim 1 or 2 which has been grafted in a twin screw extruder at a temperature in the range of 100°C-200°C.
18. A process for the preparation of a starch polyester graft co-polymer composition which comprises blending a mixture of an organic acid or anhydride of the acid with starch or a chemically modified starch and a polyester at a temperature which grafts the segments of a polyester onto the starch to form the composition.
19. The process of Claim 18 wherein the blending is in an extruder at a temperature between about 100 to 200°C.

20. The process of Claim 18 or 19 wherein the organic acid is a dibasic acid.
21. The process of Claim 18 or 19 wherein the organic acid is a dibasic acid produced in situ in the blending by reaction of an anhydride with water contained in the starch.
22. The process of Claim 18 or 19 wherein the composition in addition comprises a plasticizer.
23. The process of Claim 18 or 19 wherein in addition a peroxide initiator is mixed into the blend.
24. The process of Claim 18 wherein in addition a nanoclay is in the blend.

25. A starch based copolymer 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 organic anhydride of a dibasic organic acid and mixtures thereof, a plasticizer, a biodegradable polyester, and optionally a free radical initiator, wherein the mixture has been extruded, with heating and venting of water from the mixture.
26. The composition of Claim 24 wherein the starch is selected from the group consisting of cornstarch, potato starch, tapioca starch, rice starch, wheat starch, and cassava starch.
27. The composition of Claim 24 wherein the starch is about 5% to 90% by weight of the mixture.
28. The composition of Claim 24 wherein the starch is an unmodified, oxidized or thin boiling starch of 0 to 95 degree of fluidity.
29. The composition of Claim 24 wherein the starch has moisture content of about 0.5% to 15% by weight.

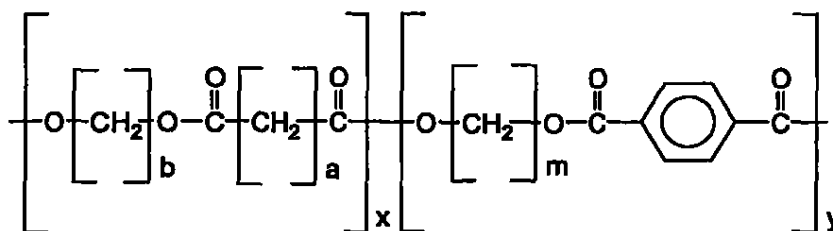
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30. The composition of Claim 24 wherein the starch is in a pulverized form.

31. The composition of Claim 24 in which the polyester is selected from the group consisting of:



where R is lower alkyl and aromatic groups containing 1 to 12 carbon atoms; n is 0 to 10; and x is 200 to 2000; and



, where a, b and m are 1 to 8; and x/y is between 3/2 and 10/1.

32. The composition of Claim 24 in which the polyester is 50 to 90 wt-% of the composition.

33. The composition as set forth in Claim 24 wherein the plasticizer is selected from the group consisting of polyhydric alcohols like glycerol, sorbitol, ethylene glycol and mixtures thereof.

34. The composition as set forth in Claim 24 further comprising a polyhydroxy organic plasticizer in an amount between 10 to 70 wt-% of the mixture.

35. The composition as set forth in Claim 24 wherein the chemical modifier is a cyclic dibasic acid anhydride.

36. The composition of Claim 24 wherein the organic anhydride or organic acid is selected from the group consisting of maleic-, succinic-, itaconic-, phthalic- and mixtures thereof.

37. The composition of Claim 24 wherein the starch is from 50% to 80% by weight of the mixture.

38. A process for preparing a starch based composition which comprises reactively extruding a mixture which comprises a mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an organic anhydride of a dibasic organic acid and mixtures thereof, a plasticizer, a biodegradable polyester resin, and optionally a free radical initiator, wherein the mixture has been extruded, with heating and venting of water from the mixture.

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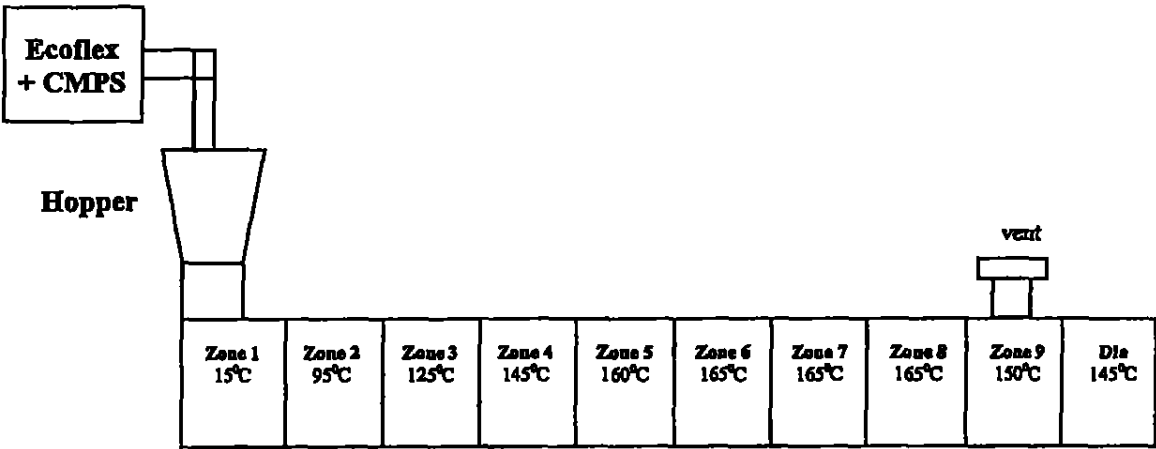
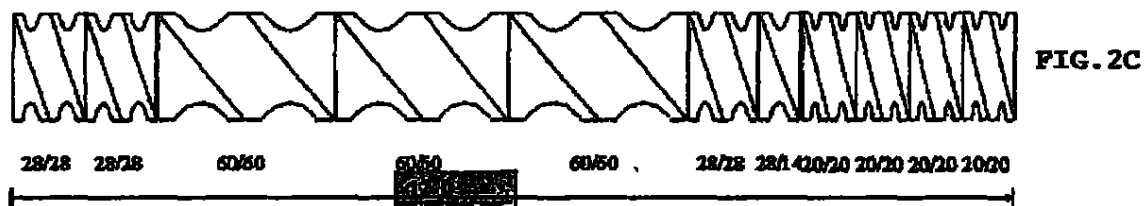
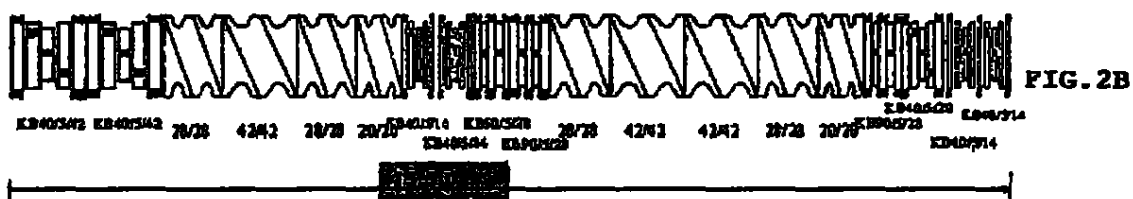
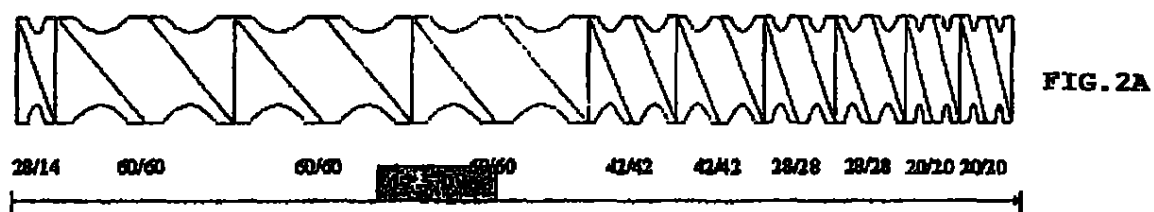


FIGURE 1



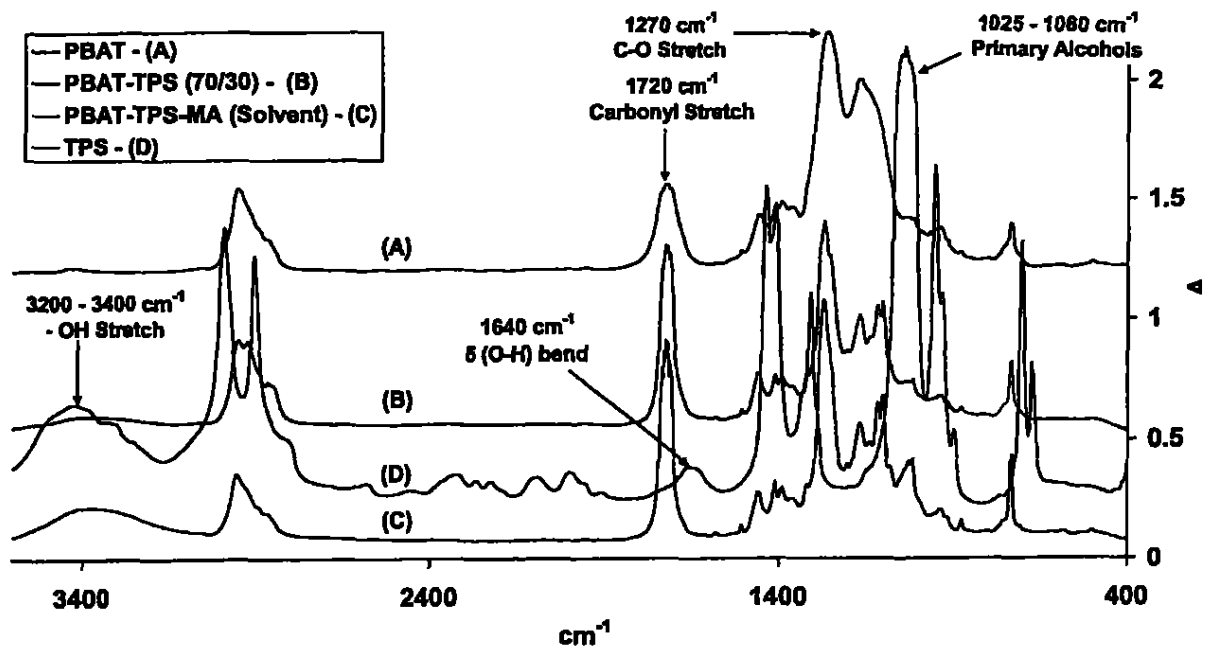


FIGURE 3

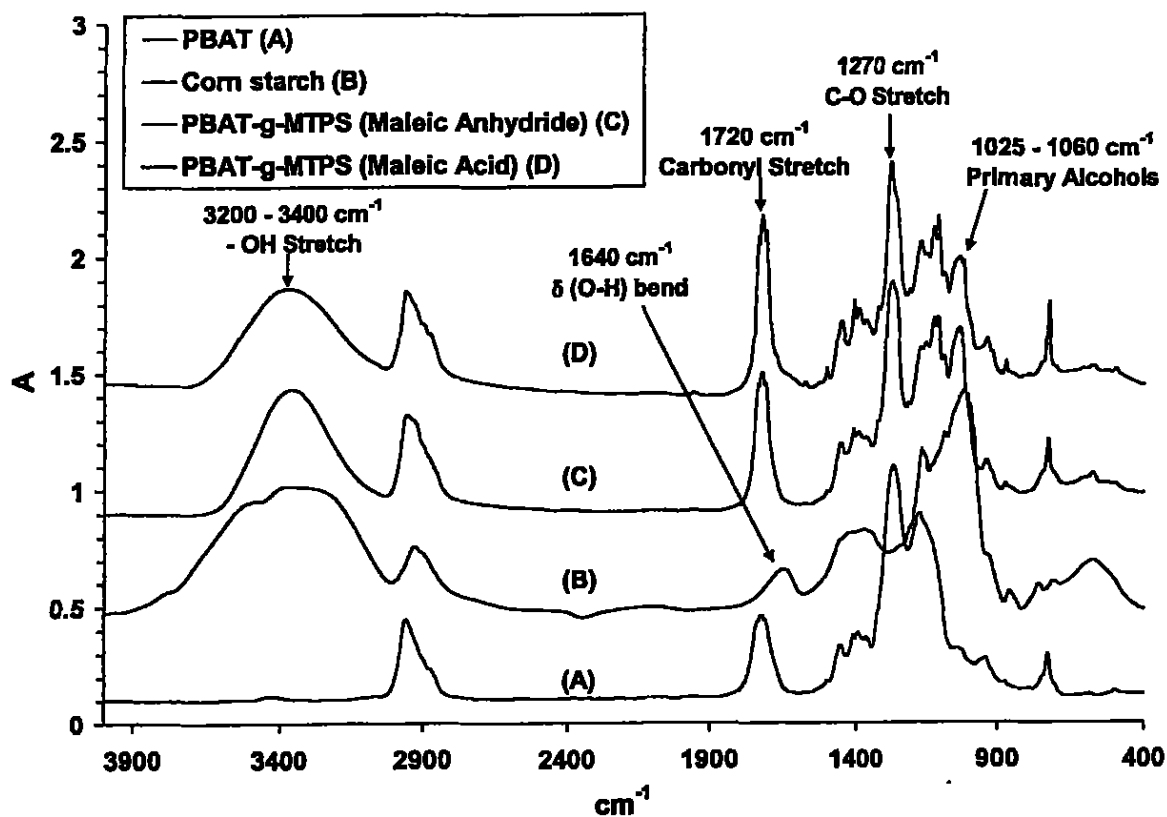


FIGURE 4

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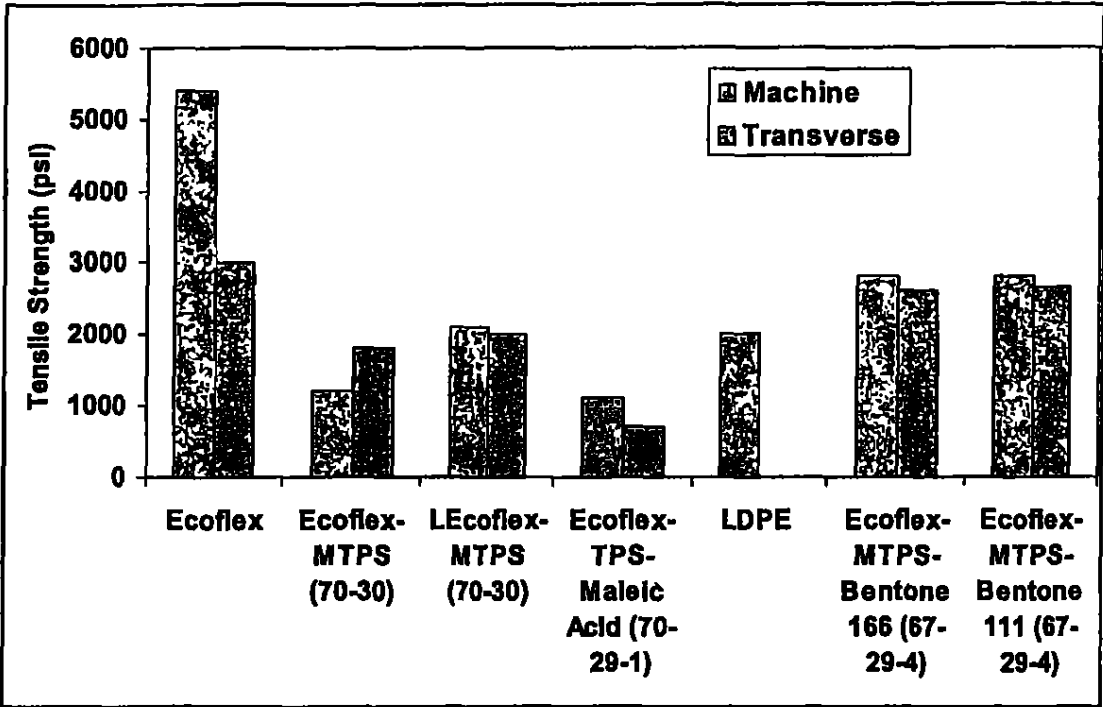


FIGURE 5

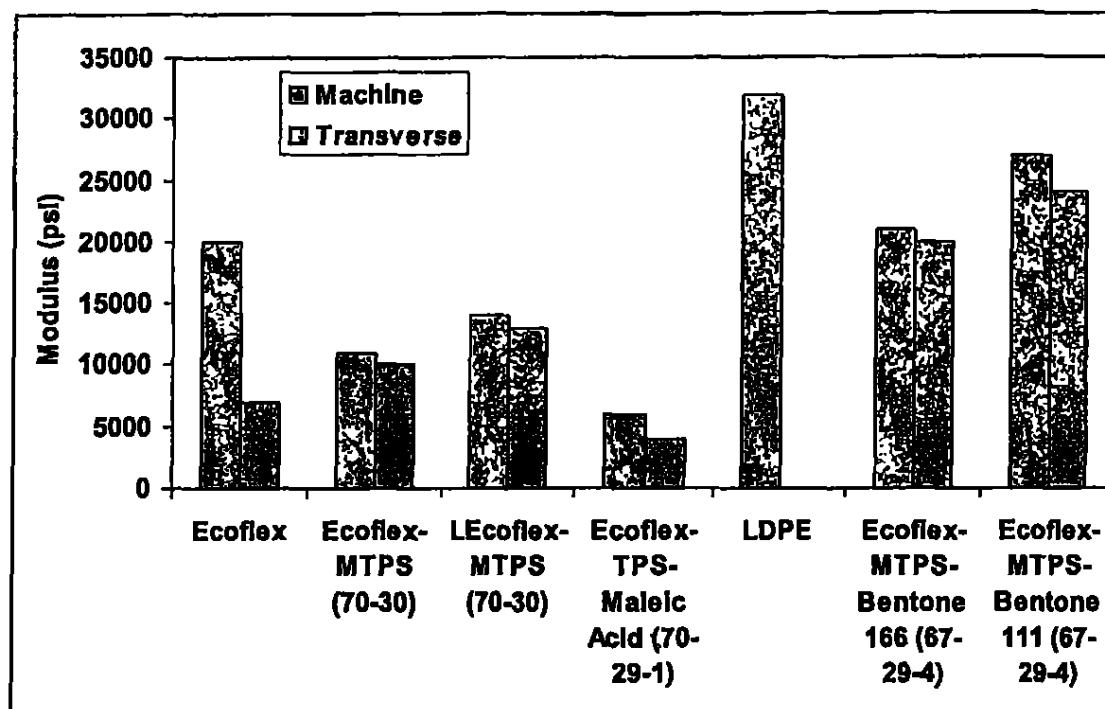


FIGURE 6

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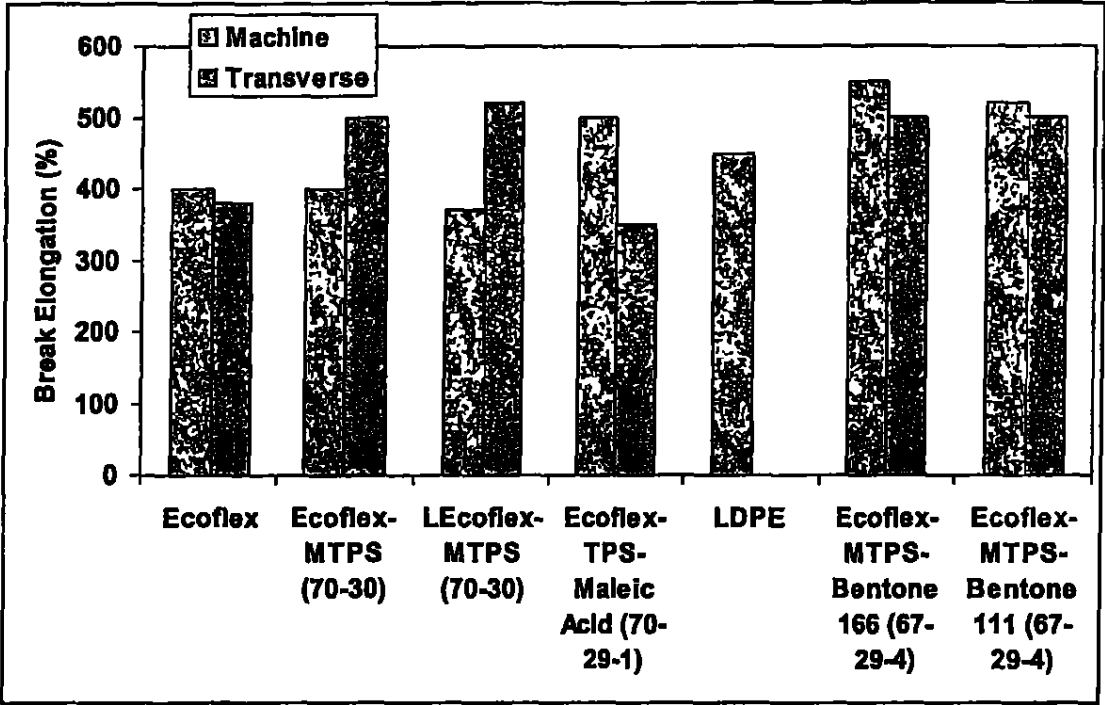


FIGURE 7

(12) SOLICITUD INTERNACIONAL PUBLICADA BAJO EL TRATADO DE COOPERACIÓN INTERNACIONAL
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(74) Agente: MCLEOD, Ian, C; McLeod & Moyne, PC,
2180 Commons Parkway, Okemos, MI 48864 (US)

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(71) Solicitante (para todos los países destinatarios con
excepción de US) MICHIGAN STATE UNIVERSITY
[US/US], 238 Administration Building, East Lansing, MI
48824 (US)

(72) Inventores, e

(75) Inventores/Solicitantes (para US únicamente)
NARAYAN, Ramani [US/US], 4275 Confer Circle,
Okemos, MI 48864 (US) BALAKRISHNAN, Sunder
[IN/US], 1836 Indian Way, Okemos, MI 48864 (US)
NABAR, Yogaraj [IN/US], 1523 Spartan Village, Apt J,
East Lansing, MI 48823 (US). RAQUEZ, Jean-Marie
[BE/US], 701 Cherry Lane, Apt 104, East Lansing, MI
48823 (US) DUBOIS, Philippe [BE/BE], Rue Grande,
1, B-4260 Ciplet (BE)

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(54) Título: COPOLÍMEROS DE INJERTO DE POLIÉSTER-ALMIDÓN, BIODEGRADABLES, Y MÉTODO DE
PREPARACIÓN DE LOS MISMOS

(57) Extracto Se describe un copolímero de injerto de poliéster-almidón y una composición de copolímero de
injerto de poliéster-almidón químicamente modificado, que comprende un almidón químicamente modificado o
un producto nanoarcilla-almidón químicamente modificado. La composición puede producirse continuamente
en una extrusora co-rotativa de doble tornillo. El copolímero de injerto de poliéster-almidón puede vaciarse con
disolvente, vaciarse por fusión y soplar en una película transparente clara, particularmente para uso en
aplicaciones desechables no retornables y ser biodegradable.

WO 2006/055505 A2

**COPOLÍMEROS DE INJERTO DE POLIÉSTER-ALMIDÓN,
BIODEGRADABLES, Y MÉTODO DE PREPARACIÓN DE LOS
MISMOS**

REFERENCIA CRUZADA A APLICACIONES RELACIONADAS

[0001] Ninguna

**DECLARACIÓN CON RESPECTO A INVESTIGACIÓN O
DESARROLLO PATROCINADOS POR EL GOBIERNO FEDERAL**

[0002] No aplicable.

DECLARACIÓN CON RESPECTO A DERECHOS DEL GOBIERNO

[0003] Ninguna

ANTECEDENTES DE LA INVENCION

(1) Campo de la Invención

[0004] La presente invención se refiere a copolímeros de injerto de poliéster-almidón. En particular, la presente invención se relaciona con un copolímero de injerto de poliéster-almidón químicamente modificado y a un copolímero de injerto de poliéster nanoarcilla-almidón. Se divulga un proceso de elaborar estos copolímeros de injerto, usando procesamiento reactivo tal como extrusión reactiva. Los copolímeros de injerto de poliéster-almidón han mejorado la procesabilidad, propiedades superficiales y un rango ampliado de propiedades mecánicas.

(2) Descripción del Arte Relacionado

[0005] El empaque plástico está sometido a presiones provenientes de las reglamentaciones ambientales y de disposición final, propuestas y existentes, y resultantes de iniciativas de sostenibilidad fundamentadas en los mercados. Plantea un problema importante de disposición final para las empresas y municipios, ya que es liviano y voluminoso y, por lo tanto, en sí, no se presta a una operación de reciclaje económicamente viable y

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ecológicamente responsable, en razón de una manipulación costosa y altos costos de transporte. No es biodegradable, lo cual hace inadmisibles la disposición final en el suelo o las operaciones de compostaje. Además, problemas tales como sostenibilidad, ecología industrial, biodegradabilidad y reciclabilidad se están volviendo consideraciones importantes en el diseño de empaques de productos de una empresa, especialmente con empaques desechables no retornables. Los biopolímeros naturales ofrecen soluciones sostenibles, biodegradables, para la fabricación de empaques desechables no retornables, de vida corta, bienes de consumo y plásticos marinos. El almidón, un polímero de anhidroglucosa, ofrece una plataforma estructural para fabricar empaques biodegradables, sostenibles. Ejemplos de patentes que divulgan la fabricación de almidón y mezclas de almidón y otros polímeros incluyen Patente de los Estados Unidos 4,673,438 a Wittwer y colaboradores; Patente de los Estados Unidos 4,095,054 a Lay y colaboradores; Patente de los Estados Unidos 5,256,711 a Tokiwa y colaboradores; Patente de los Estados Unidos 5,275,774 a Bahr y colaboradores; Patente de los Estados Unidos 5,382,611 a Stepto y colaboradores y Patente de los Estados Unidos 5,405,564 a Stepto y colaboradores. Recientemente, se han producido informes comerciales del uso de almidón termoplástico (TPS) como componente en mezclas multifase (W. Wiedmann, and E. Strobel, Starch, 43, 138 (1991); R.L. Shorgen, G.F. Fanta, and W.M. Doan, Starch, 45, 276 (1993); P. Forssell, J. Mikkila, and T. Sourtti, J.M.S. Pure Appl. Chem., A33, 703 (1996); R. Narayan, Polymers from Agricultural Co products, ACS Symp Ser. (1994); and J.J.G. Van Soest, K. Benes, and D.de. Wit, Polymer, 37, 3543 (1996). Aún otros han fabricado mezclas de almidón termoplástico, en las cuales almidón natural se combina inicialmente con una pequeña cantidad de agua y un plastificante menos volátil tal como glicerina, con el fin de formar fundiciones de almidón que se someten a un procedimiento de desgasificación antes del enfriamiento y solidificación para retirar de ellas sustancialmente la totalidad del agua. Ejemplos de tales patentes incluyen las Patentes de los Estados Unidos 5,412,005, 5,280,055, 5,288,765,

5,262,458, 5,462,980 y 5,512,378 a Bastioli y colaboradores.

[0006] Los gránulos de almidón exhiben propiedades hidrófilas y fuerte asociación intermolecular mediante enlazamiento de hidrógeno debido a los grupos hidroxilo en la superficie del gránulo. La hidrofiliidad y sensibilidad térmica hacen al polímero de almidón inapropiado para aplicaciones termoplásticas. En este respecto, algunos autores han enfatizado el hallazgo del polímero óptimo o mezcla de polímeros y otras mezclas, con el fin de "optimizar" así las propiedades del almidón. Una desventaja es que la mayoría de los polímeros y otras mezclas son en sí mismas significativamente más costosas que el almidón, lo cual tiende a aumentar el costo de tales mezclas poliméricas, comparado con fundiciones de almidón. Otra desventaja es que tales aditivos sólo estarán en capacidad de alterar marginalmente las propiedades mecánicas de las combinaciones almidón/polímero, vistas desde una perspectiva de la ciencia de materiales.

[0007] Con el fin de mejorar estas desventajas, la copolimerización de injerto de un monómero de vinilo en la línea de sostén del almidón se usó para modificar almidón. Fanta y Bagley han reseñado la síntesis y discutido algunas aplicaciones de copolímeros de injerto de almidón (G.F. Fanta and E.B. Bagley, Encyclopedia of Polymer Science, John Wiley & Sons: New York (1970); and G.F. Fanta, Block and Graft Copolymers - Vol I, John Wiley & Sons: New York (1973). Otey et al. (F.H. Otey, R.P. Westhoff and W.M. Doane, Industrial Engineering Chemistry Products Research Development, 19, 592 (1980); F.H. Otey and R.P. Westhoff, Industrial Engineering Chemistry Products Research Development, 23, 284 (1984); and F.H. Otey, R.P. Westhoff and W.M. Doane, Industrial Engineering Chemistry Products Research Development, 26, 1659 (1987)) blended starch with poly (ethylene-co-acrylic acid) (EAA). En estos documentos, los autores sugerían la formación de enlaces de hidrógeno entre el grupo carboxílico en EAA y el grupo hidroxilo en el almidón. Aumentar el nivel del almidón disminuyó el alargamiento porcentual de la

película e incrementó la velocidad de difusión del agua. Complejos similares a EAA pueden formarse también con los grupos hidroxilo del copolímero polietilen-alcohol vinílico (EVOH). Estos autores refieren una reacción entre el grupo anhídrido en el polímero sintético con los grupos -OH del almidón. La Patente de los Estados Unidos 5,462,983 a Bloembergen y *colaboradores* informa sobre mezclas y combinaciones que contienen lignocelulosas como almidón, acetato de celulosa, etc. La Patente de los Estados Unidos 5,314,934 a Tomka y *colaboradores* provee un proceso para producir una combinación polímero de almidón-poliolefina. Se empleó terpolímero etileno/acrilato/anhídrido maleico como compatibilizante. Se informó que estas combinaciones se conformaron por soplado en una película con propiedades comparables a polietileno de baja densidad (LDPE). La Patente de los Estados Unidos 5,234,977 a Bastioli y *colaboradores* divulga un material usado para la producción de artículos biodegradables en forma de película, hoja o fibra, que pueden producirse por extrusión de una masa fundida que incluye un polímero termoplástico sintético y un almidón desestructurado al cual se ha agregado un compuesto con contenido de boro, tal como ácido bórico. La Patente de los Estados Unidos 6,277,899 a Bastioli y *colaboradores* divulga una composición polimérica que comprende un relleno dispersado por fusión en una matriz que comprende un componente de almidón desestructurado, un componente polimérico termoplástico sintético y un agente fluidificante. La Patente de los Estados Unidos 5,412,005 a Bastioli y *colaboradores* divulga composiciones poliméricas biodegradables que contienen un componente a base de almidón y un componente polimérico, preferiblemente polímeros de etileno-alcohol vinílico o alcohol polivinílico.

[0008] Las Patentes de los Estados Unidos No. 6,235,816 y 6,472,497 describen combinaciones de poliéster almidón.

[0009] Otras referencias son:

(1) Ramani Narayan, Steven Bloembergen and Amit Lathia, A Method of

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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 Polyester B 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;

(6) Solicitud de Patente de los Estados Unidos presentada en forma conjunta con la presente solicitud.

OBJETOS

[0010] Es, por lo tanto, un objeto de la presente invención proveer nuevas composiciones de poliéster con almidón injertado, que poseen propiedades novedosas. Es un objeto adicional de esta invención proveer composiciones económicas y reproducibles. Éstos y otros objetos se harán cada vez más evidentes a partir de la siguiente descripción.

SUMARIO DE LA INVENCION

[0011] La presente invención se refiere a una composición de copolímero de injerto poliéster-almidón, que comprende almidón o almidón químicamente modificado, con segmentos de un poliéster injertado en el almidón. Preferiblemente, el almidón químicamente modificado es un almidón que es termoplástico. Preferiblemente, la composición comprende alrededor de 0.5 a 10% en peso de la composición de un plastificante. Preferiblemente, la composición contiene una nanoarcilla natural u orgánicamente modificada. Preferiblemente, el almidón se selecciona del grupo conformado por maíz, papa, trigo, arroz, sagú, yuca, maíz ceroso, sorgo y almidón con alto contenido de amilosa. Preferiblemente, el almidón plastificado, químicamente modificado (CMPS), se prepara de una mezcla extruida reactivamente que comprende 50% a 80% en peso del almidón, un modificador químico de 0.5% a alrededor de 10% en peso del almidón, un plastificante de 10 a 50% en peso de la composición, y, opcionalmente, un iniciador de radical libre en una cantidad que varía entre 0.01 a 2.0% en peso de la composición. Preferiblemente, el almidón plastificado químicamente modificado (CMPS), se prepara de una mezcla que comprende polímero de almidón, de 50% a 80% en peso, un modificador químico de 0.5% a alrededor de 10% en peso del polímero de almidón, más preferiblemente de 2% a 5% en peso del almidón, un plastificante de 10 a 50% en peso de la composición, una nanoarcilla, en donde las nanoarcillas se agregan en una cantidad que varía de 0.5 a 25% en peso de la composición total. Preferiblemente, el plastificante se selecciona del grupo conformado por alcoholes polihídricos como glicerol, sorbitol, y etilen glicol. Preferiblemente, el modificador se selecciona del grupo conformado por ácidos dibásicos, o sus anhídridos. Preferiblemente, la composición contiene un iniciador de radical libre. Preferiblemente, el iniciador de radical libre es un peróxido. Preferiblemente, la composición contiene una nanoarcilla seleccionada de un grupo conformado por montmorilonita, esmectita, hectorita, y sus mezclas. Preferiblemente, la composición es completamente biodegradable. Preferiblemente, la composición se ha injertado en una fase fundida en una extrusora.

Preferiblemente, la composición se ha injertado en una extrusora de doble tornillo a una temperatura en el rango de 100°C-200°C.

[0012] La presente invención se refiere igualmente a un proceso para la preparación de una composición de copolímero de injerto poliéster-almidón que comprende combinar una mezcla de un ácido orgánico p anhídrido del ácido con almidón, o almidón químicamente modificado, y un polímero de poliéster a una temperatura que injerta los segmentos de un poliéster en el almidón para formar la composición.

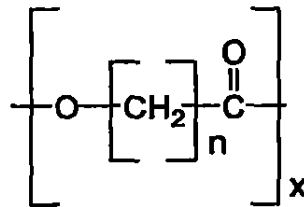
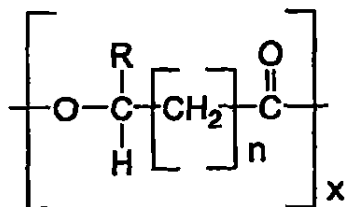
[0013] Muy preferiblemente, la presente invención se refiere a una composición de copolímero a base de almidón, que comprende una mezcla, extruida reactivamente, de un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido orgánico de un ácido orgánico dibásico y sus mezclas, un plastificante, una resina de poliéster biodegradable, una nanoarcilla y, opcionalmente, un iniciador de radical libre, en donde la mezcla se ha extruido, calentar y purgar agua de la mezcla.

[0014] Muy preferiblemente, la presente invención se refiere asimismo a un proceso para preparar una composición a base de almidón, que comprende extruir reactivamente una mezcla 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 orgánico de un ácido orgánico dibásico y sus mezclas, un plastificante, una resina de poliéster biodegradable, una nanoarcilla y, opcionalmente, un iniciador de radical libre, en donde la mezcla se ha extruido, calentar y purgar agua de la mezcla.

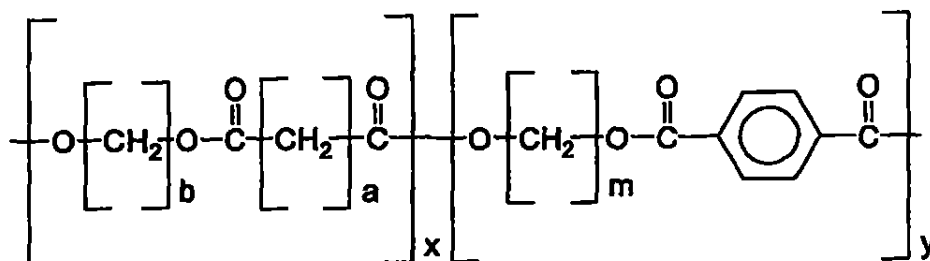
[0015] En la presente invención el mecanismo de reacción consiste en que los fragmentos de una resina de poliéster del procesamiento reaccionan con grupos hidroxilo del almidón. El ácido o anhídrido reacciona con el

polímero de poliéster para producir los fragmentos reactivos. Por lo tanto, la presente invención provee una composición única con los fragmentos del polímero de poliéster enlazado al almidón.

[0016] La presente invención provee particularmente novedosas composiciones anfífilas de copolímero de injerto de poliéster-almidón, y composiciones de copolímero de injerto poliéster-almidón químicamente modificado, que comprenden un producto de almidón químicamente modificado o de nanoarcilla-almidón químicamente modificado, producido continuamente en una extrusora co-rotativa de doble tornillo. El producto de almidón plastificado, químicamente modificado, con menor viscosidad y excelente procesabilidad y el producto nanoarcilla-almidón plastificado, químicamente modificado, se describe en la solicitud de patente copendiente. Los copolímeros de injerto de poliéster-almidón de la presente invención se pueden moldear fácilmente por soplado, vaciado por extrusión en película ("*extrusion cast into film*"), y moldeado. Ejemplos de poliésteres biodegradables incluyen poli(caprolactona) (PCL), poli(vinilacetato-co-vinilalcohol) (PVAc/VA), ácido poli(láctico) o poliláctido (PLA), ácido poli(glicólico) o poliglicólido (PGA), y copoliésteres relacionados, incluidas las diferentes combinaciones de estereoisómeros, poli(.beta.-hidroxibutirato) (PHB) sintético y bacteriano, poli(.beta.-hidroxibutirato-co-.beta.-hidroxivalerato) (PHB/V), y otros poli(.beta.-hidroxialcanoatos) (PHA), poliésteres alifáticos biodegradables, y copoliésteres alifáticos-aromáticos. Preferiblemente, el poliéster se selecciona del grupo conformado por la composición en la cual el poliéster se selecciona del grupo conformado por:



donde R es un alquilo inferior y grupos aromáticos que contienen 1 a 12 átomos de carbono; n es 0 a 10; y x es 200 a 2.000; y



donde a, b y m son 2 a 8; y x/y está entre 3/2 y 10/1.

[0017] La presente invención provee novedosos materiales poliméricos, que son ecológicamente responsables y completamente biodegradables según normas ASTM.

[0018] De acuerdo con la presente invención, se provee un producto moldeable biodegradable o película preparada de un copolímero de injerto, que contiene almidón o almidón químicamente modificado o una composición de nanoarcilla-almidón químicamente modificado y un poliéster, el cual de preferiblemente biodegradable. Se han descubierto nuevos copolímeros de injerto de poliéster-almidón con excelente alargamiento, compresibilidad y propiedades superficiales.

[0019] En una incorporación de esta invención, el almidón se extruye con co-poliéster alifático-aromático y, particularmente, polibutilenos (adipato-co-tereftalato) en la presencia de ácido maleico como catalizador de trans-esterificación para formar composiciones de copolímeros de injerto de poliéster-almidón con excelente alargamiento, compresibilidad y propiedades superficiales. En otra incorporación almidón químicamente modificado o un producto de nanoarcilla-almidón químicamente modificado se ha hecho reaccionar con copoliésteres alifáticos y alifáticos-aromáticos para proporcionar nuevos productos de copolímero de injerto con propiedades y procesabilidad mejoradas.

BREVE DESCRIPCIÓN DE LAS FIGURAS

[0020] Figura 1 es un diagrama de un aparato de extrusión para la producción de almidón injertado de poliéster.

[0021] Figuras 2A, 2B y 2C son dibujos que describen la configuración del tornillo usado para la producción de extrusión reactiva de los novedosos copolímeros de injerto. La configuración del tornillo se divide en tres secciones (Figura 2A) seguida por (Figura 2B) y luego por (Figura 2C).

[0022] Figura 3 es un gráfico que muestra los resultados FTIR de copolímeros de injerto de ECOFLEX™, (poli(butilenadipato-co-tereftalato)), obtenido de BASF (Alemania), con almidón plastificado (PS). Para validar la reactividad, se muestran asimismo las espectrometrías infrarrojas por transformada de Fourier ("*FTIR scans*") de ECOFLEX™ puro, PS y mezcla ECOFLEX™/PS (sin el catalizador).

[0023] Figura 4 es un gráfico que muestra los resultados FTIR de copolímeros de injerto de ECOFLEX™ con CMPS (elaborado usando anhídrido maleico y modificadores de ácido maleico). Para validar la reactividad, se muestran igualmente las espectrometrías infrarrojas por transformada de Fourier de ECOFLEX™ puro y almidón de maíz regular.

[0024] Figura 5 muestra gráficos de barras que representan los valores de resistencia a la tracción de ECOFLEX™, copolímero de injerto de ECOFLEX™ con CMPS, copolímero de injerto de ECOFLEX™ entrecruzado con CMPS, copolímero de injerto de ECOFLEX™ con PS y LDPE.

[0025] Figura 6 muestra gráficos de barras que representan valores del

módulo de elasticidad de ECOFLEX™, copolímero de injerto de ECOFLEX™ con CMPS, copolímero de injerto de ECOFLEX™ entrecruzado con CMPS, copolímero de injerto de ECOFLEX™ con PS y LDPE.

[0026] Figura 7 muestra gráficos de barras que representan valores de alargamiento de ruptura de ECOFLEX™, copolímero de injerto de ECOFLEX™ con CMPS, copolímero de injerto de ECOFLEX™ entrecruzado con CMPS, copolímero de injerto de ECOFLEX™ con PS y LDPE.

DESCRIPCIÓN DETALLADA DE LA INVENCION

[0027] El material de partida almidón útil en esta invención puede ser cualquiera de varios almidones, naturales o modificados. Tales almidones comprenden los derivados de cualquier fuente vegetal incluidos almidón de maíz, papa, trigo, arroz, sagú, yuca, maíz ceroso, sorgo y almidón con alto contenido de amilosa, es decir, almidón con por lo menos 40% y, más particularmente, por lo menos 65% en peso de contenido de amilosa, tal como maíz con alto contenido de amilosa, etc. En igual forma pueden usarse harinas de almidón como fuente de almidón. También se encuentran contenidos los productos de conversión derivados de cualquiera de las bases anteriores incluidos, por ejemplo, dextrina preparada por acciones hidrolíticas de ácido y/o calor; almidones oxidados preparados por tratamiento con oxidantes tales como hipoclorito de sodio; almidones de fluidez o de baja viscosidad ("*fluidity or thin boiling starches*"), preparados por conversión enzimática o acidólisis moderada; y almidones derivados y entrecruzados. El porcentaje de almidón en la mezcla final es 5% a 45% en peso y, preferiblemente, de 10% a 30% en peso.

[0028] Los plastificantes son alcoholes polihídricos, preferiblemente glicerol, sorbitol, etilen glicol y sus mezclas. La concentración de

plastificante en la mezcla final es 5% a 50% en peso y, preferiblemente, de 5% a 20% en peso.

[0029] También podrían usarse almidones modificados en esta invención. Por modificado se da a entender que el almidón puede derivarse o modificarse por procesos típicos conocidos en el arte, por ejemplo, esterificación, eterificación, oxidación, acidólisis, entrecruzamiento y conversión enzimática. Típicamente, almidones modificados incluyen ésteres, tales como acetatos y semiésteres de ácidos carboxílicos, particularmente los ácidos alquenilsuccínico; éteres, tales como los almidones hidroxietílicos e hidroxipropílicos y almidones catiónicos tales como almidón modificado con 2-dietilaminoetil cloruro (DEC) y almidón modificado con reactivos de amonio cuaternario tales como cloruro de 3-cloro-2-hidroxipropiltrimetilamonio; almidones oxidados con hipoclorito; almidones reaccionados con agentes de entrecruzamiento tales como oxiclорuro de fósforo, epiclорohidrina, y derivados de fosfato preparados por reacción con ortofosfato de sodio o potasio o tripolifosfato y sus combinaciones. Éstas y otras modificaciones convencionales de almidón se describen en publicaciones tales como "Starch: Chemistry and Technology", Second Edition, Edited by Roy L. Whistler, et al., chapter X; Starch Derivations: Production and Uses by M. W. Rutenberg, et al., Academic Press, Inc. 1984.

[0030] Ejemplos polímeros de poliéster biodegradables incluyen poli(caprolactona) (PCL), poli(acetato de vinilo-co-vinilalcohol) (PVAc/VA), ácido poli(láctico) o poliláctido (PLA), ácido poli(glicólico) o poliglicólido (PGA), y copoliésteres relacionados, incluidas las diferentes combinaciones de estereoisómeros, poli(-hidroxibutirato) sintético y bacteriano, poli(.beta.-hidroxibutirato-co-.beta.-hidroxivalerato) (PHB/V), y otros poli(.beta.-hidroxialcanoatos) (PHA), y poliésteres biodegradables alifáticos-aromáticos tales como ECOFLEX™.

[0031] En la formación de copolímeros de injerto de poliéster-almidón de esta invención, el material de partida almidón seleccionado se hace reaccionar preferiblemente con polímeros de poliéster biodegradables en la presencia de anhídrido maleico o ácido maleico o sus mezclas, que funcionan con un catalizador de trans-esterificación.

[0032] El anhídrido maleico y/o su contraparte ácido hidrolizado se combina con almidón o el almidón plastificado en una cantidad de desde alrededor de 0.1 a 10% en peso de anhídrido (o ácido) y, preferiblemente, alrededor de 0.5 a 4% de anhídrido (o ácido) basado en el peso seco del almidón. El anhídrido o ácido hidrolizado se agrega usualmente en la forma de un polvo fino y se co-extruye con el poliéster biodegradable alimentándolo directamente a la extrusora. En el caso de usar almidones tratados con maleato, el anhídrido maleico ya presente en el sistema funciona como un catalizador y, por lo tanto, no hay necesidad de agregarlo de nuevo. Pueden usarse otros diácidos orgánicos o anhídridos, tal como se describe en nuestra solicitud co-pendiente, que se incorpora aquí por referencia.

[0033] Aunque en esta invención, como ya se anotó, puede usarse cualquier almidón, los materiales de almidón que son particularmente útiles en esta invención son almidón de maíz, papa, yuca y almidón con alto contenido de amilosa; es decir, almidón que contiene por lo menos 40% en peso y, preferiblemente, por lo menos 65% en peso de amilosa. Se prefieren además los almidones que se modifican por tratamiento con maleato ("*maleation*"), especialmente anhídrido maleico o ácido maleico. Pueden emplearse combinaciones de dos o más de los materiales de partida almidón, así como un aditivo o compuestos sintéticos para mejorar las propiedades tales como resistencia en agua, fuerza, flexibilidad, color, etc.

[0034] El aparato usado para llevar a cabo el proceso de extrusión puede ser cualquier extrusora tipo tornillo. Aunque puede emplearse una

b4
b5

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 barril cilíndrico horizontal con un puerto de entrada montado en un extremo y una matriz de moldeo ("*a shaping die*") montada en el extremo de descarga. Cuando se usan tornillos dobles, éstos pueden ser co-rotativos e intercalados, o no intercalados. Cada tornillo comprenderá una aleta helicoidal ("*a helical flight*") o secciones roscadas y, típicamente, tendrá una sección de alimentación relativamente ahuecada seguida por una sección de transición ahusada, y una sección medidora de profundidad constante, comparativamente poco profunda. Los tornillos accionados por motor, ajustan por lo general cómodamente en el cilindro o barril para permitir mezclar, calentar y cortar el material a medida que pasa a través de la extrusora.

[0035] El control de la temperatura a todo lo largo del recorrido del barril de la extrusora es importante y se realiza en zonas a lo largo del recorrido del tornillo. A menudo se usan medios de intercambio de calor, típicamente un pasaje como un canal, cámara o hueco interno localizado en la pared del barril, para circular un medio calentado tal como aceite, o se emplea un calentador eléctrico tal como los calentadores Calrod® o tipo serpentín. Adicionalmente, los medios de intercambio de calor pueden instalarse en, o a lo largo del eje del dispositivo de tornillo.

[0036] Variaciones en cualquiera de los elementos utilizados en la extrusora pueden introducirse según se desee, de acuerdo con prácticas de diseño convencional. Una descripción más detallada de la extrusión y de las variaciones típicas de diseño pueden encontrarse en "Encyclopedia of Polymer Science and Engineering", Volumen 6, 1986, páginas 571 a 631.

[0037] Al llevar a cabo el proceso de extrusión, las temperaturas en la extrusora varían en función del material particular, las propiedades

deseadas y la aplicación. Éstas varían generalmente desde alrededor de 100°C a 250°C y, preferiblemente, variarán desde alrededor de 150°C a 210°C. El contenido total de humedad del almidón en la extrusora, es decir, la humedad presente en el almidón de alimentación en la boca de entrada, así como el agua en el anhídrido acuoso y/o ácido, es alrededor de 25% o menos en peso, basado en el peso del almidón. Más particularmente, el contenido total de humedad del almidón varía desde alrededor de 8 a 25%, preferiblemente alrededor de 10 a 21% y, más preferiblemente, desde alrededor de 15 a 21 % en peso, basado en el peso del almidón.

[0038] Además, los copolímeros de injerto de poliéster-almidón pueden fabricarse en un proceso de un solo paso; en donde el almidón se plastifica primeramente en una primera sección de la extrusora, seguido por la adición del poliéster junto con un catalizador de trans-esterificación para formar el copolímero de injerto de poliéster-almidón. Asimismo, el almidón puede tratarse con maleato usando anhídrido maleico o ácido maleico en la presencia de plastificante glicerol en la primera sección de la extrusora, seguido por la adición del poliéster corriente abajo para formar el copolímero de injerto de poliéster-almidón.

[0039] Cuando se utiliza el copolímero de injerto de poliéster-almidón, la temperatura general de procesamiento puede reducirse bien por debajo de la temperatura de procesamiento del componente poliéster puro. Esto es particularmente importante para la fabricación con poliésteres de alta fusión ("*high-melting polysteres*") tales como PHB y PHB/V, que se degradan térmicamente a temperaturas de procesamiento más elevadas y, por lo tanto, tienen una ventana de procesamiento más estrecha. Esta mejora se atribuye a la compatibilidad lograda por el proceso de mezcla reactiva, resultante en cambios en la micro-estructura cristalina del componente poliéster y/o la morfología del material de fase múltiple, haciéndolo así procesable a menores temperaturas de procesamiento. Es

importante que los compuestos sean compatibles.

[0040] Las composiciones de la presente invención pueden conservar su biodegradabilidad, si se emplea polímero de poliéster degradable. La resistencia en el agua del almidón y los almidones modificados se mejora por copolimerización de injerto con poliésteres biodegradables de alto peso molecular, especialmente con poliésteres sem.-cristalinos tales como PCL o PHB/V, y poliésteres biodegradables similares. Esto se logra adicionalmente diseñando con técnicas de ingeniería la composición apropiada de la mezcla, mediante la elección del poliéster, el almidón y el plastificante.

[0041] La presente invención puede procesarse por varios métodos conocidos en el arte, tales como peletización por extrusión, moldeo por inyección, y formación de película. Por ejemplo, las composiciones de copolímero de injerto de poliéster-almidón elaboradas de acuerdo con la presente invención pueden moldearse por inyección para proporcionar una variedad de productos moldeados, y vaciado por extrusión ("*extrusion cast*") o incluso vaciado de solución para proporcionar películas flexibles translúcidas, así como películas transparentes.

[0042] Los siguientes ejemplos experimentales demuestran la utilidad de la presente invención para formar productos biodegradables que contienen un almidón biodegradable o un almidón plastificado y poliéster biodegradable en la presencia de un catalizador de trans-esterificación.

[0043] Ejemplos de materiales elaborados de acuerdo con la presente invención en experimentos de compost confirman la biodegradabilidad.

Ejemplo 1

[0044] La síntesis de ECOFLEX™ (PBAT) - copolímeros de injerto con

almidón plastificado (PS) se realizó en una extrusora CENTURY co-rotativa de doble tornillo usando ácido maleico como catalizador de transesterificación. El PS se produjo por plastificación de almidón de maíz regular, obtenido de Corn Products, Inc. (Chicago, IL) (contenido de humedad de 12%) usando glicerol (20% en peso) como plastificante en la misma extrusora. Se molió ácido maleico, obtenido de Aldrich, a un polvo fino utilizando una maja y mortero y se pre-mezcló con el poliéster ECOFLEX™ (poli(butilen adipato-co-tereftalato)), obtenido de BASF (Alemania)) antes de alimentarlo al puerto de alimentación de la extrusora. La concentración de ácido maleico empleado fue de 1% en peso con respecto a la concentración total. Mientras tanto, PS, secado previamente en horno de un día para otro a 50°C, se molió a un polvo fino y se alimentó, usando un alimentador externo, al puerto de alimentación de la extrusora. Las velocidades del alimentador se ajustaron en consecuencia para obtener una relación de 70:30 (ECOFLEX™ + ácido maleico): PS. El perfil de temperatura se muestra en Figura 1 y Tabla 1, y la configuración del tornillo usada se indica en Figura 2, respectivamente. En Figuras 2A, 2B y 2C, toda la configuración del tornillo se divide en 3 secciones; sección T de 12.5D de distancia, seguida por sección 2 de 15.5D de distancia y, finalmente, sección 3 con 12D de distancia. El puerto de ventilación se mantuvo abierto para eliminar el ácido maleico que no reacción y el agua. El cordón extruido se enfrió usando un baño de agua y se granuló en línea.

[0045] Tabla 1: Condiciones de Procesamiento de Extrusión en la síntesis de copolímeros de injerto ECOFLEX-(PS/CMPS)

ZONA	PREDETERMINADO	ACTUAL	UNIDADES
ZONA 1	15	70	C
ZONA 2	95	99	C
ZONA 3	125	122	C
ZONA 4	145	149	C
ZONA 5	160	170	C

ZONA 6	165	192	C
ZONA 7	165	196	C
ZONA 8	165	193	C
ZONA 9	150	185	C
MATRIZ	145	153	C
TEMPERATURA DE FUSIÓN		153	C
VELOCIDAD DEL MOTOR		254	RPM
TORQUE		67	%
PRESIÓN		92	Psia
VELOCIDAD DEL ALIMENTADOR, CENTURY (Ecoflex + ácido maleico)		135 (~8 lb/hr)	%
VELOCIDAD DEL ALIMENTADOR, MINI			%
VELOCIDAD DEL ALIMENTADOR, EXT (TPS)		0.80 (3.4 lb/hr)	%

[0046] Los gránulos ("*pellets*") resultantes se secaron en un horno de un día para otro a 75°C. Los gránulos se extrajeron totalmente en diclorometano usando una unidad de extracción Soxhlet. La solución de copolímero de injerto extraída se vació para formar películas transparentes. Análisis FTIR (Figura 3) de las películas confirmó la reactividad y la verdadera existencia de un copolímero de injerto.

Ejemplo 2

[0047] Se siguió el procedimiento de Ejemplo 1 usando PCL™ (Poli (epsilon-caprolactona), obtenida de Dow Chemical (Midland, MI); poliéster de peso molecular de 70.000 g/mol) en lugar de ECOFLEX™. Los gránulos ("*pellets*") resultantes se secaron igualmente en un horno de un día para otro a 75°C. Los gránulos se extrajeron totalmente en diclorometano usando una unidad de extracción Soxhlet. La solución de copolímero de injerto extraída se vació para formar películas transparentes. Análisis FTIR de las películas confirmó la reactividad y la verdadera existencia de un copolímero de injerto.

Ejemplo 3

[0048] La síntesis de copolímeros de injerto de poliéster-almidón se

llevó a cabo en la siguiente forma: Almidón plastificado químicamente modificado (CMPS), producido por procesamiento de extrusión reactiva de almidón de maíz regular, obtenido de Corn Products (Chicago, IL), usando un modificador de ácido maleico, y plastificante glicerol (20% en peso) como se explica en la solicitud de patente co-pendiente, se secó al horno de un día para otro a 75°C y se molió a un polvo fino y se alimentó usando un alimentador externo al puerto de alimentación de la extrusora. Esta composición se describe en la solicitud co-pendiente del Solicitante, la cual se incorpora aquí por referencia. Se alimentó asimismo ECOFLEX™ al puerto de alimentación de la extrusora usando un alimentador CENTURY™ (Traverse City, MI). Las velocidades del alimentador se ajustaron correspondientemente para obtener una relación de 70:30 (ECOFLEX: CMPS). El perfil de temperatura y la configuración del tornillo usada son similares a Ejemplo 1. El puerto de ventilación se mantuvo abierto para eliminar el ácido maleico que no reaccionó y el agua. El cordón extruido se enfrió usando un baño de agua y se granuló en línea. Los gránulos se secaron en un horno de un día para otro a 75°C, para eliminar la humedad superficial. Los gránulos se extrajeron totalmente en diclorometano usando una unidad de extracción Soxhlet. La solución de copolímero de injerto extraída se vació para formar películas transparentes. Análisis FTIR de las películas (Figura 4) confirmó la reactividad y la verdadera existencia de un copolímero de injerto.

Ejemplo 4

[0049] La síntesis de copolímeros de injerto de poliéster-almidón se llevó a cabo en la siguiente forma: Almidón plastificado químicamente modificado (CMPS), producido por procesamiento de extrusión reactiva de almidón de maíz regular, obtenido de Corn Products, usando modificador de ácido maleico, BENTONE 166™ (BENTONE 166™ es una arcilla hectorita de alquilarilamonio, obtenida de Elementis Specialties, con características de dispersabilidad grandemente mejoradas. Ésta provee

excelente resistencia mecánica, retardo a la llama y propiedades altamente mejoradas de barrera de gas) y plastificante glicerol (20% en peso) plastificante, como se explica en la solicitud de patente co-pendiente, se secó en horno de un día para otro a 75°C y se molió a un polvo fino y se alimentó usando un alimentador externo al puerto de alimentación de la extrusora. Se alimentó igualmente ECOFLEX™ al puerto de alimentación de la extrusora usando el alimentador CENTURY™. Las velocidades del alimentador se ajustaron correspondientemente para obtener una relación de 70:30 (ECOFLEX:CMPS). El perfil de temperatura y la configuración del tornillo usada son similares a Ejemplo 1. El puerto de ventilación se mantuvo abierto para eliminar el ácido maleico y el agua. El cordón extruido se enfrió usando un baño de agua y se granuló en línea. Los gránulos se secaron en un horno de un día para otro a 75°C, para eliminar la humedad superficial.

Ejemplo 5

[0050] La síntesis de copolímeros de injerto de poliéster-almidón se llevó a cabo en la siguiente forma: Almidón plastificado químicamente modificado (CMPS), producido por el procesamiento de extrusión reactiva de almidón de maíz regular, obtenido de Corn Products, usando modificador de ácido maleico, BENTONE 111™ (BENTONE 111™ es un derivado orgánico de una arcilla esmectita especial, obtenida de Elementis Specialties. Éste proporciona excelente resistencia mecánica, retardo a la llama y propiedades de barrera de gas altamente mejoradas) y plastificante glicerol (20% en peso), como se explica en la solicitud de patente co-pendiente se secó en un horno de un día para otro a 75°C y se molió a un polvo fino y se alimentó usando un alimentador externo al puerto de alimentación de la extrusora. Se alimentó asimismo ECOFLEX™ al puerto de alimentación de la extrusora usando un alimentador CENTURY™. Las velocidades del alimentador se ajustaron correspondientemente para obtener una relación de 70:30 (ECOFLEX: CMPS). El perfil de temperatura y la

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configuración del tornillo usados son similares a Ejemplo 1. El puerto de ventilación se mantuvo abierto para eliminar ácido maleico y agua. El cordón extruido se enfrió usando un baño de agua y se granuló en línea. Los gránulos se secaron en un horno de un día para otro a 75°C, para eliminar la humedad superficial.

Ejemplo 6

[0051] Se utilizó el procedimiento dado en Ejemplo 3 empleando poliéster policaprolactona (PCL) en vez de ECOFLEX™. Los gránulos resultantes se secaron también en un horno de un día para otro a 75°C. Los gránulos se extrajeron totalmente en diclorometano usando una unidad de extracción Soxhlet. La solución de copolímero de injerto extraída se vació para formar películas transparentes. El análisis FTIR de las películas confirmó la reactividad y la verdadera existencia de un copolímero de injerto.

Ejemplo 7

[0052] ECOFLEX™ y ECOFLEX™ entrecruzado (entrecruzado usando un iniciador de radical libre) se extruyeron por fusión con PS y CMPS en diferentes proporciones de acuerdo con el procedimiento como se explica en Ejemplo 3. Todas las muestras se extrajeron en diclorometano usando un aparato Soxhlet. Los resultados de la extracción se muestran en Tabla 2.

[0053] Tabla 2: Resultados de extracción Soxhlet de ECOFLEX-copolímeros de injerto CMPS

Sistema	Poliéster (Ecoflex o LEcoflex) inicialmente presente (gm)	Componente almidón (PS o CMPS) inicialmente presente (gm)	Material extraído (gm)	% Extraído
Ecoflex/CMPS (70/30; p/p)	1.3510	0.579	1.8878	98
Ecoflex/CMPS (60/40; p/p)	1.0682	0.7122	1.7010	96
Ecoflex/CMPS (50/50; p/p)	0.7998	0.7998	0.7503	47
Ecoflex/CMPS (40/60; p/p)	0.8639	0.5759	0.5513	38.2
Ecoflex/CMPS (70/30; p/p) No se usó iniciador en la preparación de CMPS.	1.9018	0.8150	2.6530	98
Ecoflex/PS (70/30;p/p)	1.2075	0.5175	1.2595	71
LEcoflex/CMPS (65/35; p/p)	3.25	1.748	4.1272	83
LEcoflex/PS (70/30; p/p)	1.0225	0.4382	1.0602	73

[0054] Tal como se observa en la Tabla 2, se logra una extracción casi completa para EGOFLEX™/copolímeros de injerto CMPS (70/30 p/p y 60/40 p/p). Cuando esta solución se vació, se obtuvo una película transparente. Esto demuestra que ECOFLEX™ y CMPS se enlazan covalentemente haciendo el copolímero de injerto extraíble en diclorometano (disolvente en el que ECOFLEX™ es soluble, pero no el PS). Sin embargo, debido a la insolubilidad de PS en el disolvente, el copolímero de injerto forma una dispersión coloidal y no una solución transparente clara.

[0055] Este resultado es aplicable incluso a mezclas que contienen CMPS elaborado sin peróxido (véase fila 6 en Tabla 2). No obstante, para las mezclas 50/50 y 40/60, sólo se extrajeron 47% y 38% respectivamente (cerca de la respectiva cantidad de ECOFLEX™). Esto confirma el

hecho que ECOFLEX™ no reaccionó con CMPS. Por consiguiente, la reacción depende asimismo de las cantidades relativas de las fases poliéster y CMPS presentes. Además, en la Tabla 2 (filas 7 y 9), se observa claramente que cuando se emplea PS en vez de CMPS, tiene lugar una reacción mínima o no se produce reacción de ninguna clase. Esto sugiere que la reacción entre los grupos hidroxilo en el almidón y las funcionalidades éster en ECOFLEX™ ocurre sólo en la presencia de un catalizador de trans-esterificación tal como ácido maleico. Cuando el poliéster ECOFLEX™ se entrecruzó y se mezcló reactivamente con CMPS, se extrajo alrededor de 83% del poliéster. Esto podría deberse al hecho que ciertas porciones de gel (red) del poliéster entrecruzado son impermeables a reacción química.

Ejemplo 8

[0056] Varias muestras de copolímero de injerto, preparadas usando PS y CMPS de acuerdo con los procedimientos explicados en Ejemplos 1, 3, 4 y 5 se extruyeron en películas. Las películas se elaboraron empleando una unidad de soplado de película de un sólo tornillo Killion™ (Pawcatuck, CT). El diámetro del tornillo era 25.4 mm con una relación L: D de 25:1. El diámetro interno de la matriz era 50.8 mm con un tamaño de abertura de la matriz de 1.5 mm. Las condiciones de procesamiento de soplado de la película se muestran en la Tabla 3.

[0057] Tabla 3: Condiciones de Procesamiento de Soplado de Película para copolímeros de injerto ECOFLEX- (PS/CMPS)

Pre-determinado (°F)	70	350	355	360	360	395	395	300
Actual (°F)	73	351	358	357	360	380	395	300

Fundido (°F)	364
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Velocidad del tornillo (RPM)	12.4
FPM (ft/min)	5-6
Presión (psi)	500-1000

[0058] Las propiedades de tensión de las películas se determinaron usando Equipo de Pruebas Mecánicas INSTRON™ adaptado con una célula de carga de 100 lbs. La velocidad de cruceta era de 1 pulgada por minuto. Muestras rectangulares de la película, con dimensiones 4'x1', se acondicionaron a 23°C y 50% de humedad relativa durante 40 horas antes de ser ensayadas de acuerdo con las pruebas ASTM D-882. Los resultados de las muestras se muestran en Figuras 4, 5 y 6. Se observa que los valores de resistencia a la tensión y módulo de elasticidad de copolímero de injerto ECOFLEX™-PS, que contiene alrededor de 30% PS, exhiben un decremento de casi seis veces comparados con los valores de poliéster ECOFLEX™ puro. No obstante, los copolímeros de injerto ECOFLEX™/CMPS y los copolímeros de injerto ECOFLEX™ (ECOFLEX)/CMPS entrecruzados exhiben valores de tensión comparables al LDPE. Además, con la incorporación de arcilla en la producción de Ecoflex™/CMPS, la resistencia a tensión de la película aumenta adicionalmente a alrededor de 2800 - 3000 psi (dos veces tanto como ECOFLEX™/CMPS). Los valores de alargamiento a la rotura del copolímero de injerto son mayores que ECOFLEX™ y LDPE. Se encontró que las propiedades de rasgado y punzonado, determinadas de acuerdo con ASTM D1922 y ASTM F1306 respectivamente, eran comparables a LDPE. (Tabla 4)

Tabla 4: Propiedades de Rasgado y Punzonado de Copolímero de Injerto ECOFLEX-CMPS (70/30)

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Material	Espesor (in)	Rasgado (g) MD ASTM D 1922	Rasgado (g) CMD ASTM D 1922	Punzonado Máx. (1b) ASTM F 1306	Punzonado Ext. (in) ASTM F 1306
LDPE	0.0010- 0.0015	100- 300	-	1.5-3.0	-
Copolímero de injerto Ecoflex-MTPS (70/30)	0.0010- 0.0015	767.7	802.7	1.515	0.6219

[0059] Los ejemplos anteriores demuestran que la presente invención provee nuevos copolímeros de injerto a base de almidón, los cuales utilizan recursos agrícolas que pueden retornarse a la naturaleza en una forma ecológicamente sana. Los materiales poliméricos elaborados de acuerdo con la presente invención son ecológicamente compatibles, lo cual se logra diseñando mediante técnicas de ingeniería materiales completamente biodegradables que son termoplásticos, pero que se descomponen bajo condiciones ambientales apropiadas en una manera similar a sus contrapartes lignocelulósicas.

[0060] Se propone que la anterior descripción sea sólo ilustrativa de la presente invención, y que la presente invención se limite únicamente por las reivindicaciones que se incluyen a continuación.

REIVINDICAMOS:

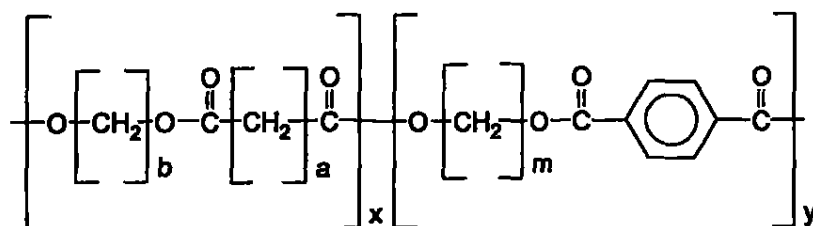
1. Una composición de copolímero de injerto de poliéster-almidón, que comprende un almidón o un almidón químicamente modificado con segmentos de un poliéster injertado en el almidón.
2. La composición de la Reivindicación 1 en donde el almidón químicamente modificado es un almidón que es termoplástico.
3. La composición de la Reivindicación 1, que comprende además alrededor de 0.5 a 25% en peso de la composición de un plastificante.
4. La composición de la Reivindicación 1, que contiene una nanoarcilla natural u orgánicamente modificada.
5. La composición de la Reivindicación 1 ó 2, en donde el almidón se selecciona del grupo conformado por almidón de maíz, papa, trigo, arroz, sagú, yuca, maíz ceroso, sorgo y almidón con alto contenido de amilosa.
6. La composición de la Reivindicación 1 ó 2, en donde el almidón es almidón químicamente modificado y se prepara de un almidón modificado extruido con 50% a 80% en peso del almidón, un modificador químico desde 0.5% a alrededor de 10% en peso del almidón, un plastificante desde 10 a 50% en peso de la composición y, opcionalmente, un iniciador de radical libre en una cantidad que varía entre 0.01 a 2.0% en peso de la composición.
7. La composición de la Reivindicación 1 ó 2 que se prepara de una mezcla que comprende polímero de almidón, desde 50% a 80% en peso, un modificador químico desde 0.5% a alrededor de 10% en peso del polímero de almidón, más preferiblemente desde 2% a 5% en peso del almidón, un plastificante desde 10 a 50% en peso de la

composición, una nanoarcilla, en donde las nanoarcillas se agregan en una cantidad que varía desde 0.5 a 25% en peso de la composición total.

8. La composición de la Reivindicación 1, en donde el poliéster se selecciona del grupo conformado por



donde R es alquilo inferior y grupos aromáticos que contienen 1 a 12 átomos de carbono; n es 0 a 10; y x es 200 a 2.000; y



donde a, b y m son 2 a 8; y x/y está entre 3/2 y 10/1.

9. La composición de la Reivindicación 1, en la cual el poliéster es 50 a 90% en peso de la composición.
10. La composición como se expone en la Reivindicación 1 ó 2, en donde el plastificante es alcohol polihídrico.
11. La composición como se expone en la Reivindicación 1 ó 2, en donde un modificante para el almidón químicamente modificado se selecciona del grupo conformado por ácidos dibásicos y sus anhídridos.
12. La composición de la Reivindicación 1 ó 2, que comprende además un iniciador de radical libre.

13. La composición de la Reivindicación 1 ó 2, que comprende además un iniciador de radical libre el cual es un peróxido.
14. La composición de la Reivindicación 1 ó 2 que, comprende además una nanoarcilla seleccionada de un grupo conformado por montmorilonita, esmectita, hectorita, y sus mezclas.
15. La composición de la Reivindicación 1 ó 2, la cual es completamente biodegradable.
16. La composición de la Reivindicación 1 ó 2, la cual se ha injertado en una fase de fusión en una extrusora.
17. La composición de la Reivindicación 1 ó 2, que se ha injertado en un extrusora de doble tornillo a una temperatura en el rango de 100°C-200°C.
18. Un proceso para la preparación de una composición de copolímero de injerto poliéster-almidón, que comprende combinar una mezcla de un ácido orgánico o anhídrido del ácido con almidón o almidón químicamente modificado y un poliéster a una temperatura que injerta los segmentos de un poliéster en el almidón para formar la composición.
19. El proceso de la Reivindicación 18, en donde la combinación se realiza en una extrusora a una temperatura entre alrededor de 100 a 200°C.
20. El proceso de la Reivindicación 18 ó 19, en donde el ácido orgánico es un ácido dibásico.

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21. El proceso de la Reivindicación 18 ó 19 en donde el ácido orgánico es un ácido dibásico producido *in situ* en la combinación por reacción de un anhídrido con agua contenida en el almidón.
22. El proceso de la Reivindicación 18 ó 19, en donde la composición comprende además un plastificante.
23. El proceso de la Reivindicación 18 ó 19, en donde adicionalmente se mezcla en la combinación un iniciador peróxido.
24. El proceso de la Reivindicación 18, en donde en la mezcla se encuentra además una nanoarcilla.
25. Una composición de copolímero a base de almidón, que comprende una mezcla extruida reactivamente de un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido orgánico de un ácido orgánico dibásico y sus mezclas, un plastificante, un poliéster biodegradable y, opcionalmente, un iniciador de radical libre, en donde la mezcla se ha extruido, calentar y purgar agua de la mezcla.
26. La composición de la Reivindicación 24, en donde el 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 de casabe.
27. La composición de la Reivindicación 24, en donde el almidón es alrededor de 5% a 90% en peso de la mezcla.
28. La composición de la Reivindicación 24, en donde el almidón es un almidón sin modificar, oxidado o de baja viscosidad de 0 a 95

grados de fluidez.

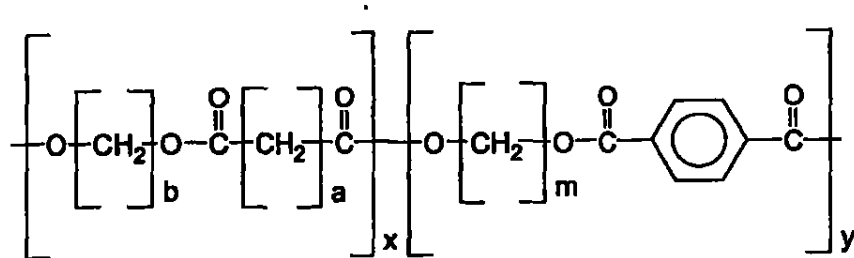
29. La composición de la Reivindicación 24, en donde el almidón tiene un contenido de humedad de alrededor de 0.5% a 15% en peso.

30. La composición de la Reivindicación 24, en donde el almidón está en forma pulverizada.

31. La composición de la Reivindicación 24, en la cual el poliéster se selecciona del grupo conformado por:



donde R es alquilo inferior y grupos aromáticos que contienen 1 a 12 átomos de carbono; n es 0 a 10; y x es 200 a 2.000; y



donde a, b y m son 1 a 8; y x/y está entre 3/2 y 10/1.

32. La composición de la Reivindicación 24, en la cual el poliéster es 50 a 90% en peso de la composición.

33. La composición como se expone en la Reivindicación 24, en donde el plastificante se selecciona del grupo conformado por alcoholes polihídricos tales como glicerol, sorbitol, etilen glicol y sus mezclas.

34. La composición como se expone en la Reivindicación 24, que

comprende además un plastificante orgánico polihidroxí en una cantidad entre 10 a 70% de la mezcla.

35. La composición como se expone en la Reivindicación 24, en donde el modificador químico es un anhídrido de ácido dibásico cíclico.

36. La composición de la Reivindicación 24, en donde el anhídrido orgánico o el ácido orgánico se seleccionado del grupo conformado por maleico, succínico, itacónico, ftálico y sus mezclas.

37. La composición de la Reivindicación 24, en donde el almidón constituye desde 50% a 80% en peso de la mezcla.

38. Un proceso para preparar una composición a base de almidón que comprende extruir reactivamente una mezcla que comprende una mezcla de un polímero de almidón biodegradable, un modificador químico seleccionado del grupo conformado por un ácido orgánico dibásico, un anhídrido orgánico de un ácido orgánico dibásico y sus mezclas, un plastificante, una resina de poliéster biodegradable y, opcionalmente, un iniciador de radical libre, en donde la mezcla se ha extruido, calentar y purgar agua de la mezcla.

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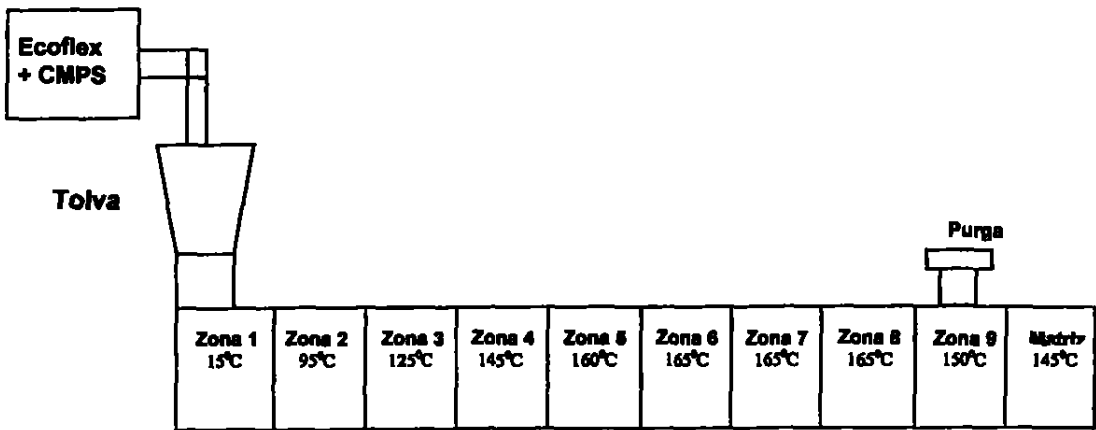
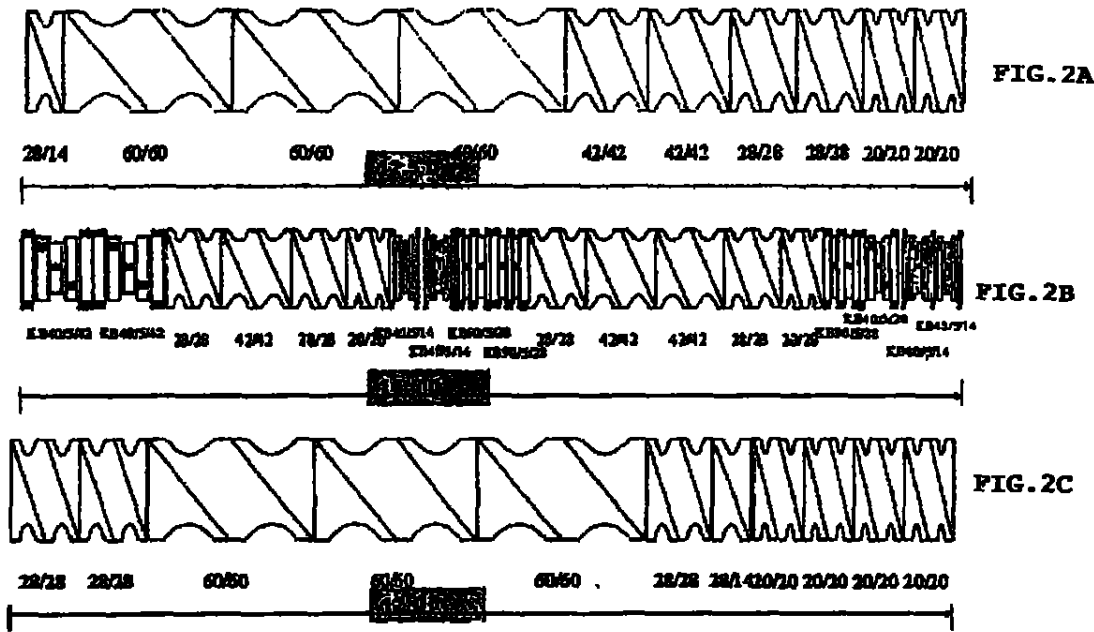


FIGURA 1



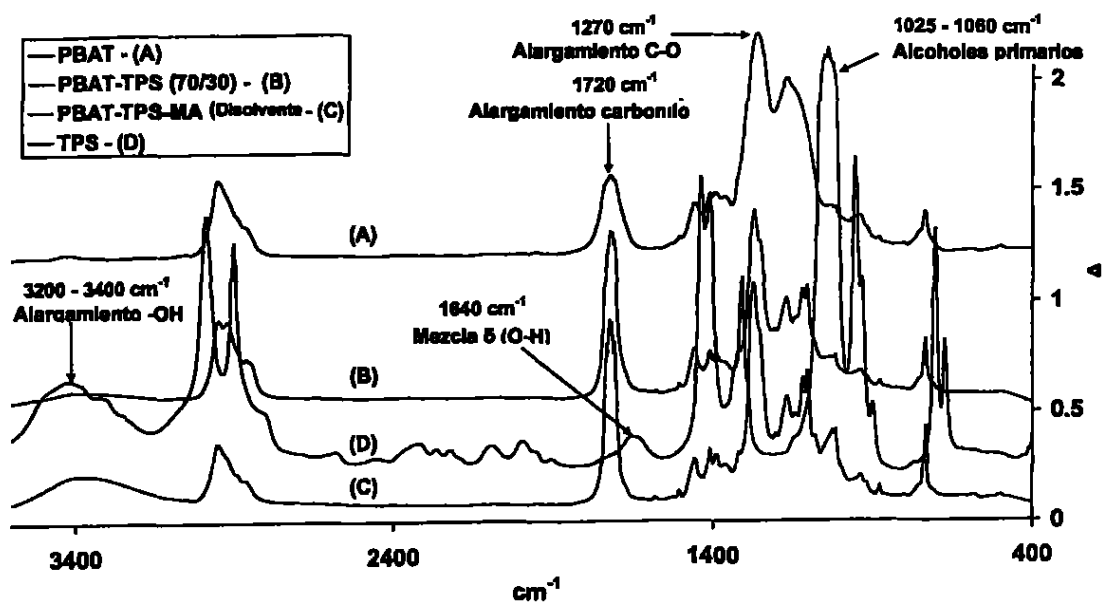


FIGURA 3

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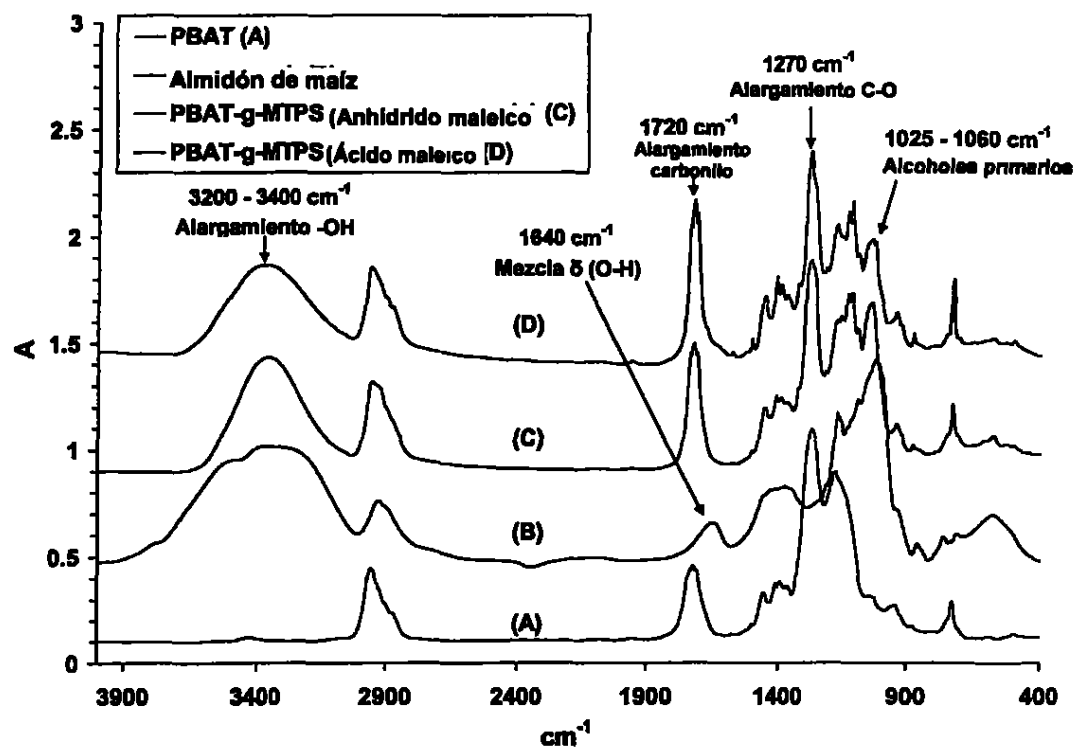


FIGURA 4

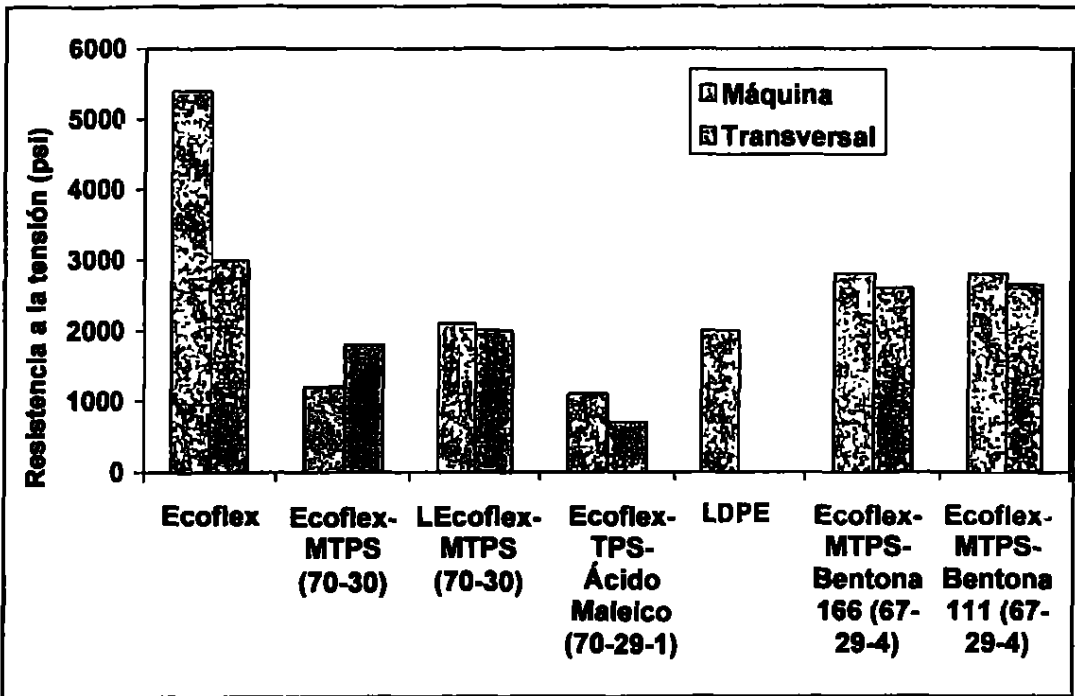


FIGURA 5

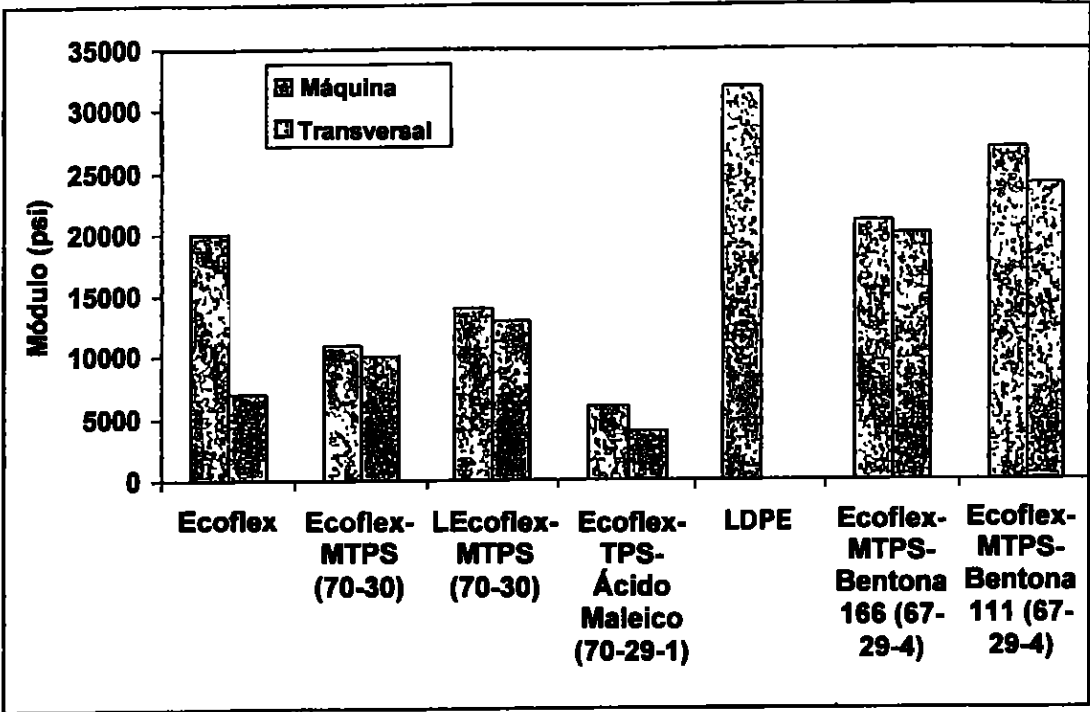


FIGURA 6

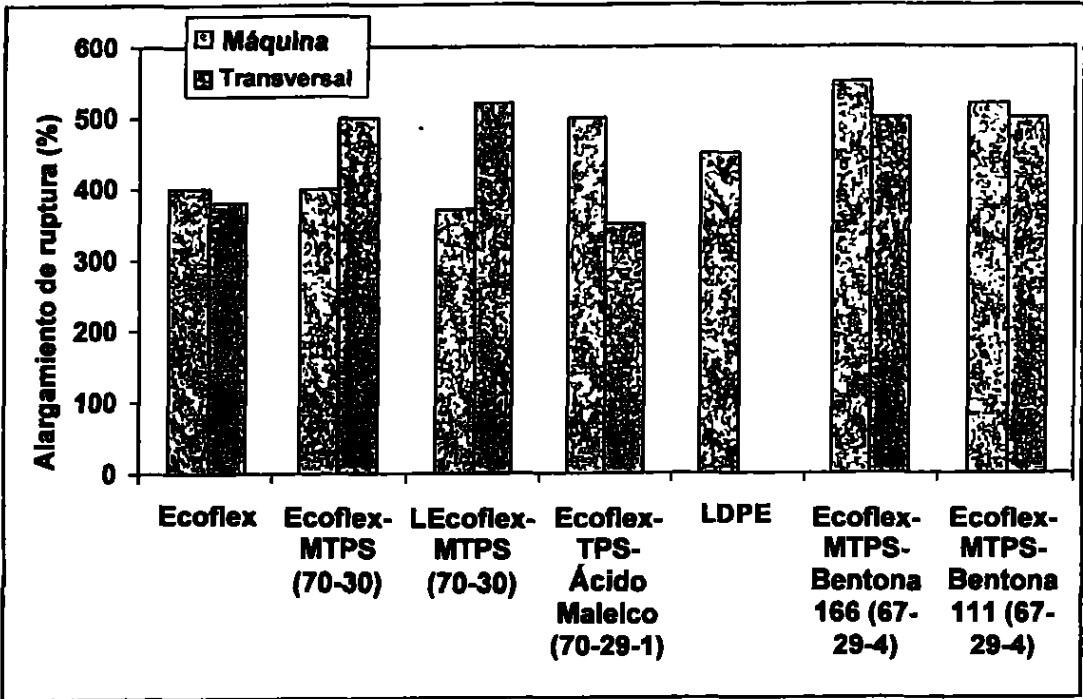


FIGURA 7

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From the INTERNATIONAL BUREAU

Ian C. McLeod

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To:

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FEB 21 2006

IAN C. McLEOD

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

Date of mailing (day/month/year) 06 February 2006 (06.02.2006)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference MSU 4:2-725 PCT	International application No. PCT/US2005/041238

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)

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Date of mailing (day/month/year) 06 February 2006 (06.02.2006)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference MSU 4.2-725 PCT	International application No. PCT/US2005/041238

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 19926, 19932 and 19934, 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 16 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 16-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 16-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(c)).

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 16-month time limit (and all other PCT time limits) is the filing date of the earliest application whose priority is claimed (Article 2(x)(b)).

TRANSMITT. LETTER TO THE
UNITED STATES RECEIVING OFFICE

Date	15 NOVEMBER 2005
International Application No.	
Attorney Docket No.	MSU 4.2-725 PCT

I. Certification under 37 CFR 1.10 (if applicable)

EQ 124511103 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	STARCH-POLYESTER BIODEGRADABLE GRAFT COPOLYMERS AND A METHOD OF PREPARATION THEREOF	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.	10/993,186	filed on	19 NOVEMBER 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
-------------------	-------------------

E. ☐ Fees as specified on attached Fee Calculation sheet form PCT/RO/101 annex

IV. ☒ A Request for Rectification under PCT 91 ☐ A Petition ☐ A Sequence Listing Diskette

V. ☐ Other (please specify):

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

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 4.2-725 PCT

Box No. I TITLE OF INVENTION STARCH-POLYESTER BIODEGRADABLE GRAFT COPOLYMERS AND A METHOD OF PREPARATION THEREOF	
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	

04

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)			
<i>If none of the following sub-boxes is used, this sheet should not be included in the request</i>			
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.) BALAKRISHNAN, 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.) 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	
State (that is, country) of nationality BE		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.) DUBOIS, Philippe Rue Grande, 1 4260 Cipleit 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			

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 <i>(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)</i>																											
Box No. VI PRIORITY CLAIM																											
The priority of the following earlier application(s) is hereby claimed <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th rowspan="2" style="width: 25%;">Filing date of earlier application (day/month/year)</th> <th rowspan="2" style="width: 20%;">Number of earlier application</th> <th colspan="3" style="text-align: center;">Where earlier application is</th> </tr> <tr> <th style="width: 20%;">national application country or Member</th> <th style="width: 20%;">regional application * regional Office</th> <th style="width: 15%;">international application receiving Office</th> </tr> <tr> <td>item (1) 19 NOVEMBER 2004 (19 11 2004)</td> <td>10/993,186</td> <td>US</td> <td></td> <td></td> </tr> <tr> <td>item (2)</td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>item (3)</td> <td></td> <td></td> <td></td> <td></td> </tr> </table>					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)	10/993,186	US			item (2)					item (3)				
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)	10/993,186	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) <i>(only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office)</i> 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 Organization for which that earlier application was filed (Rule 4.10(b)(ii))																											
Box No. VII INTERNATIONAL SEARCHING AUTHORITY																											
Choice of International Searching Authority (ISA) <i>(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)</i> ISA/US Request to use results of earlier search; reference to that search <i>(if an earlier search has been carried out by or requested from the International Searching Authority)</i> <table style="width: 100%;"> <tr> <td style="width: 40%;">Date (day/month/year)</td> <td style="width: 30%;">Number</td> <td style="width: 30%;">Country (or regional Office)</td> </tr> <tr> <td>19 NOVEMBER 2004</td> <td>10/993,186</td> <td>US</td> </tr> </table>					Date (day/month/year)	Number	Country (or regional Office)	19 NOVEMBER 2004	10/993,186	US																	
Date (day/month/year)	Number	Country (or regional Office)																									
19 NOVEMBER 2004	10/993,186	US																									
Box No. VIII DECLARATIONS																											
The following declarations are contained in Boxes Nos. VIII (i) to (v) <i>(mark the applicable check-boxes below and indicate in the right column the number of each type of declaration)</i> <table style="width: 100%;"> <tr> <th style="width: 80%;"></th> <th style="width: 20%; text-align: center;">Number of declarations</th> </tr> <tr> <td>☐ Box No. VIII (i) Declaration as to the identity of the inventor</td> <td></td> </tr> <tr> <td>☐ 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</td> <td></td> </tr> <tr> <td>☐ 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</td> <td></td> </tr> <tr> <td>☐ Box No. VIII (iv) Declaration of inventorship (only for the purposes of the designation of the United States of America)</td> <td></td> </tr> <tr> <td>☐ Box No. VIII (v) Declaration as to non-prejudicial disclosures or exceptions to lack of novelty</td> <td></td> </tr> </table>						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												
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☐ 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:	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
(a) on paper, the following number of sheets:	1 ☒ fee calculation sheet	
request (including declaration sheets) 4	2 ☐ original separate power of attorney	
description (excluding sequence listing and/or tables related thereto) 28	3 ☐ original general power of attorney	
claims 9	4 ☐ copy of general power of attorney, reference number, if any	
abstract 1	5 ☐ statement explaining lack of signature	
drawings 7	6 ☐ priority document(s) identified in Box No VI as item(s)	
Sub-total number of sheets 49	7 ☐ translation of international application into (language)	
sequence listing	8 ☐ separate indications concerning deposited microorganism or other biological material	
tables related thereto	9 ☐ sequence listing in electronic form (indicate type and number of carriers)	
(for both, actual number of sheets if filed on paper, whether or not also filed in electronic form, see (c) below)	(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)	
Total number of sheets 49	(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	
(b) ☐ only in electronic form (Section 801(a)(i))	(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column	
(i) ☐ sequence listing	10 ☐ tables in electronic form related to sequence listing (indicate type and number of carriers)	
(ii) ☐ tables related thereto	(i) ☐ copy submitted for the purposes of international search under Section 802(b-quater) only (and not as part of the international application)	
(c) ☐ also in electronic form (Section 801(a)(ii))	(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)	
(i) ☐ sequence listing	(iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column	
(ii) ☐ tables related thereto	11 ☐ other (specify)	
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the		
☐ 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 4.2-725 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 } 49
Where item (b) and (c) of Box No IX do not apply, enter Total number of sheets }

i1 first 30 sheets 1,211.00 **i1**

i2 19 x 13.00 = 247.00 **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 1,458.00 **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 2,058.00

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 13-0610

Date: 15 NOVEMBER 2005

Name Ian C McLeod

Signature Ian C McLeod

**STARCH-POLYESTER BIODEGRADABLE GRAFT
COPOLYMERS AND A METHOD OF PREPARATION THEREOF**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] None

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable.

STATEMENT REGARDING GOVERNMENT RIGHTS

[0003] None

BACKGROUND OF THE INVENTION

(1) Field of the Invention

[0004] The present invention relates to starch-polyester graft copolymers. The present invention particularly relates to a chemically modified starch-polyester graft copolymer and a chemically modified starch-nano clay polyester graft copolymer. A process of making these graft copolymers using reactive processing such as reactive extrusion is disclosed. The starch-polyester graft copolymers have improved processability, surface properties, and an extended range of mechanical properties.

(2) Description of Related Art

[0005] Plastic packaging is subjected to pressure from existing and proposed environmental and disposal regulations, and market based sustainability initiatives. It presents a major disposal problem for companies and municipalities as it is lightweight and bulky and so does not lend itself to a

99

viable economic and environmentally responsible recycling operation due to expensive handling and transportation costs. It is not biodegradable, which makes disposal in soil or composting operations untenable. Further, issues such as sustainability, industrial ecology, biodegradability, and recyclability are becoming major considerations in a company's product packaging design, especially with single use disposable packaging. Natural biopolymers provide biodegradable, sustainable solutions for the manufacture of short-life, single use disposable packaging, consumer goods, and marine plastics. Starch, an anhydroglucose polymer, offers a structural platform to manufacture sustainable, biodegradable packaging. Examples of patents that disclose the manufacture of starch and blends of starch and other polymers include U.S. Patent 4,673,438 to Wittwer et al.; U.S. Patent 4,095,054 to Lay et al.; U.S. Patent 5,256,711 to Tokiwa et al.; U.S. Patent 5,275,774 to Bahr et al.; U.S. Patent 5,382,611 to Stepto et al. and U.S. Patent 5,405,564 to Stepto et al. Lately, there have been business reports of the use of thermoplastic starch (TPS) as a component in multi phase blends (W. Wiedmann, and E. Strobel, Starch, 43, 138 (1991); R.L. Shorgen, G.F. Fanta, and W.M. Doan, Starch, 45, 276 (1993); P. Forssell, J. Mikkila, and T. Sourtti, J.M.S. Pure Appl. Chem., A33, 703 (1996); R. Narayan, Polymers from Agricultural Co products, ACS Symp Ser. (1994); and J.J.G. Van Soest, K. Benes, and D.de. Wit, Polymer, 37, 3543 (1996). Still others have manufactured thermoplastic starch blends in which native starch is initially blended with a small quantity of water and a less volatile plasticizer such as glycerin in order to form starch melts that are subjected to a degassing procedure prior to cooling and solidification in

order to remove substantially all of the water therefrom. Examples of such patents include U.S. Patents 5,412,005, 5,280,055, 5,288,765, 5,262,458, 5,462,980 and 5,512,378 to Bastioli et al.

[0006] Starch granules exhibit hydrophilic properties and strong inter-molecular association via hydrogen bonding due to the hydroxyl groups on the granule surface. The hydrophilicity and thermal sensitivity render the starch polymer unsuitable for thermoplastic applications. In this respect, some authors have emphasized on finding the optimal polymer or mixture of polymers and other admixtures in order to thereby "optimize" the properties of the starch. One drawback is that most of the polymers and other admixtures are themselves significantly more expensive than starch, which tends to increase the cost of such polymer blends compared to starch melts. Another drawback is that such additives will only be able to marginally alter the mechanical properties of the starch/polymer blends when viewed from a materials science perspective.

-[0007] In order to improve on these drawbacks, graft copolymerization of vinyl monomer on the starch backbone was used to modify starch. Fanta and Bagley have reviewed the synthesis and discussed some applications of starch graft copolymers (G.F. Fanta and E.B. Bagley, Encyclopedia of Polymer Science, John Wiley & Sons: New York (1970); and G.F. Fanta, Block and Graft Copolymers- Vol I, John Wiley & Sons: New York (1973). Otey et al. (F.H. Otey, R.P. Westhoff and W.M. Doane, Industrial Engineering Chemistry Products Research Development, 19, 592 (1980); F.H. Otey and R.P. Westhoff, Industrial Engineering Chemistry Products Research Development, 23, 284 (1984); and F.H. Otey, R.P. Westhoff and W.M. Doane, Industrial

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Engineering Chemistry Products Research Development, 26, 1659 (1987)) blended starch with poly (ethylene-co-acrylic acid) (EAA). In these papers, the authors suggested the formation of hydrogen bonds between the carboxylic group in EAA and the hydroxyl group in starch. Increasing the level of starch decreased the percentage elongation of the film and increased the diffusion rate of water. Similar complexes like EAA can also be formed with the hydroxyl groups of the polyethylene-vinyl alcohol (EVOH) copolymer. They report a reaction between the anhydride group in the synthetic polymer with the -OH groups of starch. U.S. Patent 5,462,983 to Bloembergen et al. reports on blends and alloys containing lignocelluloses like starch, cellulose acetate etc. U.S. Patent 5,314,934 to Tomka et al. provides a process to produce a polyolefin-starch polymer blend. Ethylene/acrylate/maleic anhydride terpolymer was used as a compatibilizer. These blends were reported to be blown into film with properties comparable to LDPE. U.S. Patent 5,234,977 to Bastioli et al. discloses a material used for the production of biodegradable articles in film, sheet or fiber form, which can be produced by extrusion from a molten mass that includes a synthetic thermoplastic polymer and a destructured starch to which a boron containing compound such as boric acid has been added. U.S. Patent 6,277,899 to Bastioli et al. discloses a polymeric composition comprising filler melt-dispersed in a matrix comprising, a destructure starch component, a synthetic thermoplastic polymeric component and a fluidizing agent. U.S. Patent 5,412,005 to Bastioli et al. discloses biodegradable polymeric compositions containing a starch based component and a polymeric component, preferably polymers of ethylene-vinyl alcohol or polyvinylalcohol.

[0008] U.S. Patent Nos. 6,235,816 and 6,472,497 describe starch polyester blends.

[0009] Other references are:

(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

[0010] It is therefore an object of the present invention to provide novel grafted starch polyester compositions which have

novel properties. It is further an object of this invention to provide economical and reproducible compositions. These and other objects will become increasingly apparent from the following description.

SUMMARY OF THE INVENTION

[0011] The present invention relates to a starch-polyester graft copolymer composition comprising starch or chemically modified starch with segments of a polyester grafted onto the starch. Preferably the chemically modified starch is a starch which is thermoplastic. Preferably the composition comprises about 0.5 to 10% by weight of the composition of a plasticizer. Preferably the composition contains natural or an organically modified nanoclay. Preferably the starch is selected from the group consisting of corn, potato, wheat, rice, sago, tapioca, waxy maize, sorghum and high amylose starch. Preferably the chemically modified plasticized starch (CMPS) is prepared from a reactively extruded 50% to 80% by weight of the starch, a chemical modifier from 0.5% to about 10% by weight of the starch, a plasticizer from 10 to 50 wt-% of the composition, and optionally a free radical initiator in an amount ranging between 0.01 to 2.0 wt % of the composition. Preferably the chemically modified plasticized starch (CMPS) is prepared from a blend comprising starch polymer, from 50% to 80% by weight, a chemical modifier from 0.5% to about 10% by weight of the starch polymer, more preferably from 2% to 5% by weight of the starch, a plasticizer from 10 to 50 wt-% of the composition, a nanoclay, wherein the nanoclays are added in an amount ranging from 0.5 to 25 wt% of the total composition. Preferably the plasticizer is selected from the group consisting of polyhydric

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alcohols like glycerol, sorbitol, and ethylene glycol. Preferably the modifier is selected from the group consisting of dibasic acids or their anhydrides. Preferably the composition contains a free radical initiator. Preferably the free radical initiator is a peroxide. Preferably the composition contains a nanoclay selected from a group consisting of montmorillonite, smectite, hectorite, and mixtures thereof. Preferably the composition is completely biodegradable. Preferably the composition has been grafted in a melt phase in an extruder. Preferably the composition has been grafted in a twin screw extruder at a temperature in the range of 100°C-200°C.

[0012] The present invention also relates to a process for the preparation of a starch polyester graft co-polymer composition which comprises blending a mixture of an organic acid or anhydride of the acid with starch or a chemically modified starch and a polyester polymer at a temperature which grafts the segments of a polyester onto the starch to form the composition.

[0013] Most preferably the present invention relates to a starch based copolymer 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 organic anhydride of a dibasic organic acid and mixtures thereof, a plasticizer, a biodegradable polyester resin, a nanoclay, and optionally a free radical initiator, wherein the mixture has been extruded, with heating and venting of water from the mixture.

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[0014] Most preferably the present invention also relates to a process for preparing a starch based composition which comprises reactively extruding a mixture 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 organic anhydride of a dibasic organic acid and mixtures thereof, a plasticizer, a biodegradable polyester resin, a nanoclay, and optionally a free radical initiator, wherein the mixture has been extruded, with heating and venting of water from the mixture.

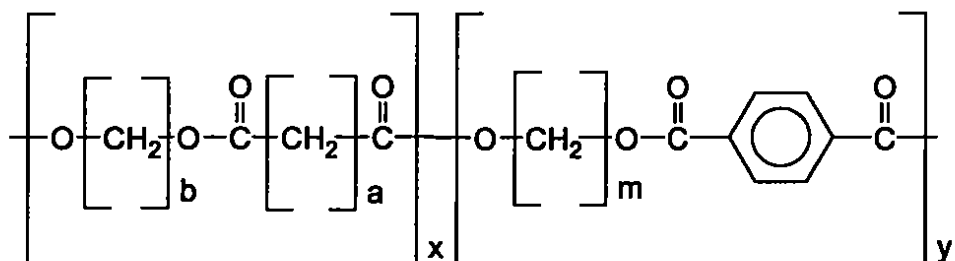
[0015] In the present invention the mechanism of reaction is that the fragments of a polyester resin from the processing react with hydroxyl groups of the starch. The acid or anhydride reacts with the polyester polymer to produce the reactive fragments. Thus the present invention provides a unique composition with the fragments of the polyester polymer bonded to the starch.

[0016] The present invention particularly provides new amphiphilic, starch-polyester graft copolymer and chemically modified starch-polyester graft copolymer compositions comprising a chemically modified starch or chemically modified starch-nanoclay product produced continuously in a twin-screw co-rotating extruder. The chemically modified plasticized starch product with lower viscosity and good processability and the chemically modified plasticized starch-nano clay product is described in the copending patent application. The starch-polyester graft copolymers of the present invention can be readily blown, extrusion cast into film, and molded. Examples of biodegradable polyesters include poly(caprolactone) (PCL),

poly(vinylacetate-co-vinylalcohol) (PVAc/VA), poly(lactic acid) or polylactide (PLA), poly(glycolic acid) or polyglycolide (PGA), and related copolyesters including the various combinations of stereoisomers, bacterial and synthetic poly(.beta.-hydroxybutyrate) (PHB), Poly(.beta.-hydroxybutyrate-co-.beta.-hydroxyvalerate) (PHB/V), and other poly(.beta.-hydroxyalkanoates) (PHA), biodegradable aliphatic polyesters, and aliphatic-aromatic copolyesters. Preferably the polyester is selected from the group consisting of the composition in which the polyester is selected from the group consisting of:



where R is lower alkyl and aromatic groups containing 1 to 12 carbon atoms; n is 0 to 10; and x is 200 to 2000; and



, where a, b and m are 2 to 8; and x/y is between 3/2 and 10/1.

[0017] The present invention provides new polymeric materials, which are environmentally responsible and fully biodegradable as per ASTM standards.

[0018] In accordance with the present invention, there is provided a biodegradable moldable product or film prepared from a graft copolymer containing starch or chemically modified starch or chemically modified starch-nano clay composition and a polyester, which is preferably biodegradable. It has been found that new starch-polyester graft copolymers with good elongation, compressibility and surface properties.

[0019] In one embodiment of this invention, starch is extruded with aliphatic-aromatic co-polyester and particularly poly butylenes (adipate-co-terephthalate) in the presence of maleic acid as a trans-esterification catalyst to form starch-polyester graft copolymers compositions with good elongation, compressibility and surface properties. In another embodiment chemically modified starch or a chemically modified starch-nano clay product has been reacted with aliphatic and aliphatic-aromatic copolyesters to provide new graft copolymer products with enhanced properties and processability.

BRIEF DESCRIPTION OF THE FIGURES

[0020] Figure 1 is a diagram of an extrusion apparatus for the production of polyester grafted starch.

[0021] Figures 2A, 2B and 2C are drawings depicting the screw configuration used for the reactive extrusion production of the novel graft copolymers. The screw configuration is divided into three sections (Figure 2A) followed by (Figure 2B)

and further followed by (Figure 2C).

[0022] Figure 3 is a graph showing the FTIR results of graft copolymers of ECOFLEX™, (poly (butylene adipate-co-terephthalate)), obtained from BASF (Germany), with plasticized starch (PS). To validate the reactivity, FTIR scans of pure ECOFLEX™, PS and ECOFLEX™/PS blend (without the catalyst) are also shown.

[0023] Figure 4 is a graph showing the FTIR results of graft copolymers of ECOFLEX™ with CMPS (made using both maleic anhydride and maleic acid modifiers). To validate the reactivity, FTIR scans of pure ECOFLEX™ and regular cornstarch are also shown.

[0024] Figure 5 shows bar graphs depicting tensile strength values of ECOFLEX™, graft copolymer of ECOFLEX™ with CMPS, graft copolymer of cross-linked ECOFLEX™ with CMPS, graft copolymer of ECOFLEX™ with PS and LDPE.

[0025] Figure 6 shows bar graphs depicting modulus of elasticity values of ECOFLEX™, graft copolymer of ECOFLEX™ with CMPS, graft copolymer of cross-linked ECOFLEX™ with CMPS, graft copolymer of ECOFLEX™ with PS and LDPE.

[0026] Figure 7 shows bar graphs depicting break elongation values of ECOFLEX™, graft copolymer of ECOFLEX™ with CMPS, graft copolymer of cross-linked ECOFLEX™ with CMPS, graft copolymer of ECOFLEX™ with PS and LDPE.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The starting starch material useful in this invention

can be any of several starches, native or modified. Such starches include those derived from any plant source including corn, potato, wheat, rice, sago, tapioca, waxy maize, sorghum and high amylose starch, i.e., starch having at least 40% and more particularly at least 65% by weight of amylose content, such as high amylose corn, etc. Starch flours can also be used as a starch source. Also included are the conversion products derived from any of the former bases including, for example, dextrin prepared by hydrolytic actions of acid and/or heat; oxidized starches prepared by treatment with oxidants such as sodium hypochlorite; fluidity or thin boiling starches prepared by enzyme conversion or mild acid hydrolysis; and derivatized and crosslinked starches. The starch percentage in the final blend is 5% to 45% by weight and preferably from 10% to 30% by weight.

[0028] The plasticizers are polyhydric alcohols, preferably glycerol sorbitol, ethylene glycol and mixtures thereof. Plasticizer concentration in the final blend is 5% to 50% by weight and preferably from 5% to 20% by weight is preferred.

[0029] Modified starches could also be used in this invention. By modified it is meant that the starch can be derivatized or modified by typical processes known in the art, e.g., esterification, etherification, oxidation, acid hydrolysis, crosslinking and enzyme conversion. Typically, modified starches include esters, such as the acetate and half-esters of dicarboxylic acids, particularly the alkenylsuccinic acids; ethers, such as the hydroxyethyl and hydroxypropyl starches and cationic starches such as starch modified with 2-diethylaminoethyl chloride (DEC) and starch modified with

quaternary ammonium reagents such as 3-chloro-2-hydroxypropyltrimethylammonium chloride; starches oxidized with hypochlorite; starches reacted with crosslinking agents such as phosphorus oxychloride, epichlorohydrin, and phosphate derivatives prepared by reaction with sodium or potassium orthophosphate or tripolyphosphate and combinations thereof. These and other conventional modifications of starch are described in publications such as "Starch: Chemistry and Technology", Second Edition, Edited by Roy L. Whistler, et al., chapter X; Starch Derivations: Production and Uses by M. W. Rutenberg, et al., Academic Press, Inc. 1984.

[0030] Examples of biodegradable polyester polymers include poly(caprolactone) (PCL), poly(vinylacetate-co-vinylalcohol) (PVAc/VA), poly(lactic acid) or polylactide (PLA), poly(glycolic acid) or polyglycolide (PGA), and related copolyesters including the various combinations of stereoisomers, bacterial and synthetic poly(-hydroxybutyrate) poly(.beta.-hydroxybutyrate-co-.beta.-hydroxyvalerate) (PHB/V), and other poly(.beta.-hydroxyalkanoates) (PHA), and aliphatic-aromatic biodegradable polyesters such as ECOFLEX™.

[0031] In forming starch-polyester graft copolymers of this invention, the selected starch starting material is preferably reacted with biodegradable polyester polymers in the presence of maleic anhydride or maleic acid or mixtures thereof, which functions as a trans-esterification catalyst.

[0032] The maleic anhydride and/or its hydrolyzed acid counterpart is combined with the starch or the plasticized starch in an amount of from about 0.1 to 10% by weight of

anhydride (or acid) and preferably about 0.5 to 4% anhydride (or acid) based on the dry weight of starch. The anhydride or hydrolyzed acid is usually added in the form of a fine powder and is co-extruded with the biodegradable polyester by adding it directly to the extruder. In the case of using maleated starches, maleic anhydride already present in the system functions as a catalyst and hence there is no need to add again. Other organic diacids or anhydrides can be used as described in our copending application, which is incorporated herein by reference.

[0033] While any starch may be used in this invention as noted previously, the starch materials that are particularly useful in this invention are corn, potato, tapioca and high amylose starch; i.e., starch containing at least 40% by weight and preferably at least 65% by weight of amylose. Further preferred are the starches that are modified by maleation, especially using maleic anhydride or maleic acid. Blends of two or more of the starch starting materials may be used as well as additive or synthetic compounds to improve properties such as water resistance, strength, flexibility, color, etc.

[0034] The apparatus used in carrying out the extrusion process can be any screw type extruder. While the use of a single or twin screw extruder can 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.

[0035] 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.

[0036] Variations in any of the elements used in the extruder can 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.

[0037] In carrying out the extrusion process, temperatures in the extruder vary depending on the particular material, desired properties and application. They generally range from about 100°C to 250°C, and preferably will range from about 150°C to 210°C. The total moisture content of the starch in the extruder, i.e., moisture present in the inlet feed starch as well as water in the aqueous anhydride and/or acid, is about 25% or less by weight, based on the weight of starch. More

particularly, the total moisture content of the starch ranges from about 8 to 25% preferably about 10 to 21% and more preferably from about 15 to 21 % by weight, based on the weight of starch.

[0038] Further, the starch-polyester graft copolymers can be manufactured in a one-step process; wherein the starch is first plasticized in a first section of the extruder followed by addition of the polyester along-with a trans-esterification catalyst to form the starch-polyester graft copolymer. Further, starch can be maleated using maleic anhydride or maleic acid in the presence of glycerol plasticizer in the first section of the extruder, followed by addition of the polyester downstream to form the starch-polyester graft copolymer.

[0039] By utilizing the starch-polyester graft copolymer, the overall processing temperature can be reduced to well below the processing temperature of the pure polyester component. This is particularly important for manufacturing with high-melting polyesters such as PHB and PHB/V, which thermally degrade at higher processing temperatures and therefore have a narrower processing window. This improvement is attributed to the compatibility achieved by the reactive blending process, resulting in changes in the crystalline microstructure of the polyester component and/or the morphology of the multi-phase material thereby rendering it processable at lower processing temperatures. It is important that the compounds be compatible.

[0040] The compositions of the present invention can retain their biodegradability if a degradable polyester polymer is used. The water resistance of the starch and modified starches

is improved by graft copolymerization with high molecular weight biodegradable polyesters, especially with semi-crystalline polyesters such as PCL or PHB/V, and similar biodegradable polyesters. This is further achieved by engineering the appropriate blend composition, through the choice of polyester, starch and plasticizer.

[0041] The present invention can be processed by various methods known in the art, such as extrusion pelletizing, injection molding, and film forming. For example, the starch-polyester graft copolymer compositions made in accordance with the present invention can be injection molded to give a variety of molded products, and extrusion cast or even solution cast to give translucent flexible films, as well as transparent films.

[0042] The following experimental examples demonstrate the utility of the present invention for forming biodegradable products containing a biodegradable starch or plasticized starch and biodegradable polyester in the presence of a transesterification catalyst.

[0043] Examples of materials made in accordance with the present invention in compost experiments confirm biodegradability.

Example 1

[0044] The synthesis of ECOFLEX™(PBAT) - plasticized starch (PS) graft copolymers was accomplished in a twin-screw co-rotating CENTURY extruder using maleic acid as a transesterification catalyst. PS was produced by plasticization of regular corn-starch, obtained from Corn Products, Inc. (Chicago, IL) (moisture content of 12%) using glycerol (20-wt

%) as a plasticizer in the same extruder. Maleic acid, obtained from Aldrich, was ground to a fine powder using a mortar and pestle and pre-blended with the ECOFLEX™ polyester (poly (butylene adipate-co-terephthalate)), obtained from BASF (Germany)) before being fed to the feed port of the extruder. The concentration of maleic acid used was 1-wt% with respect to the total concentration. Meanwhile, PS, previously oven dried overnight at 50°C, was ground to a fine powder and fed using an external feeder to the feed port of the extruder. The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (ECOFLEX™ + Maleic acid): PS. The temperature profile is shown in Figure 1 and Table 1, and the screw configuration used is shown in Figure 2, respectively. In Figures 2A, 2B and 2C, the entire screw configuration is divided into 3 sections; section 1 of 12.5D distance followed by section 2 of 15.5D distance and finally section 3 with 12D distance. The vent port was kept open to remove unreacted maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line.

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[0045] Table 1: Extrusion Processing Conditions in the synthesis of ECOFLEX-(PS/CMPS) graft copolymers

ZONE	SET	ACTUAL	UNITS
ZONE1	15	70	C
ZONE2	95	99	C
ZONE3	125	122	C
ZONE4	145	149	C
ZONE5	160	170	C
ZONE6	165	192	C
ZONE7	165	196	C
ZONE8	165	193	C
ZONE9	150	185	C
DIE	145	153	C
MELT TEMP.		153	C
MOTOR SPEED		254	RPM
TORQUE		67	%
PRESSURE		92	Psia
FEEDER SPEED, CENTURY (Ecoflex + Maleic acid)		135 (~8 lb/hr)	%
FEEDER SPEED, MINI			%
FEEDER SPEED, EXT (TPS)		0.80 (3 4 lb/hr)	%

[0046] The resulting pellets were dried in an oven overnight at 75°C. The pellets were totally extracted in Dichloro methane using a Soxhlet extraction unit. The extracted graft copolymer solution was cast to form transparent films. FTIR analysis (Figure 3) of the films confirmed reactivity and the true existence of a graft copolymer.

Example 2

[0047] The procedure of Example 1 was followed using PCL™ (Poly (epsilon-caprolactone), obtained from Dow Chemical (Midland, MI); Molecular weight of 70,000 g/mol) polyester instead of ECOFLEX™. The resulting pellets were also dried in an oven overnight at 75°C. The pellets were totally extracted in Dichloro methane using a Soxhlet extraction unit. The extracted graft copolymer solution was cast to form transparent films. FTIR analysis of the films confirmed reactivity and the true existence of a graft copolymer.

Example 3

[0048] The synthesis of starch-polyester graft copolymers was carried out as follows: Chemically modified plasticized starch (CMPS), produced by reactive extrusion processing of regular corn-starch, obtained from Corn Products (Chicago, IL), using maleic acid modifier, and glycerol (20-wt%) plasticizer as explained in the co-pending patent application was oven dried overnight at 75°C and ground to a fine powder and fed using an external feeder to the feed port of the extruder. This composition is described in Applicants' co-pending application which is incorporated herein by reference. ECOFLEX™ was also fed to the feed port of the extruder using CENTURY™ feeder (Traverse City, MI). The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (ECOFLEX: CMPS). The temperature profile and the screw configuration used are similar to Example 1. The vent port was kept open to remove unreacted maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at 75°C, to remove surface moisture. The pellets were

totally extracted in Dichloro methane using a Soxhlet extraction unit. The extracted graft copolymer solution was cast to form transparent films. FTIR analysis of the films (Figure 4) confirmed reactivity and the true existence of a graft copolymer.

Example 4

[0049] The synthesis of starch-polyester graft copolymers was carried out as follows: Chemically modified plasticized starch (CMPS), produced by reactive extrusion processing of regular corn-starch, obtained from Corn Products, using maleic acid modifier, BENTONE 166™ (BENTONE 166™ is an alkylaryl ammonium hectorite clay, obtained from Elementis Specialties, with greatly improved dispersibility characteristics. It provides excellent mechanical strength, flame retardancy and highly improved gas barrier properties) and glycerol (20-wt%) plasticizer as explained in the co-pending patent application was oven dried overnight at 75°C and ground to a fine powder and fed using an external feeder to the feed port of the extruder. ECOFLEX™ was also fed to the feed port of the extruder using the CENTURY™ feeder. The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (ECOFLEX: CMPS). The temperature profile and the screw configuration used are similar to Example 1. The vent port was kept open to remove maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at 75°C, to remove surface moisture.

Example 5

[0050] The synthesis of starch-polyester graft copolymers was

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carried out as follows: Chemically Modified plasticized starch (CMPS), produced by reactive extrusion processing of regular corn-starch, obtained from Corn Products, using maleic acid modifier, BENTONE 111™ (BENTONE 111™ is an organic derivative of a special smectite clay, obtained from Elementis Specialties. It provides excellent mechanical strength, flame retardancy and highly improved gas barrier properties) and glycerol (20-wt%) plasticizer as explained in the co-pending patent application was oven dried overnight at 75°C and ground to a fine powder and fed using an external feeder to the feed port of the extruder. ECOFLEX™ was also fed to the feed port of the extruder using CENTURY™ feeder. The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (ECOFLEX: CMPS). The temperature profile and the screw configuration used are similar to Example 1. The vent port was kept open to remove maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at 75°C, to remove surface moisture.

Example 6

[0051] The procedure given in Example 3 was followed using polycaprolactone (PCL) polyester instead of ECOFLEX™. The resulting pellets were also dried in an oven overnight at 75°C. The pellets were totally extracted in dichloromethane using a Soxhlet extraction unit. The extracted graft copolymer solution was cast to form transparent films. FTIR analysis of the films confirmed reactivity and the true existence of a graft copolymer.

Example 7

[0052] ECOFLEX™ and cross-linked ECOFLEX™ (Cross-linked using a free radical initiator) were melt extruded with PS and CMPS in different proportions according to the procedure as explained in Example 3. All the samples were extracted in dichloromethane using a Soxhlet apparatus. The results of the extraction are shown in Table 2.

[0053] Table 2: Soxhlet Extraction results of ECOFLEX-CMPS graft copolymers

System	Polyester (Ecoflex or LEcoflex) initially present (gm)	Starch component (PS or CMPS) initially present (gm)	Material extracted (gm)	% Extracted
Ecoflex/CMPS (70/30;w/w)	1.3510	0.579	1.8878	98
Ecoflex/CMPS (60/40;w/w)	1.0682	0.7122	1.7010	96
Ecoflex/CMPS (50/50;w/w)	0.7998	0.7998	0.7503	47
Ecoflex/CMPS (40/60;w/w)	0.8639	0.5759	0.5513	38.2
Ecoflex/CMPS (70/30;w/w) No Initiator used in the preparation of CMPS.	1.9018	0.8150	2.6530	98
Ecoflex/PS (70/30;w/w)	1.2075	0.5175	1.2595	71
LEcoflex/CMPS (65/35;w/w)	3.25	1.748	4.1272	83
LEcoflex/PS (70/30;w/w)	1.0225	0.4382	1.0602	73

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[0054] As seen from Table 2, almost complete extraction is achieved for ECOFLEX™/CMPS (70/30 w/w and 60/40 w/w) graft copolymers. When this solution was cast, a transparent film was obtained. This proves that ECOFLEX™ and CMPS are covalently linked making the graft copolymer extractable in Dichloromethane (solvent wherein ECOFLEX™ is soluble, but PS is not). However, due to the insolubility of PS in the solvent, the graft copolymer forms a colloidal dispersion and not a clear transparent solution.

[0055] This result is applicable even to blends containing CMPS made with no peroxide (see row 6 in Table 2). However, for the 50/50 and 40/60 blends, only 47% and 38% respectively (close to the respective ECOFLEX™ amount) were extracted out. This confirms the fact that ECOFLEX™ has not reacted with CMPS. Thus, the reaction is also dependent on the relative amounts of the polyester and CMPS phases present. Also, from Table 2 (rows 7 and 9), it is clearly seen that when PS is used instead of CMPS, there is very minimal or no reaction taking place. This suggests that the reaction between the hydroxyl groups in starch and the ester functionalities in ECOFLEX™ occurs only in the presence of a trans-esterification catalyst such as maleic acid. When ECOFLEX™ polyester was cross-linked and reactively blended with CMPS, around 83% of the polyester was extracted out. This could be due to the fact that certain gel (network) portions of the cross-linked polyester are impermeable to chemical reaction.

Example 8

[0056] Several graft copolymer samples, prepared using both

PS and CMPS according to procedures explained in Examples 1, 3, 4 and 5 were extruded into films. Films were made using a Killion™ (Pawcatuck, CT) single-screw blown film unit. The screw diameter was 25.4 mm with L: D ratio of 25:1. The die inner diameter was 50.8 mm with a die gap size of 1.5 mm. The blown film processing conditions are shown in Table 3.

[0057] Table 3: Blown Film Processing Conditions for ECOFLEX-(PS/CMPS) graft copolymers

Set (°F)	70	350	355	360	360	395	395	300
Actual (°F)	73	351	358	357	360	380	395	300

Melt (°F)	364
Screw Speed (RPM)	12.4
FPM (ft/min)	5-6
Pressure (psi)	500-1000

[0058] Tensile properties of the films were determined using INSTRON™ Mechanical Testing Equipment fitted with a 100 lbs load cell. The crosshead speed was 1 inch per minute. Rectangular film samples, 4'x1' dimension were conditioned at 23°C and 50% Relative Humidity for 40 hours before being tested according to ASTM D-882 testing. The results of the testing are shown in Figures 4, 5 and 6. It is observed that the tensile strength and modulus of elasticity values of ECOFLEX™-PS graft copolymer, containing around 30% PS, exhibit almost a six fold decrease as compared to pure ECOFLEX™ polyester values. However, ECOFLEX™/CMPS graft copolymers and cross-linked

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ECOFLEX™ (ECOFLEX)/CMPS graft copolymers exhibit tensile values comparable to LDPE. Also, on incorporation of clay in the production of Ecoflex™/CMPS, the film tensile strength further improves to about 2800 - 3000 psi (twice as much as ECOFLEX™/CMPS). Break elongation values of the graft copolymer are higher than ECOFLEX™ and LDPE. Tear and Puncture properties, determined according to ASTM D1922 and ASTM F1306 respectively, were found to be comparable to LDPE. (Table 4)

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Table 4: Tear and Puncture properties of ECOFLEX-CMPS (70/30) graft copolymer

Material	Thickness (in)	Tear (g) MD ASTM D 1922	Tear (g) CMD ASTM D 1922	Puncture Max. (lb _f) ASTM F 1306	Puncture Ext. (in) ASTM F 1306
LDPE	0.0010- 0.0015	100- 300	-	1.5-3.0	-
Ecoflex-MTPS (70/30) graft copolymer	0.0010- 0.0015	767.7	802.7	1.515	0.6219

[0059] The above examples demonstrate that the present invention provides new starch-based graft copolymers which utilize agricultural resources that can be returned back to nature in an environmentally sound manner. The polymeric materials made in accordance with the present invention are environmentally compatible, this being achieved by designing and engineering fully biodegradable materials that are

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thermoplastic, yet breakdown under appropriate environmental conditions in a manner similar to their lignocellulosic counterparts.

[0060] 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 starch-polyester graft copolymer composition comprising starch or chemically modified starch with segments of a polyester grafted onto the starch.
2. The composition of Claim 1 wherein the chemically modified starch is a starch which is thermoplastic.
3. The composition of Claim 1 further comprising about 0.5 to 25% by weight of the composition of a plasticizer.
4. The composition of Claim 1 containing natural or an organically modified nanoclay.
5. The composition of Claim 1 or 2 wherein the starch is selected from the group consisting of corn, potato, wheat, rice, sago, tapioca, waxy maize, sorghum and high amylose starch.
6. The composition of Claim 1 or 2 wherein the starch is chemically modified starch and is prepared from a reactively extruded 50% to 80% by weight of the starch, a chemical modifier from 0.5% to about 10% by weight of the starch, a plasticizer from 10 to 50 wt-% of the

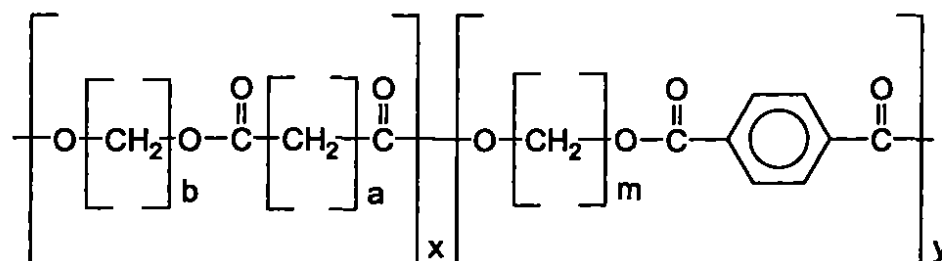
composition, and optionally a free radical initiator in an amount ranging between 0.01 to 2.0 wt % of the composition.

7. The composition of Claim 1 or 2 which is prepared from a blend comprising starch polymer, from 50% to 80% by weight, a chemical modifier from 0.5% to about 10% by weight of the starch polymer, more preferably from 2% to 5% by weight of the starch, a plasticizer from 10 to 50 wt-% of the composition, a nanoclay, wherein the nanoclays are added in an amount ranging from 0.5 to 25 wt % of the total composition.

8. The composition of Claim 1 wherein the polyester is selected from the group consisting of



where R is lower alkyl and aromatic groups containing 1 to 12 carbon atoms; n is 0 to 10; and x is 200 to 2000; and



, where a, b and m are 2 to 8; and x/y is between 3/2 and 10/1.

9. The composition of Claim 1 in which the polyester is 50 to 90 wt-% of the composition.

10. The composition as set forth in Claim 1 or 2 wherein the plasticizer is polyhydric alcohol.

11. The composition as set forth in Claim 1 or 2 wherein a modifier for the chemically modified starch is selected from the group consisting of dibasic acids and their anhydrides.

12. The composition of Claim 1 or 2 further comprising a free radical initiator.

13. The composition of Claim 1 or 2 further comprising a free radical initiator which is a peroxide.

14. The composition of Claim 1 or 2 further comprising a nanoclay selected from a group consisting of montmorillonite, smectite, hectorite, and mixtures thereof.
15. The composition of Claim 1 or 2 which is completely biodegradable.
16. The composition of Claim 1 or 2 which has been grafted in a melt phase in an extruder.
17. The composition of Claim 1 or 2 which has been grafted in a twin screw extruder at a temperature in the range of 100°C-200°C.
18. A process for the preparation of a starch polyester graft co-polymer composition which comprises blending a mixture of an organic acid or anhydride of the acid with starch or a chemically modified starch and a polyester at a temperature which grafts the segments of a polyester onto the starch to form the composition.
19. The process of Claim 18 wherein the blending is in an extruder at a temperature between about 100 to 200°C.

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20. The process of Claim 18 or 19 wherein the organic acid is a dibasic acid.

21. The process of Claim 18 or 19 wherein the organic acid is a dibasic acid produced in situ in the blending by reaction of an anhydride with water contained in the starch.

22. The process of Claim 18 or 19 wherein the composition in addition comprises a plasticizer.

23. The process of Claim 18 or 19 wherein in addition a peroxide initiator is mixed into the blend.

24. The process of Claim 18 wherein in addition a nanoclay is in the blend.

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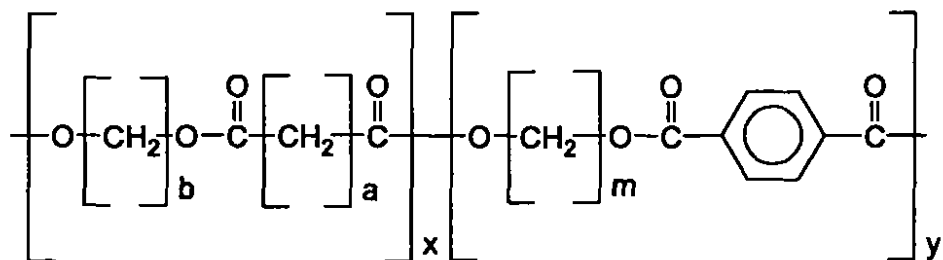
25. A starch based copolymer composition which comprises a reactively extruded mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an organic anhydride of a dibasic organic acid and mixtures thereof, a plasticizer, a biodegradable polyester, and optionally a free radical initiator, wherein the mixture has been extruded, with heating and venting of water from the mixture.
26. The composition of Claim 24 wherein the starch is selected from the group consisting of cornstarch, potato starch, tapioca starch, rice starch, wheat starch, and cassava starch.
27. The composition of Claim 24 wherein the starch is about 5% to 90% by weight of the mixture.
28. The composition of Claim 24 wherein the starch is an unmodified, oxidized or thin boiling starch of 0 to 95 degree of fluidity.
29. The composition of Claim 24 wherein the starch has moisture content of about 0.5% to 15% by weight.

30. The composition of Claim 24 wherein the starch is in a pulverized form.

31. The composition of Claim 24 in which the polyester is selected from the group consisting of:



where R is lower alkyl and aromatic groups containing 1 to 12 carbon atoms; n is 0 to 10; and x is 200 to 2000; and



, where a, b and m are 1 to 8; and x/y is between 3/2 and 10/1.

32. The composition of Claim 24 in which the polyester is 50 to 90 wt-% of the composition.

33. The composition as set forth in Claim 24 wherein the plasticizer is selected from the group consisting of polyhydric alcohols like glycerol, sorbitol, ethylene glycol and mixtures thereof.

34. The composition as set forth in Claim 24 further comprising a polyhydroxy organic plasticizer in an amount between 10 to 70 wt-% of the mixture.

35. The composition as set forth in Claim 24 wherein the chemical modifier is a cyclic dibasic acid anhydride.

36. The composition of Claim 24 wherein the organic anhydride or organic acid is selected from the group consisting of maleic-, succinic-, itaconic-, phthalic- and mixtures thereof.

37. The composition of Claim 24 wherein the starch is from 50% to 80% by weight of the mixture.

38. A process for preparing a starch based composition which comprises reactively extruding a mixture which comprises a mixture of a biodegradable starch polymer, a chemical modifier selected from the group consisting of a dibasic organic acid, an organic anhydride of a dibasic organic acid and mixtures thereof, a plasticizer, a biodegradable polyester resin, and optionally a free radical initiator, wherein the mixture has been extruded, with heating and venting of water from the mixture.

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ABSTRACT OF THE DISCLOSURE

A starch-polyester graft copolymer and chemically modified starch-polyester graft copolymer composition comprising a chemically modified starch or chemically modified starch-nanoclay product is described. The composition can be produced continuously in a twin-screw co-rotating extruder. The starch-polyester graft copolymer can be solvent cast, melt cast and blown into clear transparent film particularly for use in single use disposable applications and can be biodegradable.

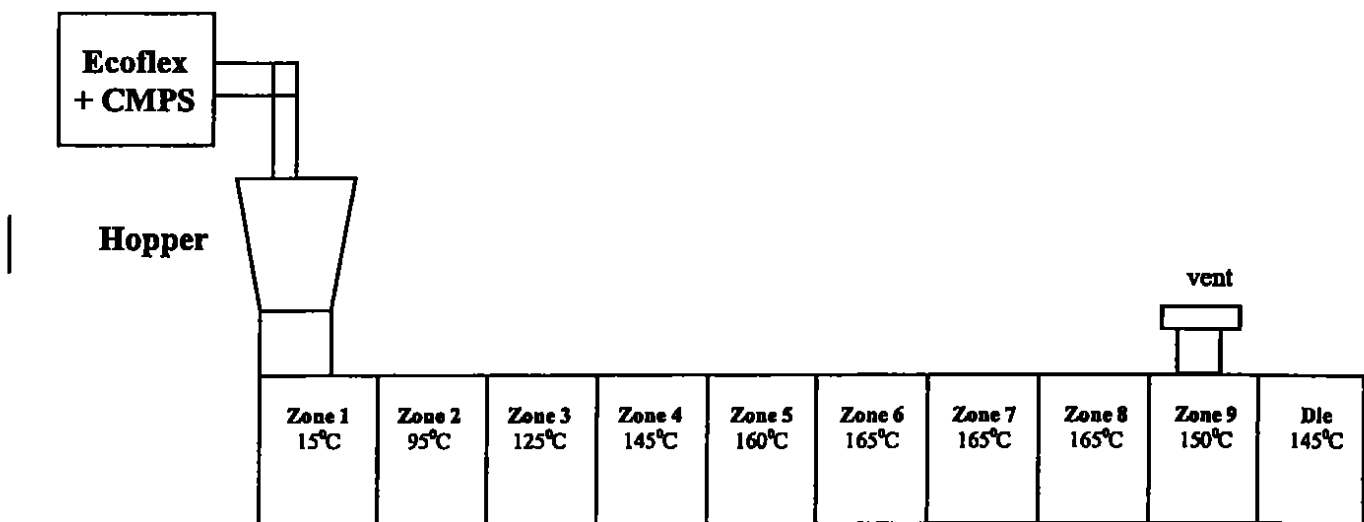


FIGURE 1



FIG. 2A

28/14 60/60 60/60 60/60 42/42 42/42 28/28 28/28 20/20 20/20



FIG. 2B

KB40/S42 KB40/S42 28/28 42/42 28/28 20/20 KB40/S14 KB90/S28 28/28 42/42 42/42 28/28 20/20 KB90/S28 KB40/S14 KB40/S14



FIG. 2C

28/28 28/28 60/60 60/60 60/60 28/28 28/14 20/20 20/20 20/20 20/20

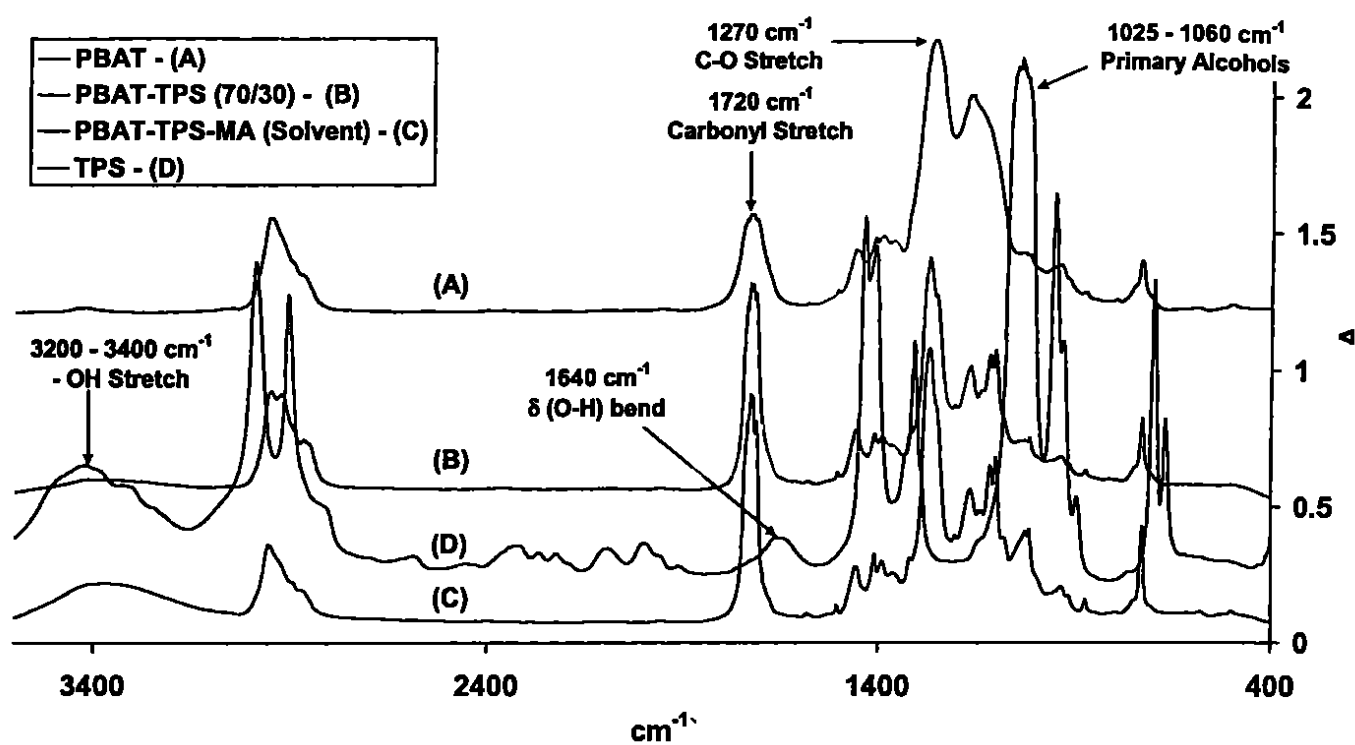


FIGURE 3

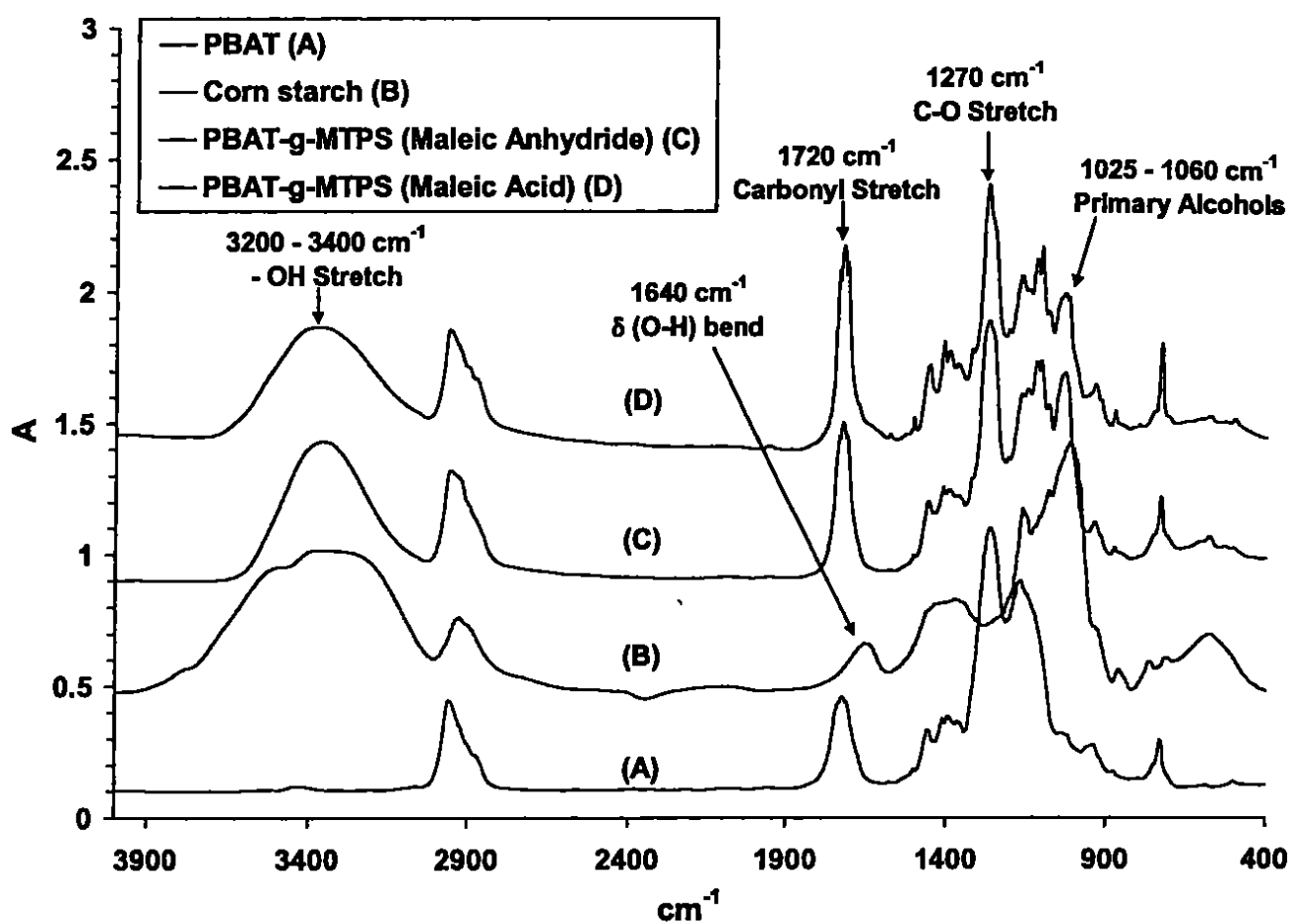


FIGURE 4

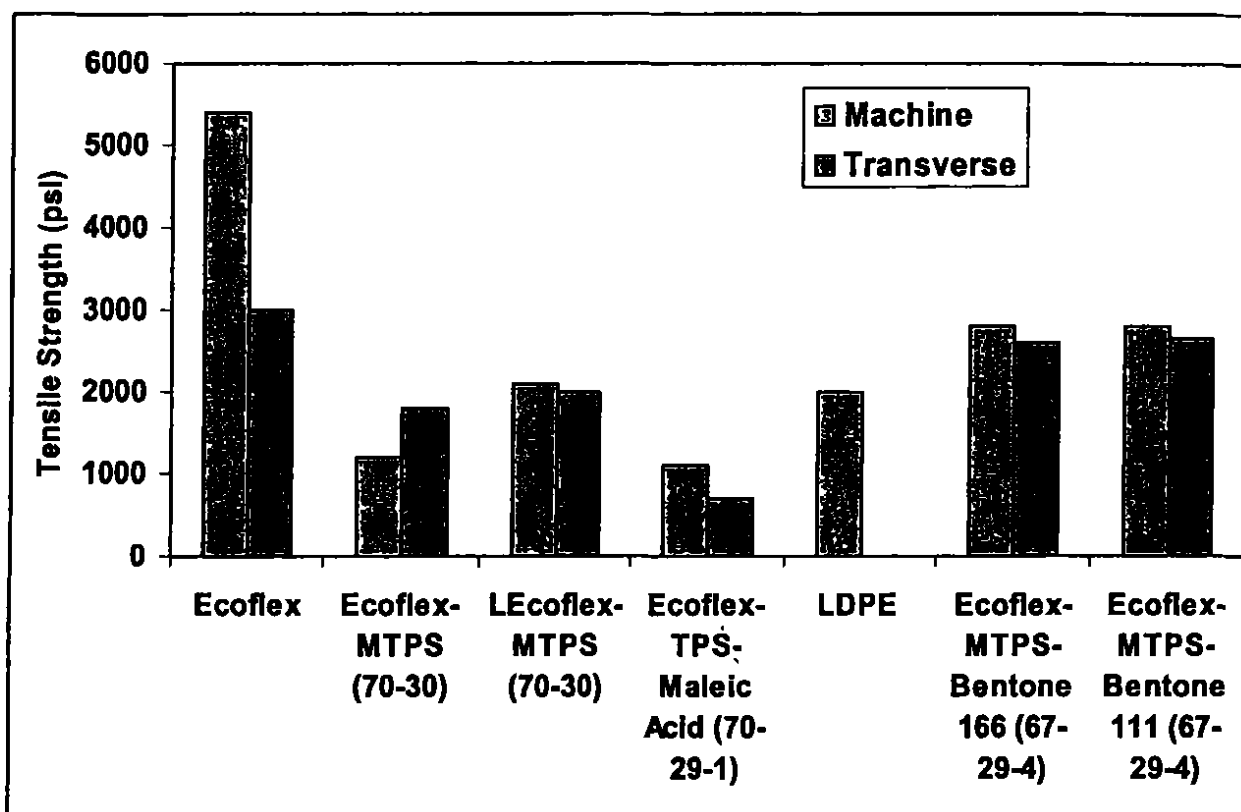


FIGURE 5

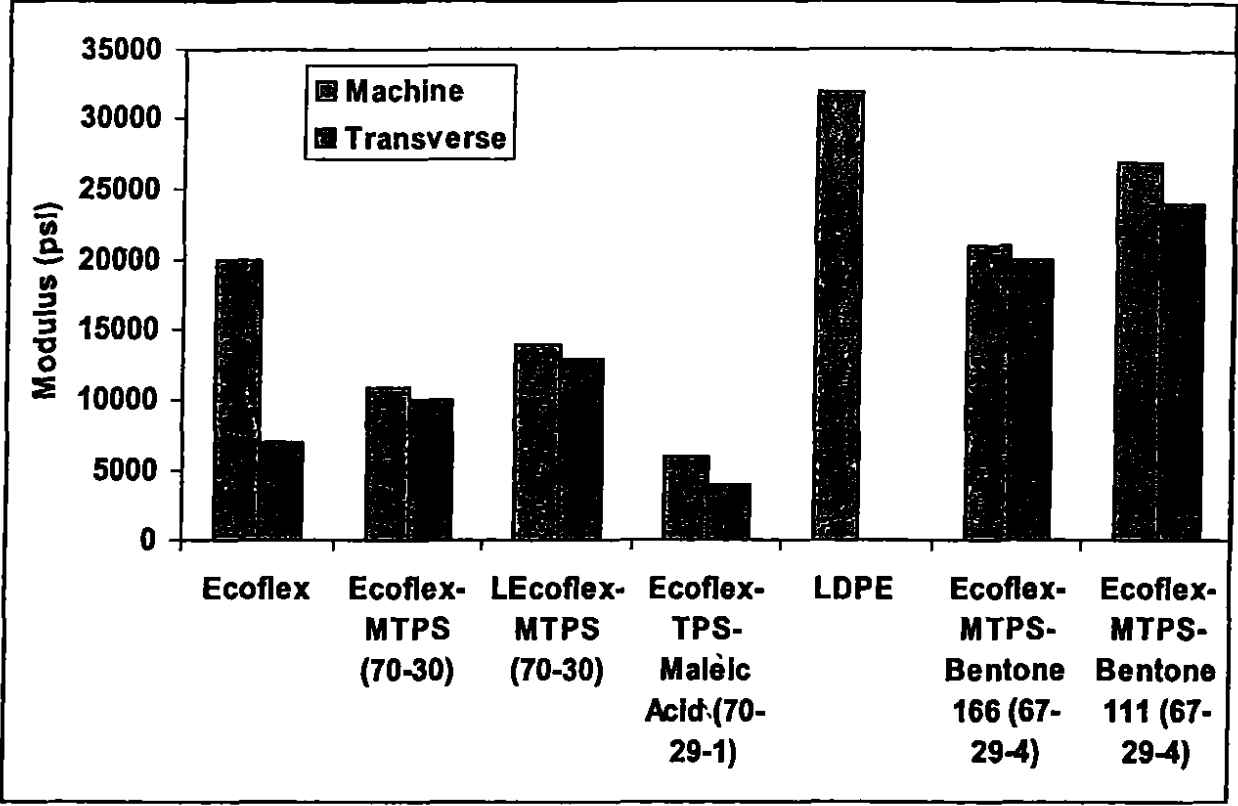


FIGURE 6

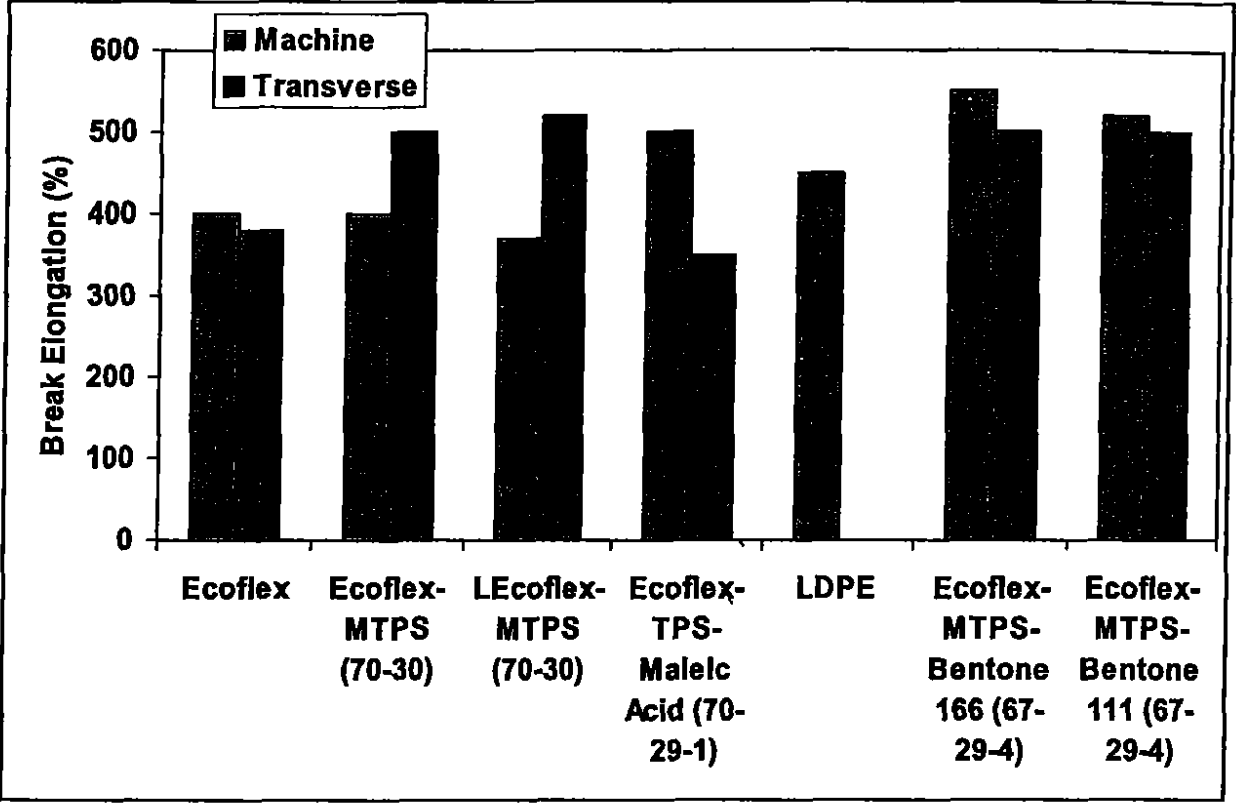


FIGURE 7

REQUISITOS MINIMOS PARA ADMISION A TRAMITE
PCT

PATENTE DE INVENCION ☒

MODELO DE UTILIDAD ☐

- ◆ Indicación de que se solicita la concesion de una patente ☒
- ◆ Datos de identificacion del solicitante o de la persona que presenta la solicitud ☒
- ◆ Descripción de la invencion ☒
- ◆ 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 identificacion del solicitante o de la persona que presenta la solicitud ☐
- ◆ Representación gráfica y fotografica del Diseno 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 identificacion del solicitante o de la persona que presenta la solicitud ☐
- ◆ Representación grafica del esquema trazado ☐
- ◆ Comprobante de pago de las tasas establecidas ☐

COMPLETA ☐

INCOMPLETA ☐


Firma Responsable

Fecha 13 JUL. 2008

Carrera 13 No 27-00 Piso 5 7 y 10
Conmutador 3 82 08 40
Fax 350 52 20
E mail info@sic.gov.co
www.sic.gov.co
Bogotá D C Colombia

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REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
CADENA SARMIENTO JUAN PABLO

REFERENCIA	Radicación No.	6 68308
	Solicitud internacional	US2005/041238
	Fecha inicio fase nacional	20/06/2006
	Trámite	11
	Evento	378
	Actuación	430
	Oficio No.	10463

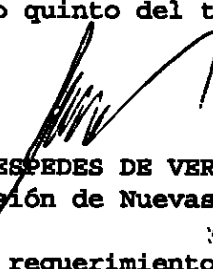
Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se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

2. La solicitud no contiene el poder debidamente otorgado, con el lleno de los requisitos exigidos por los artículos 63 y subsiguientes del Código de Procedimiento Civil. Adicionalmente, deberá presentar el documento que acredita la existencia y representación legal de la sociedad solicitante, cuando ésta fuere persona jurídica.

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.


ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la división de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista de fecha 15 SET. 2006
adpall