

No. 07-045686- -00005-0000

Fecha: 2012-07-04 16:24:29 Dep. 2020 DIR.NUEVASOR
Tra. 11 PATENTEYII Eve: 379 FASENACIONALI
Act. 523 RESPUESTA Folios: 30

Act. 523 RESPUESTA Folios: 29

As. 103.671

Señor

**DIRECTOR DIVISIÓN DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO**

E.

S.

D.

REF: Expediente No. **07 045686**– solicitud de patente de invención a favor de **MICHIGAN STATE UNIVERSITY**. Título **COMPOSICIONES DE ALMIDÓN PLASTIFICADO, MODIFICADO QUÍMICAMENTE POR PROCESAMIENTO CON EXTRUSIÓN**.

RESPUESTA A EXAMEN DE FONDO

JUAN PABLO CADENA SARMIENTO, portador de la tarjeta profesional No. 57.492 del C.S.J., obrando como apoderado de la sociedad solicitante me permito dar respuesta al oficio número 05551 relacionado con la patentabilidad de la presente invención y notificado por fijación en lista el 11 de abril de 2012.

Con el ánimo de subsanar las objeciones planteadas por el señor Examinador, me permito presentar un nuevo pliego reivindicatorio de 1-30 reivindicaciones, en donde no se amplía en ningún momento la materia inicialmente divulgada y encuentra entero sustento en la descripción.

1. Claridad

En primer lugar, observamos que todos los componentes incluidos en el pliego reivindicatorio se encuentran divulgados y debidamente sustentados en la descripción, tanto en términos de los componentes químicos específicos empleados como sus cantidades respectivas. Particularmente, referimos al señor Examinador al **párrafo 31** donde se divulgan los **almidones**, **párrafo 32** en donde se mencionan los **plastificantes**,

párrafo 33 en donde se especifican los **ácidos orgánicos dibásicos y sus anhídridos**, párrafo 34 para **iniciadores de radicales libres**, y al párrafo 36 en donde se discute las **nanoarcillas**. En este orden de ideas, todos los términos objetados por el señor Examinador se encuentran completamente sustentados en la descripción y deben ser aceptados. Igualmente notamos que los ejemplos contenidos en la descripción son únicamente configuraciones particulares que ilustran la invención que se encuentra divulgada en la *totalidad* de la descripción.

En efecto, la Decisión 486 requiere que se presente la mejor manera conocida por el solicitante de llevar cabo la invención, pero esto no significa que los ejemplos sean limitativos de la materia divulgada; estos son meramente ilustrativos. Consecuentemente no se puede decir que los ejemplos sean el único sustento de la invención ya que el solicitante presentó un capítulo descriptivo completo para soportar su invención. Por lo tanto solicitamos al señor Examinador evaluar el soporte de la invención basado en la descripción como un todo y no solamente en algunas configuraciones ilustrativas.

En cuanto a las cantidades específicas solicitadas en el oficio técnico, advertimos que el conocimiento de una persona versada en la materia junto con las enseñanzas de la descripción permiten escoger la cantidad apropiada de cada uno de los componentes dependiendo de las condiciones en planta. Notamos además que la descripción de la presente solicitud proporciona una guía para obtener las cantidades óptimas de los componentes (párrafos 31 a 36). En cualquier caso, las reivindicaciones 25 y 29 divulgan cantidades altamente específicas para cada uno de los componentes.

Dice además el señor Examinador que las expresiones empleadas abarcan amplias posibilidades de compuestos además de ser nombrados en términos de su función y por lo tanto no son adecuadas. Al respecto, nos permitimos señalar que todos los componentes de la composición se encuentran divulgados en términos de su nombre común o químico y no en términos de su función. En este sentido, la identidad de los componentes contenidos en el pliego reivindicatorio es absolutamente clara para el técnico versado en la materia. Insistimos además en que la descripción proporciona una definición más específica y varios ejemplos para cada uno de los componentes reivindicados:

- “Almidón” es un nombre común ampliamente utilizado en el campo de la química, y la descripción clarifica la estructura del almidón en términos de los componentes poliméricos amilosa y amilopectina;
- “Ácido orgánico dicarboxílico” (modificado en la descripción y en las reivindicaciones de acuerdo a la sugerencia del señor Examinador) y “anhídrido”

tienen una definición química estructural ampliamente conocida y se ilustran en detalle en la descripción (ácidos orgánicos con dos grupos ácidos carboxílicos y anhídridos de los mismos);

- El término “modificador químico” se especifica dentro de las reivindicaciones como siendo seleccionado del grupo conformado por un ácido orgánico dicarboxílico, un anhídrido del ácido orgánico dicarboxílico, y sus mezclas;
- “Alcohol polihídrico” es un componente con una estructura química bien definida cuyo significado también se encuentra revelado en la descripción (un alcohol con dos o más grupos hidroxilo);
- El “Peróxido orgánico” también tiene una estructura reconocida en el campo de la química e “iniciador de radicales libres” es un término de uso común en el campo de la invención, además de que la descripción proporciona varios ejemplos representativos de estos componentes;
- “Nanoarcilla” es un término ampliamente conocido y empleado en el campo de la invención, y la descripción provee numerosos ejemplos de minerales de nanoarcilla comunes.

En este sentido, todos los términos empleados en el capítulo reivindicatorio son usados comúnmente en el estado de la técnica y se encuentran divulgados y ejemplificados en la descripción, por lo que son claros y precisan de manera adecuada el alcance de la invención.

Hacemos mención especial al término “combinar reactivamente” o “mezclar reactivamente” el cual según la descripción representa el mezclado de una mezcla de componentes bajo condiciones apropiadas para hacer reaccionar al menos una parte de los componentes de la mezcla para formar un producto de dicha reacción. Por ejemplo, la mezcla puede ser mezclada reactivamente en un extrusor a temperaturas elevadas para formar el producto de reacción. Las condiciones específicas de operación (temperaturas, presión, velocidad de extrusión, etc.) pueden ser derivadas por el técnico versado en la materia basado en la aplicación deseada y en los materiales de partida empleados (descripción, párrafos 37 a 41).

Por último, notamos que las reivindicaciones no mencionan limitaciones de viscosidad, no contienen las expresiones “opcionalmente” y “alrededor de” y las condiciones de extrusión han sido eliminadas de las reivindicaciones de producto, tal y como fue requerido por el señor Examinador.

En vista de los comentarios anteriores consideramos que el nuevo pliego reivindicatorio es completamente claro y encuentra sustento en la descripción.

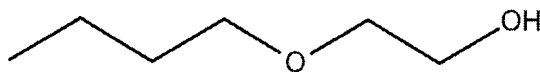
2. Novedad

Notará el señor Examinador que la antigua reivindicación 1 ha sido eliminada, y que la reivindicación principal de producto es la antigua reivindicación 2 con más restricciones. Por este motivo enfocaremos la novedad de la invención sobre la antigua reivindicación 2.

Ahora bien, la nueva reivindicación 1 revela una composición a base de almidón que comprende un producto de reacción de una mezcla reactivamente mezclada que comprende (i) un polímero de almidón biodegradable, (ii) un modificador químico seleccionado del grupo conformado por un ácido orgánico dicarboxílico, un anhídrido del ácido orgánico dicarboxílico, y sus mezclas, y (iii) un alcohol polihídrico plastificante.

Nos permitimos observar que ninguna de las anterioridades citadas menciona el tercer componente de la mezcla reactivamente mezclada, es decir el alcohol polihídrico plastificante. El documento US20030144637 (D2) no hace ninguna mención sobre un alcohol polihídrico, como plastificante o con cualquier otra función.

En cuanto al documento US 4011392 (D1), dice el señor Examinador que la divulgación de *cellosolve* es análoga al alcohol polihídrico en la presente solicitud. Al respecto, notamos que en el contexto de D1 el *cellosolve* no es un plastificante sino que por el contrario es un co-solvente usado con agua para crear una dispersión de ésteres de almidón como composición de recubrimiento. Además de esta diferencia, advertimos que cellosolve es el nombre comercial del compuesto químico 2-butoxietanol¹, el cual tiene únicamente un grupo hidroxilo (-OH) y por lo tanto no es un alcohol polihídrico, como se requiere en las reivindicaciones de la presente solicitud:



[2-butoxietanol]

Por otra parte, notamos que D1 divulga el uso de etilenglicol y propilenglicol como componentes opcionales de la composición de recubrimiento. Es importante señalar que, al igual que el 2-butoxietanol, dichos componentes opcionales no son plastificantes. Por el

¹ <http://www.dow.com/productsafety/finder/egbe.htm>

contrario, se incluyen como inhibidores de congelación en solución con el medio de recubrimiento líquido, y por tanto no plastifican los ésteres de almidón mixtos de D1.

3. Nivel Inventivo

Como quedo establecido anteriormente, ninguna de las referencias citadas como estado de la técnica revela o sugiere cualquiera de (a) una reacción entre (i) un polímero biodegradable de almidón, (ii) un modificador químico que comprende un ácido/anhídrido dicarboxílico y (iii) un alcohol polihídrico plastificante (como se requiere en la reivindicación 19), ó (b) una composición basada en almidón con una estructura que corresponde al producto de reacción de los componentes mezclados reactivamente (como se requiere en la nueva reivindicación 1). Esto es, incluso si se asume que D1 o D2 mencionen algún compuesto que pudiese ser tomado como alcohol polihídrico, dicho compuesto estaría simplemente mezclado, sin reaccionar, con los demás componentes.

Más específicamente, el almidón hidrolizado y el agente acilante de D1 se hacen reaccionar en una primera etapa en ausencia de otros compuestos (como por ejemplo 2-butoxietanol, etilenglicol y/o propilenglicol) para formar los ésteres de almidón mezclados; los ingredientes opcionales, como etilenglicol o propilenglicol, son combinados posteriormente con los ésteres de almidón mezclados en una etapa que no incluye ningún tipo de mezcla reactiva.

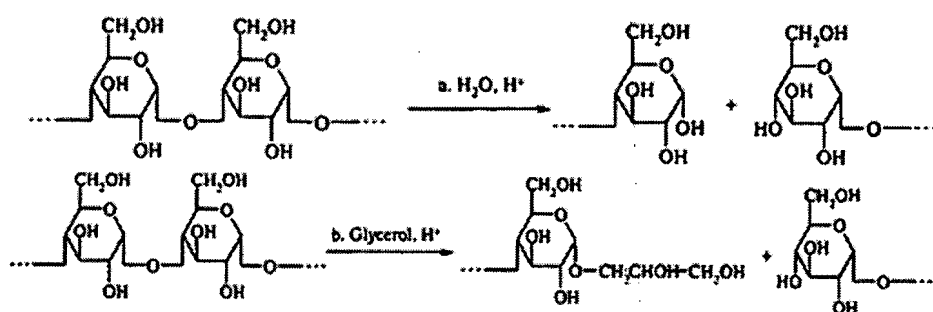
En este sentido, el producto químico resultante del proceso de D1 es completamente diferente a un producto obtenido mediante el proceso de (i) mezclar reactivamente un polímero biodegradable de almidón con un modificador químico que comprende un ácido/anhídrido dicarboxílico, seguido de (ii) mezclar el producto de la etapa (i) con un alcohol polihídrico plastificante.

Para justificar la afirmación anterior, anexamos a la respuesta una declaración del co-inventor Ramani Narayan que fue empleada en el equivalente estadounidense de la presente solicitud. Esta declaración explica la publicación académica de Raquez et al., "Almidón termoplástico maleado por extrusión reactiva", *Polímeros de Carbohidratos*, vol. 74 (2008), p. 159-169 (en donde el inventor Ramani Narayan también es coautor; publicación también adjunta para referencia del señor Examinador) en donde se ilustran las diferencias estructurales de las composiciones basadas en almidones modificados químicamente que resulta de la mezcla reactivamente mezclada.

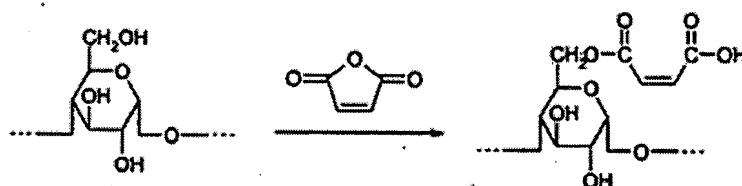
Particularmente, la mezcla reactiva de almidón, ácidos/anhídridos orgánicos dicarboxílicos y un alcohol polihídrico plastificante involucra múltiples reacciones para que se pueda formar la composición basada en almidón que se reivindica en la presente solicitud:

1. La reacción del grupo hidroxilo en la posición C-6 del almidón con el ácido/anhídrido orgánico dicarboxílico para formar un éster unido a la columna de almidón que además incluye una funcionalidad de ácido carboxílico (por ejemplo, para hacer posteriormente un injerto en el almidón y producir así un polímero tipo poliéster);
2. Hidrolisis parcial catalizada con ácido de la columna de almidón inducida por el ácido/anhídrido orgánico dicarboxílico para formar fragmentos de almidón que tienen un peso molecular reducido;
3. Glucosilación catalizada por ácido de la columna de almidón resultante de la reacción del alcohol polihídrico plastificante con la columna de almidón hidrolizado para formar unidades de alcohol polihídrico plastificante enlazadas covalentemente con los fragmentos de almidón de peso molecular reducido en la posición C-1 del almidón y que tiene una funcionalidad de acetal.

Así las cosas, además de proporcionar una funcionalidad de ácido carboxílico, la composición basada en almidón químicamente modificada se caracteriza por comprender fragmentos de almidón de bajo peso molecular y residuos del alcohol polihídrico plastificante enlazados covalentemente a los fragmentos de almidón de bajo peso molecular. Estas características estructurales distintivas se ilustran de mejor manera en los siguientes esquemas de reacción, tomados del artículo académico adjunto.



Esquema 1. Hidrolisis (a) y glucosilación (b; por claridad, solo se representa la reacción entre el almidón y la función hidroximetileno del glicerol) reacciones presentes durante la maleación de TPS *in situ*.



Esquema 2. Reacción de esterificación de almidón con MA en la posición C6 (la posición más preferida, ver texto)

En otras palabras, la mezcla posterior de un alcohol polihídrico plastificante con un producto de la reacción de almidón con ácido/anhídrido dicarboxílico resulta simplemente en una mezcla física de los dos componentes. Es decir, con la combinación de enseñanzas de D1 y D2 propuesta por el señor Examinador, no habría ningún enlace covalente de ningún residuo de alcohol/glicol a los ésteres mezclados de almidón después de la etapa post-reacción de mezclado para formar la composición de recubrimiento incluyendo los ésteres mezclados de almidón.

Consideramos que los argumentos anteriores representan una distinción más que suficiente entre la composición de almidón mezclada reactivamente que se reivindica en la presente invención y el estado de la técnica, tanto en términos del proceso como de la estructura resultante contenida en la composición.

Adicionalmente, se ha demostrado que existen beneficios técnicos inesperados alcanzados con la presente invención, que constituyen indicios adicionales de nivel inventivo. Específicamente, el proceso y composición reivindicados proporcionan un almidón químicamente modificado plastificado en el cual (i) tanto el modificador químico como el alcohol polihídrico plastificante están injertos en el almidón, y (ii) la viscosidad del almidón se reduce sustancialmente (ver descripción, párrafos 45-54). La reducción en la viscosidad y la inserción del alcohol polihídrico plastificante no se encuentran sugeridas en ninguna de las referencias citadas. Además, como se observa en la descripción de la presente solicitud existen varias ventajas sobre el estado de la técnica, como por ejemplo (i) prevención de la obstrucción de la boquilla del extrusor por de la masa fundida de almidón plastificado, (ii) la prevención de formación de espuma en el almidón plastificado fundido en la boquilla del extrusor, y (iii) la formación de una composición biodegradable, obtenidas gracias a las características reivindicadas en la presente invención.

Finalmente hacemos notar al señor Examinador que las reivindicaciones dependientes 25 y 29 divulgan cantidades específicas para los componentes que se mezclan reactivamente para formar la composición final, incluyendo las características divulgadas en la reivindicación original 11 (10% a 50% en peso del plastificante en la mezcla reactivamente mezclada). Notamos que la reivindicación original 11 no fue objetada por novedad ni nivel inventivo. En este orden de ideas, las nuevas reivindicaciones 25 y 29, las cuales son altamente específicas e incluyen limitaciones de la antigua reivindicación 11, deberían ser aceptadas -en adición a los argumentos anteriores- por esta razón.

En vista de lo anteriormente expuesto, respetuosamente solicitamos el retiro de las objeciones de la presente solicitud y la concesión del privilegio solicitado, ya que en opinión del solicitante cumple con todos los requisitos establecidos en la decisión 486.

Anexos

Nuevo pliego reivindicatorio.

Declaración del co-inventor Ramani Narayan

Artículo académico de Raquez et al.

Del Señor Director

Atentamente,



JUAN PABLO CADENA SARMIENTO

T.P. No. 57.492 del C.SJ.

C.C. 80.410.337 de Usaquén

Calle 70 A No. 4 - 41

REIVINDICACIONES

1. Una composición a base de almidón que comprende un producto de reacción de una mezcla reactivamente mezclada que comprende (i) un polímero de almidón biodegradable, (ii) un modificador químico seleccionado del grupo conformado por un ácido orgánico dicarboxílico, un anhídrido del ácido orgánico dicarboxílico, y sus mezclas, y (iii) un alcohol polihídrico plastificante.
2. La composición de la Reivindicación 1 en donde la mezcla reactivamente mezclada comprende adicionalmente un peróxido orgánico iniciador de radicales libres.
3. La composición de cualquiera de las Reivindicaciones 1 o 2 en donde la mezcla reactivamente mezclada comprende adicionalmente una nanoarcilla.
4. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el polímero de almidón biodegradable se selecciona del grupo conformado por almidón de maíz, almidón de papa, almidón de yuca, almidón de arroz, almidón de trigo y almidón de casabe.
5. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el polímero de almidón biodegradable en la mezcla está presente en una cantidad entre 5% a 90% en peso de la mezcla.
6. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde polímero de almidón biodegradable es un almidón no modificado, oxidado o almidón hidrolizado en medio ácido con una viscosidad reducida en caliente ("thin boiling starch") de 0 a 95 grados de fluidez.
7. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el polímero de almidón biodegradable tiene un contenido de humedad de 0.5% a 15% en peso.
8. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el polímero de almidón biodegradable está en forma pulverizada.
9. La composición de una cualquiera de las Reivindicaciones 1, 2, ó 3 en donde el alcohol polihídrico plastificante está presente en una cantidad entre 10 a 50 % en peso de la mezcla.

10. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el modificador químico es el ácido orgánico dicarboxílico.
11. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el modificador químico es el anhídrido del ácido orgánico dicarboxílico.
12. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el modificador químico está presente en una cantidad entre 0.5% a 10% en peso del polímero de almidón biodegradable.
13. La composición de la Reivindicación 3 en donde la nanoarcilla se selecciona del grupo conformado por montmorillonita, esmectita, hectorita y sus mezclas.
14. La composición de la Reivindicación 3 en donde la nanoarcilla está presente en una cantidad de entre 0.5 a 25 % en peso de la mezcla.
15. La composición de la Reivindicación 2 en donde el peróxido orgánico iniciador de radicales libres es 2,5-bis(terc-butilperoxi)-2,5-dimetilhexano.
16. La composición de la Reivindicación 2 en donde el peróxido orgánico iniciador de radicales libres está presente en la mezcla en una cantidad entre 0.01 a 2.0 % en peso de la mezcla.
17. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el modificador químico es seleccionado del grupo conformado por ácido maleico, ácido succínico, ácido itacónico, ácido ftálico, anhídrido maleico, anhídrido succínico, anhídrido itacónico, anhídrido ftálico, y mezclas de los mismos.
18. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el modificador químico está presente en 2% a 5% en peso del polímero de almidón de la mezcla.
19. Un proceso para preparar una composición a base de almidón, el proceso comprendiendo:

mezclar reactivamente una mezcla que comprende (i) un polímero de almidón biodegradable, (ii) un modificador químico seleccionado del grupo conformado por un ácido orgánico dicarboxílico, un anhídrido de un ácido orgánico dicarboxílico y sus mezclas, y (iii) un alcohol polihídrico plastificante, formando así la composición a base de almidón como producto de reacción:

en donde la mezcla se extruye con calentamiento y purga de agua de la mezcla.

20. El proceso de la Reivindicación 19 en donde el polímero de almidón biodegradable y el modificador químico se mezclan como polvos.
21. El proceso de la Reivindicación 19 en donde la extrusión tiene lugar a una temperatura de entre 130°C y 180°C.
22. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el alcohol polihídrico plastificante es glicerol.
23. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el alcohol polihídrico plastificante está presente en 15% a 30% en peso de la composición.
24. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde el modificador químico se selecciona del grupo conformado por ácido maleico, anhídrido maleico, y combinaciones de los mismos.
25. La composición de una cualquiera de las Reivindicaciones 1, 2, o 3 en donde:
 - (i) el polímero de almidón biodegradable en la mezcla está presente en una cantidad de entre 5% a 90% de la mezcla;
 - (ii) el modificador químico está presente en una cantidad de entre 0,5% a 10% en peso del polímero de almidón biodegradable;
 - (iii) el alcohol polihídrico plastificante está presente en una cantidad de entre 10% a 50% en peso de la mezcla;
 - (iv) el peróxido orgánico iniciador de radicales libres, cuando se encuentra incluido en la mezcla, está presente en la mezcla una cantidad de entre 0,01% a 2,0% en peso de la mezcla; y
 - (v) la nanoarcilla, cuando se encuentra incluida en la mezcla, está presente en una cantidad de entre 0,5% a 25% en peso de la mezcla.
26. La composición de la Reivindicación 25, en donde:
 - (i) el polímero de almidón biodegradable se selecciona del grupo formado por almidón de maíz, almidón de papa, almidón de yuca, almidón de arroz, almidón de trigo y almidón de casabe, y combinaciones de los mismos;
 - (ii) el modificador químico se selecciona del grupo formado por ácido maleico, ácido succínico, ácido itacónico, ácido ftálico, anhídrido maleico, anhídrido succínico, anhídrido itacónico, anhídrido ftálico, y mezclas de los mismos;
 - (iii) el alcohol polihídrico plastificante comprende glicerol;
 - (iv) el peróxido orgánico iniciador de radicales libres, cuando se incluye en la mezcla, comprende 2,5-bis (terc-butilperoxi) -2,5-dimetilhexano; y
 - (v) la nanoarcilla, cuando se incluye en la mezcla, se selecciona del grupo que consiste de montmorillonita, esmectita, hectorita, y mezclas de los mismos.

27. El proceso de la Reivindicación 19 en donde la mezcla reactivamente mezclada comprende además un peróxido orgánico iniciador de radicales libres.
28. El proceso de cualquiera de las Reivindicaciones 19 o 27 en donde la mezcla reactivamente mezclada comprende además un nanoarcilla.
29. El proceso de cualquiera de las Reivindicaciones 19, 27 o 28, en donde:
 - (i) el polímero de almidón biodegradable en la mezcla está presente en una cantidad de entre 5% a 90% en peso de la mezcla;
 - (ii) el modificador químico está presente en una cantidad de entre 0,5% a 10% en peso del polímero de almidón biodegradable;
 - (iii) el alcohol polihídrico plastificante está presente en una cantidad de entre 10% en peso a 50% en peso de la mezcla;
 - (iv) el peróxido orgánico iniciador de radicales libres, cuando se incluye en la mezcla, está presente en la mezcla en una cantidad de entre 0,01% en peso a 2,0% en peso de la mezcla, y
 - (v) la nanoarcilla, cuando se incluye en la mezcla, está presente en una cantidad de entre 0,5% en peso a 25% en peso de la mezcla.
30. El proceso de la Reivindicación 29, en donde:
 - (i) el polímero de almidón biodegradable se selecciona del grupo conformado por almidón de maíz, almidón de papa, almidón de yuca, almidón de arroz, almidón de trigo y almidón de casabe, y combinaciones de los mismos;
 - (ii) el modificador químico se selecciona del grupo formado por ácido maleico, ácido succínico, ácido itacónico, ácido ftálico, anhídrido maleico, anhídrido succínico, anhídrido itacónico, anhídrido ftálico, y mezclas de los mismos;
 - (iii) el alcohol polihídrico plastificante comprende glicerol;
 - (iv) el peróxido orgánico iniciador de radicales libres, cuando se incluye en la mezcla, comprende 2,5-bis (terc-butilperoxi) -2,5-dimetilhexano; y
 - (v) la nanoarcilla, cuando se incluye en la mezcla, se selecciona del grupo conformado por montmorillonita, esmectita, hectorita, y mezclas de los mismos.

PATENT

IN THE UNITED STATES PATENT
AND TRADEMARK OFFICE

Serial No.: 12/592,996)
)
 Applicants: Ramani Narayan, Sunder)
 Balakrishnan, Yogaraj Nabar,)
 Jean-Marie Raquez and)
 Philippe Dubois)
)
 Filed: December 7, 2009)
)
 Title: STARCH-POLYESTER)
 BIODEGRADABLE GRAFT)
 COPOLYMERS AND A METHOD)
 OF PREPARATION THEREOF)
)
 Group Art Unit: 1796)
)
 Confirmation No.: 4238)
)
 Customer No.: 35684)
)
 Examiner: Ana L. Woodward)
)
 Attorney Docket No.: MSU 4.1-906)
 (000059910-0850)

DECLARATION OF PROFESSOR RAMANI NARAYAN UNDER 37 C.F.R. § 1.132

Mail Stop Amendment
 Commissioner for Patents
 P.O. Box 1450
 Alexandria, Virginia 22313-1450

Dear Sir:

I, Ramani Narayan, an inventor in the above application, state as follows:

[0001] I received a doctorate from Bombay University in organic chemistry (polymer science and engineering) in 1975. I am a member of the faculty of the Department of Chemistry Chemical Engineering and Materials Science at Michigan State University; currently, I am a University Distinguished Professor of Chemical and Biochemical Engineering. My research focuses on polymeric materials from renewable resources; biodegradable polymer systems; engineering and design of natural-synthetic polymer graft and block copolymers; polymer blends; studies in reactive extrusion processing, biobased and recyclable composites. I have authored/co-

authored numerous refereed publications, invented/co-invented numerous patents, and edited three books of in the area of bio-based polymeric materials.

[0002] I am familiar with the contents of the above-identified application, the pending claims, and the current office action dated March 8, 2010. I make this declaration (a) to present work performed by me or at my direction related to the formation of starch-polyester graft copolymers within the scope of the pending claims and (b) to clarify the differences between the chemically modified starch recited in the claims and the compositions of the cited Shiraishi et al. U.S. Patent No. 6,150,438 ("Shiraishi") and Halley et al. U.S. Publication No. 2004/0122135 ("Halley") publications.

[0003] The pending claims recite a chemically modified starch that comprises a reactively blended mixture comprising: (i) a starch, (ii) a trans-esterification catalyst comprising one or more of a dibasic organic acid and an anhydride thereof, and (iii) a plasticizer comprising a polyhydric alcohol. We have unexpectedly found that the reactive blending of these three components undergoes multiple reactions that result in a chemically modified starch having a structure distinct from anything disclosed or suggested by the combination of Shiraishi and Halley.

[0004] Raquez et al., "Maleated thermoplastic starch by reactive extrusion," *Carbohydrate Polymers*, vol. 74 (2008), p. 159-169 ("Raquez"), which is co-authored by me and is attached hereto as Appendix A, illustrates the distinct structural characteristics of the recited chemically modified starch as exemplified by the case when the dibasic organic acid/anhydride is maleic anhydride and the polyhydric alcohol plasticizer is glycerol. The specific reactions that occur during the reactive blending process include:

1. Reaction of the starch C-6 hydroxyl group with the dibasic organic acid/anhydride to form an ester linked to the starch backbone that further includes a carboxylic acid functionality for subsequent grafting to the recited polyester (see Raquez p. 163, col. 1, p. 163 (Figure 2, structure D), and p. 164 (Scheme 2));
2. Acid-catalyzed partial hydrolysis of the starch backbone induced by the dibasic organic acid/anhydride to form starch fragments having a reduced molecular weight (see Raquez p. 162, and p. 164 (Scheme 1a)); and
3. Acid-catalyzed glucosidation of the starch backbone resulting from the reaction of the polyhydric alcohol plasticizer with the hydrolyzed starch

backbone to form polyhydric alcohol plasticizer units covalently bonded to the reduced molecular weight starch fragments at the starch C-1 position and having an acetal functionality (see Raquez p. 163, col. 2, p. 163 (Figure 2, structure C), and p. 164 (Scheme 1b)).

[0005] More specifically, the reactive blending of starch and glycerol in the presence of maleic anhydride/maleic acid results in an unusual reaction system as shown in Raquez Schemes 1a, 1b, and 2. The starch granules are first disrupted, which typically results from a physical blend with glycerol. However, in the presence of an acid functionality provided by the maleic anhydride/maleic acid (or more generally a dibasic organic acid/anhydride), the starch polymer chains break down, and the resultant end group reacts with the glycerol (or more generally a hydroxyl group of a polyhydric alcohol) forming an acetal linkage. The glycerol is now covalently bonded to the starch backbone and the viscosity is reduced based on the reduction in molecular weight. This chemically modified starch is highly reactive and allows for a polyester subsequently to covalently bond to the starch backbone and form the recited starch-polyester graft copolymer (i.e., whether the polyester to be grafted is an aliphatic polyester or an aliphatic-aromatic copolyester).

[0006] Proof for the covalent linking of glycerol to starch is evidenced from soxhlet extraction studies – glycerol is not generally extracted from the chemically modified starch as opposed to simply plasticizing starch with glycerol in a physical blend in which case the glycerol can be extracted. See Raquez, p. 161, col. 2 and Table 1 (in particular comparing entry 2 (a physical blend of starch and 20% glycerol; “TPS”) with entry 3 (a chemically modified starch including 2.5% maleic anhydride and 20% glycerol; “MTPS”). A reduction in the intrinsic viscosity (η) for MTPS compared to TPS further shows the reduction in molecular weight of the starch. See *id.*

[0007] The composition and method of Shiraishi shows some grafting of a polyester through the carboxylic acid moiety to a biomass material similar to item 1 of paragraph [0004] above. Since the biomass material (e.g., wood flour or starch as shown in Shiraishi’s examples) has *not* been plasticized (i.e., it retains its granular structure), however, the grafting would mostly be surface grafting, which results in poor performance properties.

[0008] In the case of Halley, a pre-plasticized mixture of starch and a polyol plasticizer (e.g., generally glycerol) was used. However, the plasticization using

glycerol is a physical phenomenon as is typical with plasticizers, and the granular crystalline structure disrupted to form an amorphous material. The glycerol is *not* covalently bonded to the starch backbone as shown by the fact that it can be readily solvent extracted from the glycerol plasticized starch. The reaction of polyesters with such thermoplastic starch is a *physical blending and intercalation* with the starch chains and does not represent true covalent bonding.

[0009] The grafting reaction of aliphatic polyesters like polycaprolactone (PCL) or polylactic acid (PLA) with the highly reactive chemically modified starch at the C-6 position (i.e., via the dibasic organic acid/anhydride ester-linked to the starch backbone at the C-6 position) is high, and covalent grafting of the polyester chains to the starch backbone has been established using soxhlet extraction studies. The following describes experiments for the formation of a PCL-starch graft copolymer using a chemically modified starch according to the application disclosure.

[0010] *Preparation of Chemically Modified Starch:* Regular silver medal pearl corn-starch, obtained from Cargill Inc., was reactively modified using maleic anhydride/maleic acid in a twin-screw co-rotating CENTURY extruder with a screw diameter of 30 mm and an L/D ratio of 40. Maleic anhydride/acid(MA) was ground to a fine powder using a mortar and pestle and mixed with the starch (800 gm starch + 20, 40, or 80 gm maleic anhydride/acid) using a kitchen blender for 15 minutes before being fed to the feed port of the extruder. A mixture of glycerol and 2,5-bis (tert-butylperoxy)-2,5-dimethylhexane (LUPEROX 101 peroxide initiator) (200 gm glycerol + 1.6 gm LUPEROX 101) was also added to the starch/MA mixture in the extruder to form the chemically modified starch in the form of a maleated thermoplastic starch ("MTPS"). Due to the low viscosity of the extruded strand, the MTPS was collected in aluminum pans and ground to a fine powder. Ground MTPS was stored in an oven at 75°C. The extrusion processing conditions for the reactive maleation is outlined in Table 1 below.

Table 1: Extrusion processing conditions for the reactive maleation of starch using maleic anhydride/maleic acid modifier in the presence of glycerol plasticizer

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

[0011] Preparation of Starch-Aliphatic Polyester Graft Copolymer. The synthesis of graft copolymers between polycaprolactone (PCL TONE 787) and MTPS was accomplished in a twin-screw co-rotating CENTURY extruder. MTPS was produced by reactive plasticization of regular corn-starch using MA modifier and glycerol (20-wt%) plasticizer as explained above. MTPS, previously oven dried overnight at 75°C, was ground to a fine powder and mixed with PCL to obtain various ratios: 70:30, 80:20, and 90:10 (PCL:MTPS). The temperature used is shown in Table 2 below. The vent port was kept open to remove maleic acid and water. The extruded strand ("PCL-MTPS" graft copolymer) was cooled using a water bath and pelletized in line.

Table 2: Extrusion processing conditions in the synthesis of PCL-MTPS graft copolymers

ZONE	SET	ACTUAL	UNITS
ZONE1	15	37	°C
ZONE2	95	96	°C
ZONE3	125	132	°C
ZONE4	150	150	°C
ZONE5	160	164	°C
ZONE6	165	176	°C
ZONE7	170	173	°C
ZONE8	170	169	°C
ZONE9	170	169	°C
DIE	150	152	°C
MELT TEMP.		155	°C
MOTOR SPEED		150	RPM
TORQUE		75	%
PRESSURE		95	Psia
FEEDER SPEED, CENTURY (PCL)		250	%
FEEDER SPEED, MINI			%
FEEDER SPEED, EXT (MTPS)			%

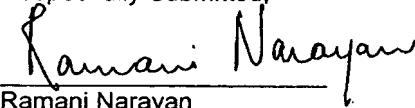
[0012] Demonstration of Grafting and Soxhlet Extraction: The above PCL-MTPS graft copolymers were extracted in dichloromethane (DCM) solvent. Around 2-3 grams of the sample were accurately weighed into a cellulose extraction thimble (33 mm x 94 mm) and placed into the thimble holder. The evaporated solvent condensed into the thimble containing the sample. The extraction was performed for 24 hours. After extraction, the thimble, along with the sample, was removed and dried to constant weight. The aim of the extraction was to selectively remove the unreacted PCL from the PCL-MTPS graft copolymers. The soxhlet extraction results of PCL-MTPS graft copolymers are shown in Table 3 below. As seen from the table, almost complete extraction is achieved for PCL/MTPS graft copolymers, no matter at what ratios they were mixed. This confirms the fact that PCL has reacted with the modified thermoplastic starch. As is well known, starch is insoluble in dichloromethane, so the fact that all of the material was extracted in dichloromethane leaving no starch residue requires that the PCL is extensively grafted onto the starch. An unmodified thermoplastic starch (i.e., starch physically blended/plasticized with glycerol but with no chemical modification) was also reacted with TONE 787 PCL

using the same process conditions. In this case, starch was left behind as a residue upon extraction with dichloromethane indicating the absence of grafting.

Table 3: Proof of grafting by Soxhlet Extraction

System	PCL initially present (gm)	MTPS initially present (gm)	Material extracted (gm)	% Extracted
70PCL-30MTPS	1.34	0.57	1.89	98.95
70PCL-30MTPS, Duplicated	1.73	0.74	2.44	98.79
80PCL-20MTPS	1.61	0.40	2.01	99.90
80PCL-20MTPS, Duplicated	1.74	0.43	2.16	99.54
90PCL-10MTPS	1.97	0.22	2.18	99.54
90PCL-10MTPS, Duplicated	1.94	0.22	2.15	99.54

[0013] I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully Submitted,


Ramani Narayan

September 7, 2010

Date

Attachment: Appendix A (Raquez et al., "Maleated thermoplastic starch by reactive extrusion," *Carbohydrate Polymers*, vol. 74 (2008), p. 159-169)

Maleated thermoplastic starch by reactive extrusion

Jean-Marie Raquez^{a,d,*}, Yogaraj Nabar^b, Madhusudhan Srinivasan^b,
Boo-Young Shin^c, Ramani Narayan^b, Philippe Dubois^a

^a Center of Innovation and Research in Materials & Polymers (CIRMAP), Laboratory of Polymer and Composite Materials,
University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium

^b Department of Chemical Engineering & Material Science, 2527 Engineering Building, Michigan State University, East Lansing, MI 48824, USA

^c Department of Chemical Engineering and Technology, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Republic of Korea

^d Ecoles des Mines de Douai, 941 Rue Charles Bourseul, BP 10838, F-59508 Douai, France

Received 17 November 2007; received in revised form 28 January 2008; accepted 29 January 2008

Available online 6 February 2008

Abstract

Novel maleated thermoplastic starch (MTPS) with both improved processing and reactivity useful in the melt-blending with biodegradable polyester was prepared through *in situ* reactive modification of thermoplastic starch (TPS) with maleic anhydride (MA) as esterification agent. Glycerol was used as plasticizer. Physico-chemical parameters of MTPS were determined at different MA contents, while keeping both the content in glycerol (20 wt% by starch), and the processing temperature constant (150 °C). Soxhlet extraction attested for the complete incorporation of glycerol into the starch backbone during the maleation process at low content in MA. In addition, two-dimensional liquid-phase NMR measurements attested for the preferential esterification of starch backbone at C6, together with the occurrence of some hydrolysis and glucosidation reactions. Such reactions promoted by MA moieties reduced the intrinsic viscosity of the MTPS, expecting an improvement in its processability. WAXS diffraction analyses confirmed the complete disruption of the granular structure of native starch in MTPS during the reactive extrusion processing.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Extrusion; Starch; Maleation

1. Introduction

Over the past decades, starch, anhydroglucosidic polymer, has attracted considerable attention as an interesting structural platform for the manufacture of sustainable and biodegradable plastic packaging due to its natural abundance and low cost (Gross, 2002; Reddy, Ghai, & Rashmi, 2003). Starch composed by two isomers (amylose – linear one and amylopectine – highly branched one) is derived from renewable resource (Mohanty, Misra, & Hinrichsen, 2000). This represents an elegant way to prevent

the depletion of petrochemical feedstock and the emission of fossil fuel-derived CO₂. As biomaterial, thermoplastic starch (TPS) can be prepared in specific extrusion conditions using plasticizers (de Graaf, Karman, & Janssen, 2003; Forssell, Mikkila, Suortti, Seppala, & Poutanen, 1996; Narayan, 1994; Nayak, 1999; Shogren, Fanta, & Doane, 1993; Stepto, 2003; Van Soest, Benes, & de Witt, 1996). The most widely used plasticizers are glycerol and water. The role of plasticizers is to *destructure* granular starch by breaking hydrogen bonds between the starch macromolecules, accompanying with a partial depolymerization of starch backbone, in order to lower the melting and the glass transition temperatures of starch below its decomposition temperature (230 °C) (Souza & Andrade, 2002; Stepto, 2003). However, its hydrophilic nature makes TPS susceptible to moisture attacks and significant changes in dimensional stability and mechanical properties.

* Corresponding author. Address: Center of Innovation and Research in Materials & Polymers (CIRMAP), Laboratory of Polymer and Composite Materials, University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium. Tel.: +32 65 37 3371; fax: +32 65 37 3484.

E-mail address: jean-marie.raquez@umh.ac.be (J.-M. Raquez).

To impart hydrophobicity to TPS, some authors have tried to overcome these weaknesses by melt-blending starch with a moisture resistant polymer with good mechanical properties, while maintaining the biodegradability of the overall product. Therefore, hydrophobic biodegradable polymers such as poly(ϵ -caprolactone) and cellulose acetate have largely been utilized in starch-based formulations (Averous, Moro, Dole, & Fringant, 2000; Fang & Hanna, 2000, 2001a, 2001b; Martin, Schwach, Averous, & Couturier, 2001; Neumann & Seib, 1993; Shogren, 1996; Wang & Shogren, 1997; Willett & Shogren, 2002; Xu & Doane, 1998). Recently, poly(butylene adipate-co-terephthalate) (PBAT), biodegradable aliphatic-aromatic copolyester, has shown to be a valuable candidate for melt-blending with starch-based products due to its interesting thermal and mechanical properties (Nabar, Raquez, Dubois, & Narayan, 2005; Nabar, Draybuck, & Narayan, 2006).

Developing such melt-blends with satisfactory overall physico-mechanical behavior depends on the ability to control interfacial tension, to generate a small dispersed phase size and strong interfacial adhesion, and to improve the stress transfer between the component phases (Barlow & Paul, 1984). In this respect, most of researches have focused on the grafting of highly reactive functions such as maleic anhydride (MA) onto the polymeric backbone using different methods (Bratawidjaja, Gitopadmoyo, Watanabe, & Hatakeyama, 1989; Ho, Su, Wu, & Chen, 1993; Mani, Battacharya, & Tang, 1999; Minoura, Ueda, Mizunuma, & Oba, 1969; Oliphant, Russel, & Baker, 1995; Rengarajan, Parameshwar, Lee, & Rinaldi, 1990; Ruggeri, Aglietto, Petramani, & Ciardelli, 1983; Shi et al., 2001; Singh, 1992; Vijayakumar, Reddy, & Joseph, 1985; Xie, Yu, Liu, & Chen, 2006). These grafted functions can react with the hydroxyl groups of starch macromolecules to form covalent bonds; and thus, they provide better control of the size of phase and strong interfacial adhesion. However, although many have attempted for years to discover the “perfect” starch/polymer blend that would yield an environmentally sound polymer while, at the same time, fulfilling desired mechanical and cost criteria, such a combination has been difficult to achieve. The reason is that the emphasis has been on finding the optimal polymer or mixture of polymers and other admixtures in order to thereby “optimize” the properties of the starch/polymer blend.

Furthermore, a major issue that most of authors have not addressed yet, is that the morphology (particularly, the size of dispersed domain) that depends on the difference of melt-viscosity for different polymeric partners, can strongly affect the mechanical properties for the resulting melt-blends. It is very critical since starch plasticized or not (Wu et al., 1995) exhibits high melt-viscosity related to its high molecular weight (ranging from 100,000 to 500,000 g/mol and more than millions, respectively, for amylose and amylopectin). As a consequence, at least 20% plasticizer are required in the preparation of plasti-

cized starch-based melt-blends at temperature close to 130 °C (Tomasik, Wang, & Jane, 1995).

Acid derivatization of starch is a well-known technique to obtain lower viscosity products, which are dispersible at higher solids than one made from the native starch, and one whose dispersions are still able to be pumped and handled (Caldwell, Hills, & Wurzburg, 1953; Miladinov & Hanna, 2000; Radley, 1976; Tomasik et al., 1995). Interestingly, cyclic dibasic acid anhydrides such as maleic anhydride can yield starch esters containing a free carboxylic group that be able to promote acid-catalyzed transesterification reactions with biodegradable polyesters, leading to the formation of a graft copolymer. Tomasik et al. (Tomasik et al., 1995) reported a similar chemical modification of corn starch using MA and the like, and by varying amounts of water (18%, 20% and 30%) as plasticizer, the whole process was carried out by extrusion. Carbonate buffer, either at pH 8 or pH 9, was added. It resulted that extrusion of starch with cyclic anhydrides in alkaline medium presented a facile method for the preparation of anionic thermoplastic starches. However, such modified hydrophilic thermoplastic contained large amounts in water, rendering difficult their melt-blending with hydrophobic polyester, for instance poly(butylene adipate-co-terephthalate).

This paper aims at investigating the one-step and continuous plasticization and maleation reaction of starch by reactive extrusion. Glycerol was used as a plasticizer, and was kept at a constant content (20 wt%) with respect to starch. Maleic anhydride content has been changed, and its effect on the physico-chemical parameters for the resulting maleated thermoplastic starch (MTPS) has thoroughly been studied. Solution viscometry, two-dimensional liquid-phase NMR methods (DEPT, ^1H - ^{13}C HMQC and g-COSY), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and wide angle X-ray scattering (WAXS) analysis were used as main characterization tools.

2. Experimental section

2.1. Materials

Regular silver medal pearl corn starch (unmodified) was obtained from Cargill-grade SMP 1100 (MN, USA), with equilibrium moisture content of about 12 percent (w/w). Anhydrous glycerol (99.9%) and maleic anhydride (MA, 99%) were obtained from J.T. Baker (NJ, USA) and Sigma-Aldrich (WI, USA), respectively.

2.2. Preparation of maleated thermoplastic starch (MTPS)

Regular silver medal pearl corn starch was reactively modified using MA as an esterification agent in a twin-screw co-rotating CENTURY ZSK-30 extruder with a screw diameter of 30 mm and a L/D ratio of 42. MA was ground to a fine powder using a mortar and pestle, and

mixed with starch (800 g starch + [20 (2.5 wt%)/40 (5 wt%)/64 (8 wt%) g] MA) using a kitchen blender for 15 min before being introduced to the feed port of the extruder. Glycerol as a plasticizer was pumped to the extruder through a peristaltic pump for a mass composition of starch/glycerol close to 80:20. Vacuum (using water jets) was applied at the vent port downstream to remove out the unreacted MA and excess moisture. The temperature profile used was 15/95/125/145/160/165/165/165/150/145 from the feed throat to the die, and the melt temperature was 153 °C. The screw speed employed was 120 rpm corresponding to a mean residence time of around 7 min. A cylindrical filament die 2.7 mm in diameter and 8.1 mm in length, with a cooling sleeve was assembled to the extruder for collecting the extruded samples. The resulting MTPS was stored in an oven at 50 °C. For FTIR and NMR characterizations, unreacted MA and excess glycerol were extracted from MTPS samples through Soxhlet extraction carried out in acetone for 3 days.

2.3. Characterization and analyses

¹H and ¹³C NMR spectra were recorded using a Varian 500 MHz superconducting NMR spectrometer operating at 499.955 MHz interfaced with a Sun Microsystems Ultra2 UNIX console in dimethylsulfoxide-*d*₆ (DMSO-*d*₆; Sigma–Aldrich WI, USA, 99%) at 60 °C. FTIR analysis was conducted on samples of MTPS from 400 cm^{−1} to 4000 cm^{−1} using a Perkin-Elmer Model 2000 FTIR. One percent of MTPS was mixed with 99% KBr powder and pressed using a pellet maker to a fine transparent disk. This disk was directly put into the sample holder in FTIR to obtain the spectrum. The intrinsic viscosity of starch, extracted TPS and MTPS samples were determined using a Cannon Ubbelohde viscometer (size 0B) in DMSO solvent (Sigma–Aldrich, WI, USA, 99.5%) at 25 °C following the Huggins method. A high resolution thermal gravimetric analyzer (TGA) 2950 from TA Instruments was used to determine the degradation temperature of the starch, TPS and the MTPS samples under nitrogen flow. The sample was heated to 550 °C at a rate of 10 °C/min. A high resolution differential scanning calorimeter (DSC) 2920 from TA Instruments was used to determine the thermal transitions of the MTPS under nitrogen flow. MTPS samples were heated to 200 °C at a rate of 10 °C/min, cooled to −50 °C and then reheated to 200 °C. Second scan data were taken for analysis. X-ray diffraction analysis was performed with a Rigaku Rotaflex Ru-200BH wide angle X-ray (WAXS) diffractometer operated at 45 kV, 100 mA with a nickel filtered Cu K_{α1} radiation and a θ compensating slit. Data were acquired in 0.02° 2 θ , at the rate of 1°/min. The spacing of crystals, *d*, was calculated using the Bragg's equation, $\lambda = 2d \sin \theta (\lambda(\text{CuK}_{\alpha 1}) = 0.15406 \text{ nm})$. Samples were used in the form of a powder. The samples were equilibrated in a constant environment room at 23 ± 1 °C and 50 ± 2% RH for at least 72 h before testing.

3. Results and discussion

3.1. Maleated thermoplastic starch (MTPS)

In situ chemical modification of thermoplastic starch (TPS) was accomplished through reactive extrusion, in the presence of glycerol as plasticizer (20 wt% by starch), and at different contents in maleic anhydride (MA) as esterification agent (0, 2.5, 5, and 8 wt% by starch), in an attempt to produce reactive functional groups onto the starch backbone. Such an approach is expected to improve the interfacial adhesion between starch and other biodegradable polyesters.

Table 1 reports the intrinsic viscosity ($[\eta]$) and the recovery yield for the resulting maleated TPS (MTPS) after Soxhlet extraction. For the sake of comparison, the recovery yield and $[\eta]$ for TPS, together with $[\eta]$ of pure regular corn starch are reported. The Soxhlet extraction was employed solely as a qualitative tool in the purification of MTPS and TPS, and was carried out for extraction of unreacted MA and excess glycerol (not strongly physically/chemically bound) in acetone for 3 days. The ester derivatives from reactions between MA and glycerol in MTPS could be also extracted since they had shown to be soluble in acetone as determined by selective solubilization experiments (not reported here). It is pointing out that some attempts to purify MTPS were carried out by solubilization of crude MTPS in dimethylsulfoxide (DMSO), and then precipitation in different solvents (water and acetone) miscible with DMSO. However, for MTPS prepared with higher content in MA, a suspension solution was obtained on precipitation, rendering it difficult for recovery.

From Table 1, by comparison to that of TPS (85 wt% recovery yield), the amount of residues for MTPS (96 wt%) was much higher when 2.5 wt% MA was added (entries 2 and 3, Table 1). This attested for the reaction of glycerol with starch during the maleation process. Surprisingly, increasing MA content decreased the amount of residues for the resulting MTPS (entries 3–5, Table 1). This could be explained by the reduction in the relative molecular weight of starch, to such extent that some fractions of modified starch were soluble in acetone (used for Soxhlet extraction). This was supported by the decrease in intrinsic viscosity ($[\eta]$) for the resulting MTPS. For

Table 1
Effect of MA content on $[\eta]$ and recovery yield of MTPS prepared at different MA contents, and TPS after Soxhlet extraction

Entry	Nature	Recovery yield (%) ^a	$[\eta]$ ^b (dL/g)
1	Corn Starch	–	1.51
2	TPS	85	1.19
3	MTPS (2.5 wt% MA)	96	0.27
4	MTPS (5 wt% MA)	92	0.24
5	MTPS (8 wt% MA)	85	0.18

^a By gravimetry after Soxhlet extraction carried out in acetone for 3 days.

^b By solution viscometry in DMSO at 25 °C (after Soxhlet extraction).

instance, $[\eta]$ of MTPS prepared with 2.5 and 8 wt% MA were of 0.27 and 0.18 dL/g, respectively. This reduction in $[\eta]$, and thus in relative molecular weight, could be ascribed to some acid-catalyzed reactions of starch with water and glycerol, occurring during the maleation of starch. These reactions will be discussed hereafter (see determination of MTPS structure). By comparison to $[\eta]$ of corn starch, unmodified starch underwent some partial depolymerization reactions (reducing the molecular weight of starch) after its plasticization (Stepito, 2003) as attested by the slight decrease in $[\eta]$ (entries 1 and 2 Table 1).

Fig. 1 shows the expanded FTIR spectrum of extracted MTPS modified with 8 wt% MA, together with those of corn starch and TPS (entries 1–2 and 5, Table 1). The unreacted MA and excess glycerol was previously extracted from MTPS by Soxhlet extraction in acetone as aforementioned (see Section 2). For the native granular corn starch, a relevant band from 3200 to 3400 cm^{-1} could be observed due to the stretching of inter- and intramolecular bonding hydroxyl groups of starch. When glycerol was used as a plasticizer, two additional peaks at 2984 and 2912 cm^{-1} appeared due to the formation of inter- and intramolecular bonds between starch and glycerol hydroxyl groups. The most striking feature is that the extracted MTPS exhibited a carbonyl stretch peak at 1720 cm^{-1} , attesting that MA was covalently linked to the starch backbone. Moreover, the MTPS sample did not display the peak at 1787 cm^{-1} corresponding to the ring anhydride carbonyl functions, which suggested that MA ring was fully reacted and opened.

To determine the structure of MTPS, two-dimensional liquid-phase NMR methods (DEPT, ^1H – ^{13}C HMQC and g-COSY) have been employed in the characterization of MTPS derivatives. Fig. 2 shows the ^1H – ^{13}C HMQC NMR spectrum of extracted MTPS modified with 8 wt%

MA (entry 5, Table 1). The carbon atoms C1–1' (100.3, 100.1, and 99.7 ppm), C2 (71.7 ppm), C3 (73.0 ppm), C4 (78.6 and 79.0 ppm), C5 (71.3 ppm), C6 (60.7 and 60.2 ppm) were readily assigned to the glucosidic unit of starch (present in linear amylose and branched amylopectin), and were accordingly correlated to their respective protons H1–1' (5.2 and 5.1 ppm), H2–5, (3.5–3.6 ppm) and H6 (3.3 ppm) in a good agreement with the literature (Chakraborty, Sahoo, Teraoka, Miller, & Gross, 2005; Dais & Perlin, 1982; Gidley, 1985). Small resonance peaks characteristic to glycerol, which reacted with starch (see hereafter), could be also observed (^{13}C NMR: 72.4 (–CHOH–; C7) and 63.5 ppm (–CH₂–OH; C8/8'); ^1H NMR: 3.5 ppm (–CHOH–; H7) and 3.1 and 3.8 ppm (–CH₂–OH; H8/8')), but unreacted MA was absent from the ^1H – ^{13}C HMQC NMR spectrum (^{13}C NMR: 164.5 (–C(O)O–) and 136.8 ppm (C=C); ^1H NMR: 7.0 ppm (–CH=CH–)). Two cross-peaks at 70.1/3.0 ppm (C4'/H4') and at 98.6/4.7 ppm (C1''/H1'') assigned to the non-reducing terminal units of starch and the hydroxyl anomeric carbon, respectively, attested for the partial hydrolysis of the starch backbone during the maleation process (Scheme 1a). These signals were almost absent in the ^1H – ^{13}C HMQC NMR spectrum of unmodified TPS extracted by Soxhlet (entry 2, Table 1; not shown here). In addition to hydrolysis reactions, starch backbone underwent some glucosidation reactions with glycerol as promoted by MA (Scheme 1b). This was supported by the presence of cross-peaks at 102.9/4.6 ppm (C1'''/H1'''), 62.8–62.3/3.3–3.5 ppm (C6''/H6'') and at 74.9/3.4 ppm (C5'/H5' and C2'/H2', broad signal). Such a behavior has already been reported in the case of *starch-derived glycol and glycerol glucosides* (Chong, Xing, Philipps, & Corke, 2001). In the presence of acid functions resulting from, e.g. MA grafting onto the starch backbone by esterification, the reaction of

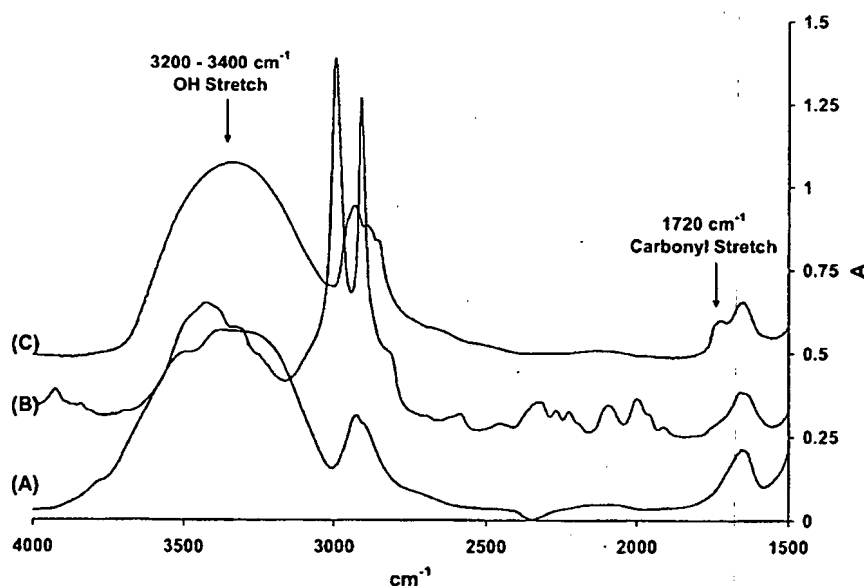


Fig. 1. Expanded FTIR spectra of extracted MTPS (C) modified with 8 wt% MA, TPS (B) and corn starch (A) (see Table 1).

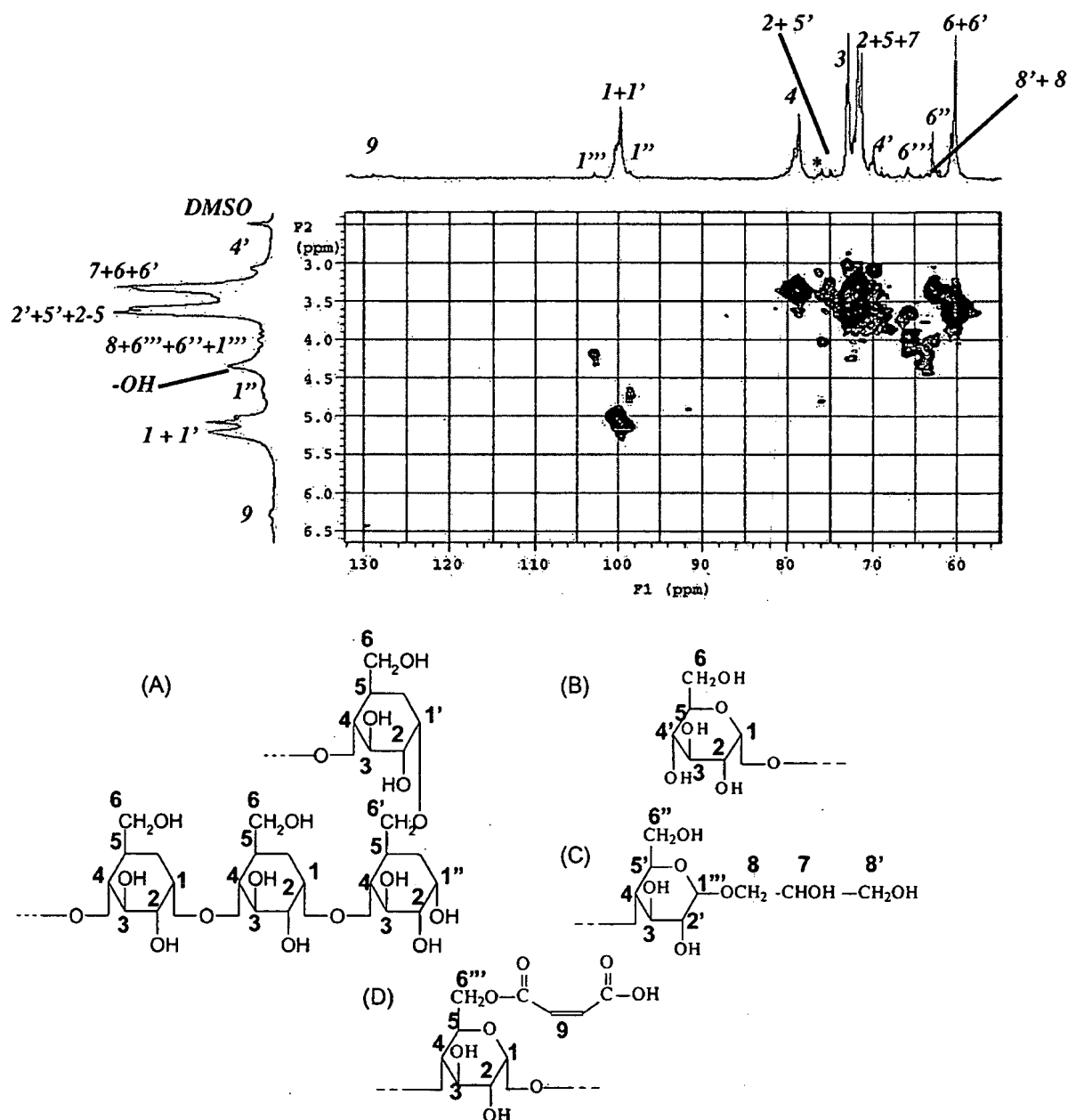
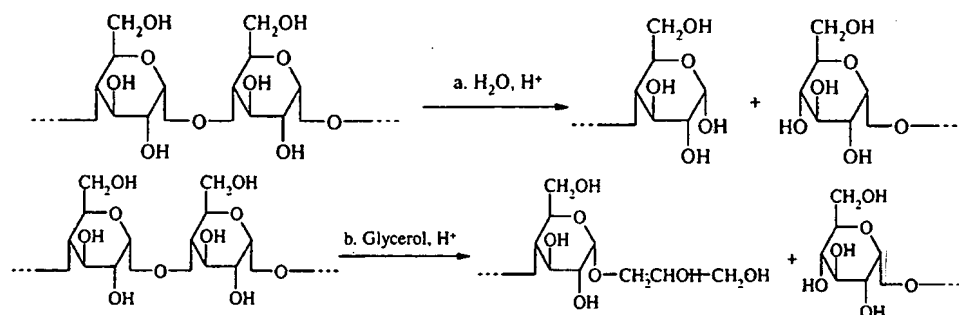


Fig. 2. ^1H - ^{13}C HMQC NMR spectrum of extracted MTPS prepared with 8 wt% MA (entry 5, Table 1) determined in $\text{DMSO}-d_6$ at 60°C (see depictions hereafter for assignment; *ester carbon derived from maleated-starch ring).

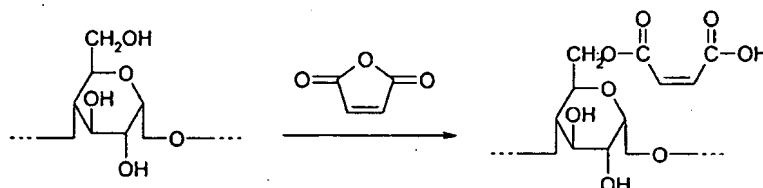
starch with glycol/glycerol at elevated temperature yields glucosides with chemical properties of acetal functions.

Within the limit of resolution in the NMR spectra, one could not exclude that glucosidation reactions might occur through both CH_2 and CH groups of glycerol. The most striking feature was the presence of a downfield shift originated from a CH_2 group (evidenced by DEPT analysis, not shown here) at 65.8/4.1 ppm ($\text{C6}''/\text{H6}''$), which attested for the esterification, of starch backbone with MA. This occurred mainly at the C6 positions of glucose units (Scheme 2).

According to the literature (Gidley, 1985), this was supported by the cross-peak at 129.5/6.4 ppm ($\text{C9}/\text{H9}$) characteristic to the vinyl functions of open MA moieties grafted onto starch backbone. However, from the ^1H NMR spectrum (Fig. 2, right), the resonance peak at 6.4 ppm appeared broad due to a heterogeneous chemical environment for the $\text{C}=\text{C}$ group (Mani et al., 1999), i.e. the formation of different types of ester functions (mono- and diester). Indeed, as observed from the ^1H - ^1H g-COSY NMR spectrum of extracted MTPS modified with 8 wt% MA (Fig. 3), the presence of a small cross-peak at



Scheme 1. Hydrolysis (a) and glucosidation (b; for sake of clarity, only the reaction between starch and the hydroxymethylene function from glycerol is represented) reactions present during the *in situ* maleation of TPS.



Scheme 2. Esterification reaction of starch with MA occurring at the C6 position (the most preferential position, see text).

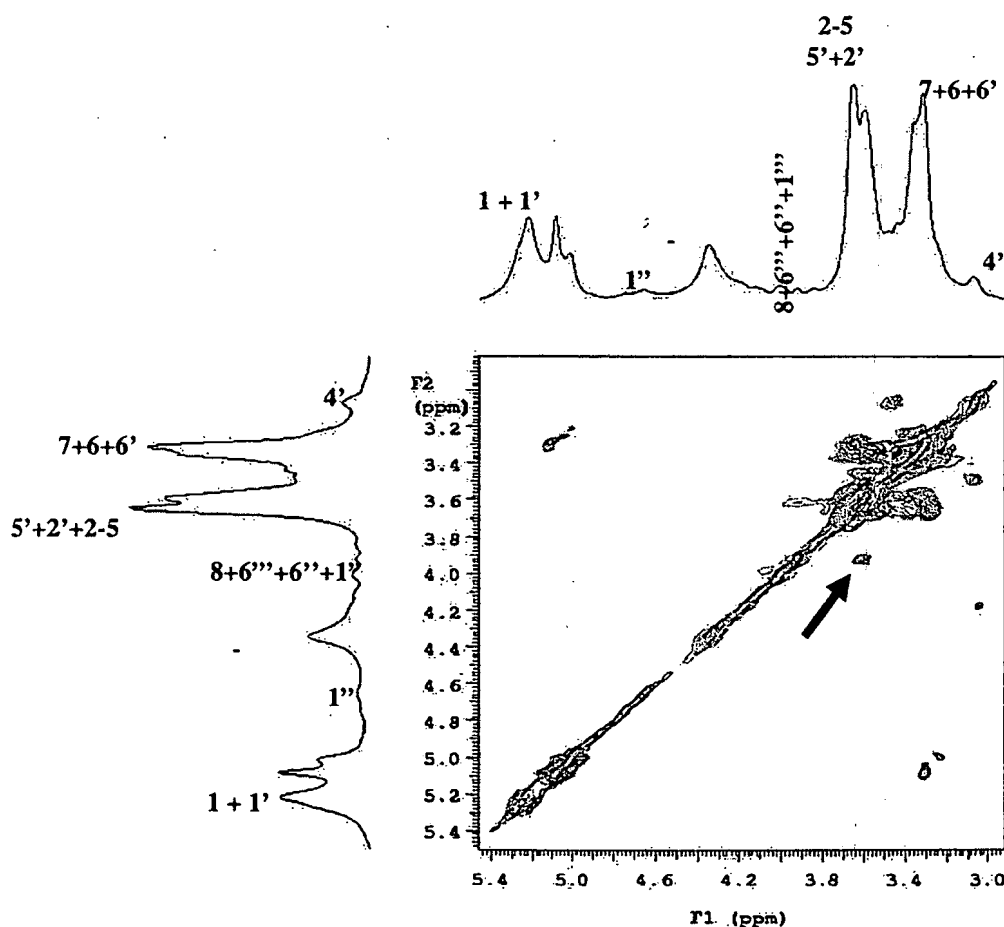


Fig. 3. ^1H - ^1H g-COSY NMR spectrum of extracted MTPS prepared with 8 wt% MA (entry 5, Table 1) determined in $\text{DMSO}-d_6$ at 60 $^\circ\text{C}$ (see depictions for assignment; arrow represents ester proton of maleated-starch ring).

3.9 ppm, characteristic to ester functions, correlated to the glucosidic unit protons H2–5 (3.5–3.6 ppm) attested that some MA molecules had directly reacted onto the starch ring. However, due to the heterogeneity of MTPS (glucosidation and hydrolysis), it was impossible to determine the degree of substitution as obtained by maleation of starch backbone.

3.2. Thermal analyses

DSC thermograms of corn starch, TPS and MTPS modified with 2.5 wt% MA are shown in Fig. 4. From Fig. 4, one cannot detect any melting temperature for native starch, attesting for the thermal degradation of starch before it melted (Forssell et al., 1996). This occurred mainly during the first heating scan (see Section 2). However, in the presence of plasticizers, the native starch was destructurized under heating and shearing, which broke the hydrogen bonds in starch, so-destroying partially its initial crystalline nature. Accordingly, a broad melting endotherm was observed for TPS, whereas two sharp melting endotherms were observed for MTPS. The melting temperature of MTPS was around 153 °C, i.e. 10 °C higher than TPS. This difference in melting behavior for MTPS was attributed to the maleation process, which had chemi-

cally modified the whole structure of native starch backbone.

The thermal stability of MTPS, cornstarch, and TPS were assessed by thermogravimetric analyses (TGA) under inert atmosphere (nitrogen). However, the results derived from TGA curves showed that the thermal behavior for MTPS was complicated (not shown here), due to the concomitant occurrence of secondary thermal processes such as water and glycerol evaporation with the main degradation of MTPS. In this respect, derivatived TGA results of cornstarch, TPS and MTPS prepared at different contents in MA were reported in Figs. 5 and 6 to get a better insight based on the maximum temperature corresponding to the thermal degradation of starch backbone (ca. 350 °C). From Fig. 5, it can be observed that the maximum temperature corresponding to the thermal degradation of starch backbone was higher for TPS and MTPS modified with 2.5 wt% MA than native cornstarch. In other words, MTPS and TPS were both more thermally stable than native cornstarch. However, MTPS showed a slightly higher thermal stability than TPS based on the weight composition at the maximum degradation temperature. At a temperature of approximately 350 °C, 66 wt% of TPS were degraded compared to 58 wt% for MTPS. Both TPS and MTPS showed additional weight loss due to the presence

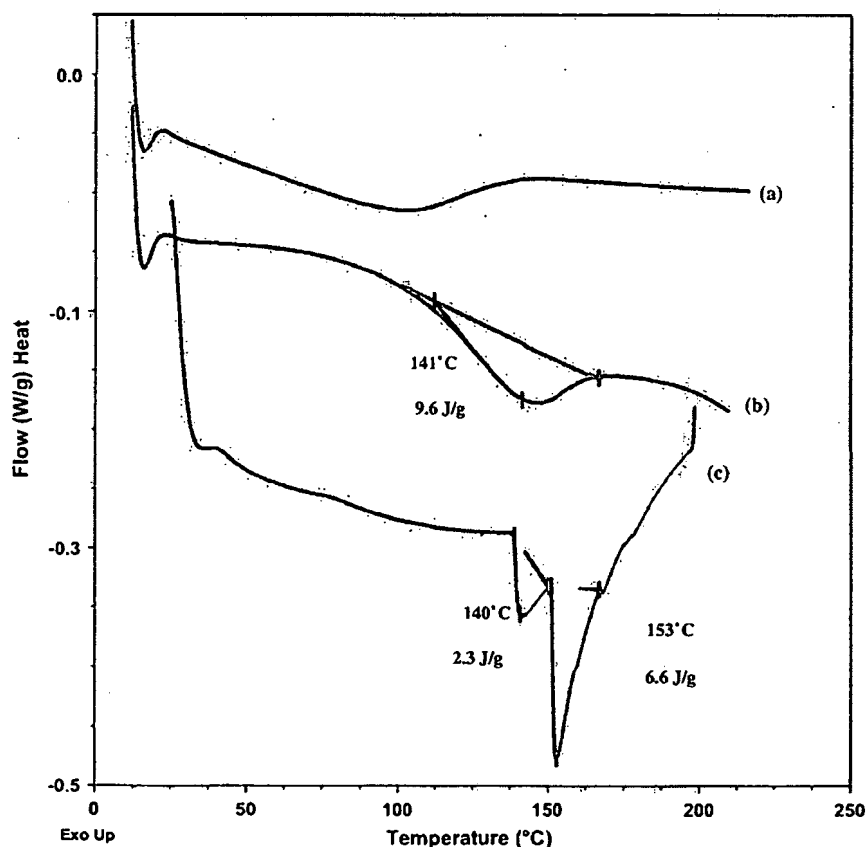


Fig. 4. DSC thermograms of starch (a), TPS (b) and MTPS modified with 2.5 wt% MA (c) (entries 1–3, Table 1; determined from –50 °C to 200 °C at a heating rate of 10 °C/min under nitrogen flow, second scan).

26
27

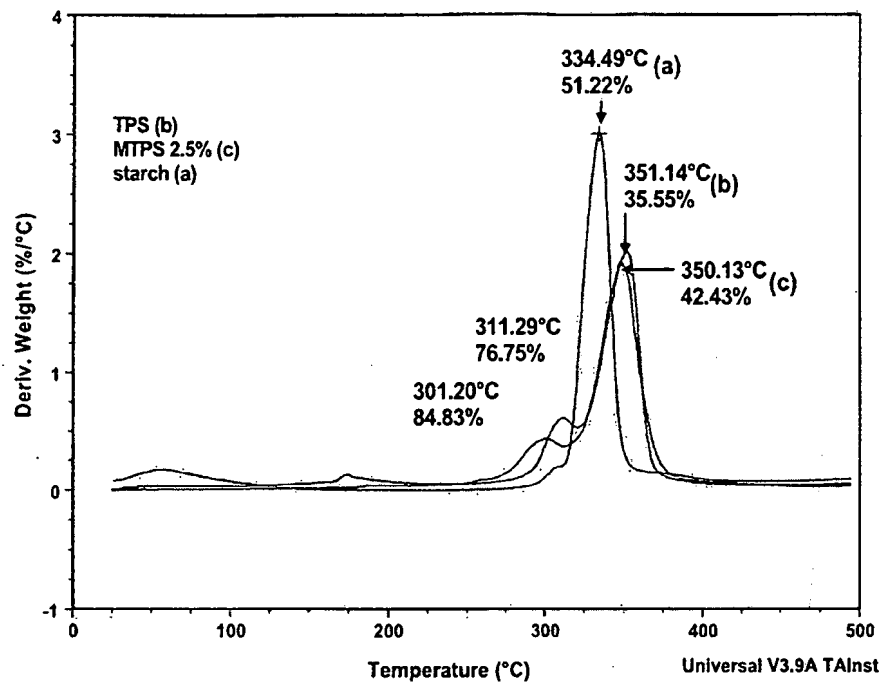


Fig. 5. TGA results of starch (a), TPS (b) and MTPS samples modified with 2.5 wt% MA (c) (entries 1–3, Table I; from r.t. to 500 °C at a heating rate of 20 °C/min under helium flow).

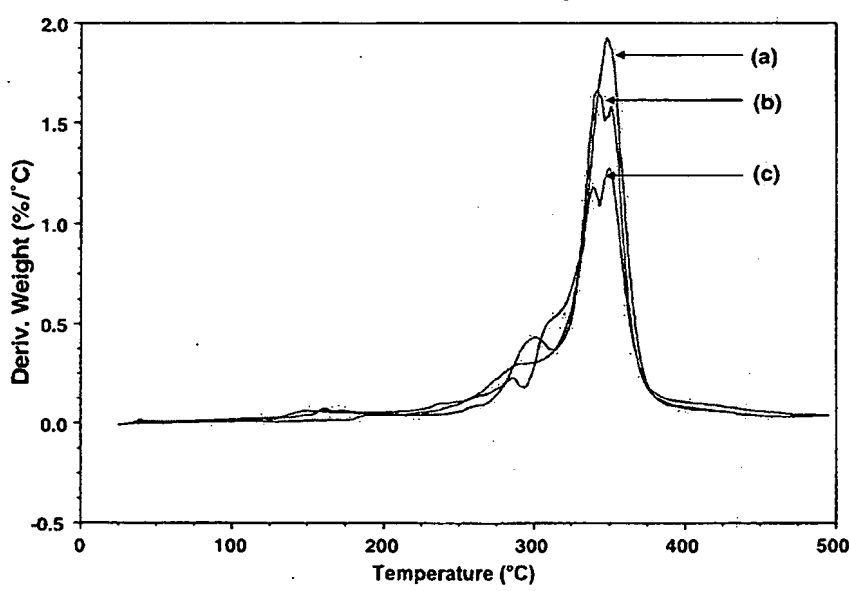


Fig. 6. TGA results of MTPS samples modified with 2.5 (a), 5 (b) and 8 wt% (c) MA (entries 3–5, Table I; from r.t. to 500 °C at a heating rate of 20 °C/min under helium flow).

of glycerol as observed at ca. 305 °C. From Fig. 6, MTPS samples modified with 5% and 8% MA exhibited two peaks in the derivative curve for the degradation of starch as opposed to one peak for MTPS modified with 2.5% MA. This observation supports the fact that the structure of starch backbone was significantly modified after maleation (see next paragraph).

3.3. X-ray diffraction patterns for regular corn starch, TPS and MTPS

WAXS diffractograms for regular corn starch and plasticized starch are shown in Fig. 7. Native starches are bio-synthetically assembled as semi-crystalline granules. The type of native, crystalline structure, labeled as A-, B-, or

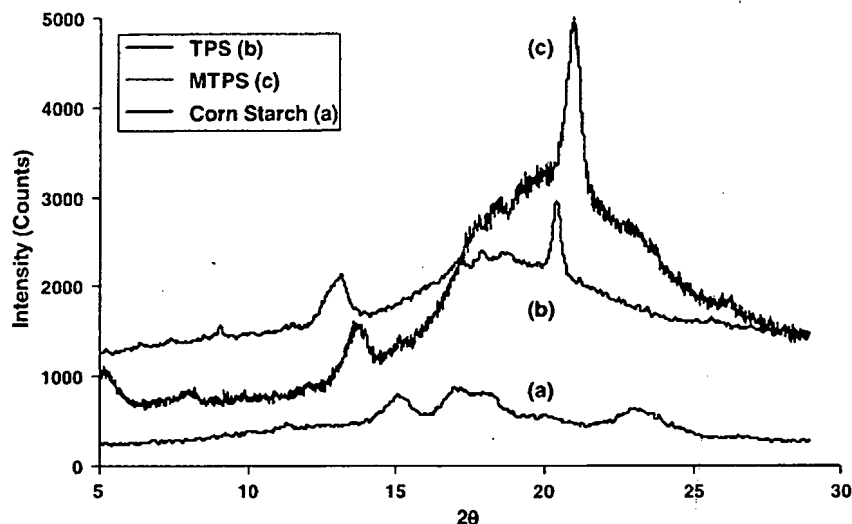


Fig. 7. WAXS diffraction patterns for granular starch (a), TPS (b), and MTPS modified with 8 wt% MA (c) (entries 1–2 and 5, Table 1).

C-type, depends on the starch source (Carr, 1991). As shown in Fig. 7(a), two single peaks at 14.8° and 22.6° and the double peak corresponding to 16.6° and 17.7° are characteristic to A-type crystals observed in starches from grains (as in corn). B-starches are found in tuberous plants (as in potato), while the C-type structure is more rare and is thought to be an intermediate form occurring in some plant sources such as pea starch (Muhrbeck, 1991; Ratnayake, Hoover, & Warkentin, 2002; Sarko & Wu, 1978; Vermeylen, Goderis, Reynaers, & Delcour, 2004). Native A- and B-type crystal lattices consist of double helical, sixfold structures. The difference between the A-type and B-type crystallinity is the packing density of the double helices in the unit cell (Imberty, Buleon, Tran, & Perez, 1991).

TPS that is prepared by kneading, extrusion, compression molding, or injection molding of several native starches with glycerol as a plasticizer, may exhibit two types of distinguished crystallinity directly after processing.

- (1) Residual crystallinity: native A-, B-, or C-type crystallinity caused by incomplete melting of starch during processing.
- (2) Processing-induced crystallinity: amylose V_H -, V_A -, or V-glycerol-type crystallinity, which is formed during thermo-mechanical processing.

The amount of residual crystallinity depends on processing conditions like processing temperature and applied shear stress. The composition of the starch/plasticizer mixture influences indirectly the amount of residual crystallinity. Lower amounts of glycerol reduce residual crystallinity. The effects are attributed to an increase in the melt viscosity at decreasing plasticizer content, which promotes an enhancement of the shear stress on the melt (Van Soest, 1996). Processing-induced crystallinity, also influenced by processing parameters, is caused by the fast recrystalliza-

tion of the complex formed between amylose and glycerol into single-helical structures. An increase in the screw speed during extrusion or increasing residence time during kneading triggers an increase in the single-helical type of crystallinity [48]. Several V-type structures have been reported for low and medium moisture starch food products such as bread and several extrusion cooked starch products (Chinnaswamy, Hanna, & Zobel, 1989; Lai & Kokini, 1991).

Residual A-type crystallinity was observed for TPS ($\sim 17^\circ$) (Fig. 7(b)), though diminished, dependent on the native crystal structure. These structures occur when the energy input is lower than necessary to completely melt the native crystals. By X-ray diffraction, three processing-induced crystal structures of single-helical amylose type (V_H -, V_A -, or V-glycerol) have been observed for TPS materials (Radley, 1976). On plasticization, the new processing-induced characteristic crystalline starch peaks were observed at 13.2° and 20.5° . By comparison to the diffraction data for TPS with those in the literature, the diffraction pattern observed was assigned to the V_A structure. Its lattice is indexed as an orthorhombic unit cell with the dimensions: $a = 13.0$, $b = 22.5$, $c = 7.9 \text{ \AA}$ (Winter & Sarko, 1974).

Fig. 7(c) shows the X-ray diffraction pattern of the MTPS. It resulted that the residual crystalline peaks for the native starch crystals at $\sim 17^\circ$ were absent (within the resolution limits provided by WAXS equipment), suggesting that the inherent granular, crystalline structure of the native cornstarch was completely disrupted. Since the MTPS had a lower shear viscosity, the energy input in the extruder was sufficient to plasticize the native starch completely. However, the processing-induced crystallinity of type V_A -caused by the fast recrystallization of amylose complexed with glycerol into single-helical structures was retained, and was observed in the form of individual peaks at 13.5° and 20.8° .

4. Concluding remarks

Novel MTPS was prepared by *in situ* reactive modification of TPS in the presence of MA as an esterification agent and glycerol as plasticizer through reactive extrusion. The influence of different content in MA was first studied over the physico-chemical parameters of MTPS prepared at ca. 150 °C, and at 20 wt% glycerol (by starch). When 2.5 wt% MA was used, reaction of some glycerol to starch backbone occurred during the maleation process. This was supported by the fact that an almost complete recovery yield was obtained for the resulting MTPS after Soxhlet extraction. Increasing MA content decreased the recovery yield for resulting MTPS, due to their partial solubilization in the solvent used for Soxhlet extraction (acetone). Accordingly, intrinsic viscosity, FTIR and two-dimensional liquid-phase NMR measurements proved the occurrence of some hydrolysis and glucosidation reactions promoted by MA moieties grafted onto the starch backbone. This reduced the melt-viscosity, and therefore the relative molecular weight of MTPS. WAXS diffraction analyses also confirmed the complete disruption for the granular structure of native starch in the thermoplastic starch maleate during reactive extrusion. Interestingly, *in situ* esterification reactions prepared MTPS bearing a free carboxylic group mainly at the C6 position of starch carbon. This characteristic feature will be explored for promoting acid-catalyzed transesterification reactions upon melt-blending MTPS with biodegradable aliphatic–aromatic copolyesters (Raquez, Nabar, Dubois, & Narayan, Nara).

Acknowledgments

This research was partly funded by Corn Products International during the JMR's post-doctoral stay at Michigan State University (USA). Authors are very grateful to "Région Wallonne" and European Community (FEDER, FSE) for general support in the frame of "Objectif 1-Hainaut: Materia Nova". This work was partly supported by the Belgian Federal Government Office of Science Policy (SSTC-PAI 6/27).

References

- Averous, L., Moro, L., Dole, P., & Fringant, C. (2000). Properties of thermoplastic blends: Starch–polycaprolactone. *Polymer*, 41, 4157.
- Barlow, J. W., & Paul, D. R. (1984). Mechanical compatibilization of immiscible blends. *Polymer Engineering and Science*, 24, 525.
- Bratawidjaja, A. S., Gitopadmoyo, I., Watanabe, Y., & Hatakeyama, T. (1989). Adhesive property of polypropylene modified with maleic anhydride by extrusion molding. *Journal of Applied Polymer Science*, 37, 1141.
- Caldwell, C. G., Hills, F., & Wurzburg, O. B. (1953). US 2,661,349.
- Carr, M. (1991). Starch-derived glycol and glycerol glucosides prepared by reactive extrusion processing. *Journal of Applied Polymer Science*, 42(1), 45.
- Chakraborty, S., Sahoo, B., Teraoka, I., Miller, L. M., & Gross, R. A. (2005). Enzyme-catalyzed regioselective modification of starch nanoparticles. *Macromolecules*, 38, 61.
- Chinnaswamy, R., Hanna, M. A., & Zobel, H. F. (1989). Microstructural, physicochemical, and macromolecular changes in extrusion-cooked and retrograded corn starch. *Cereal Foods World*, 34, 415.
- Chong, C. K., Xing, J., Philipps, D., & Corke, H. (2001). Development of NMR and Raman spectroscopic methods for the determination of the degree of substitution of maleate in modified starches. *Journal of Agricultural and Food Chemistry*, 49, 2702.
- Dais, P., & Perlin, A. (1982). High-field, ¹³C-NMR spectroscopy of b-D-glucans, amylopectin, and glycogen. *Carbohydrate Research*, 100, 103.
- de Graaf, R., Karman, A., & Janssen, L. (2003). Material properties and glass transition temperatures of different thermoplastic starches after extrusion processing. *Starch/Stärke*, 55, 80.
- Fang, Q., & Hanna, M. A. (2000). Functional properties of polylactic acid starch-based loose-fill packaging foams. *Cereal Chemistry*, 77(6), 779.
- Fang, Q., & Hanna, M. A. (2001a). Preparation and characterization of biodegradable copolyester starch-based foams. *Bioresource Technology*, 78, 115.
- Fang, Q., & Hanna, M. A. (2001b). Characteristics of biodegradable Mater-Bi®-starch based foams as affected by ingredient formulations. *Industrial Crops and Products*, 13, 219.
- Forssell, P., Mikkilä, J., Suortti, T., Seppälä, J., & Poutanen, K. (1996). Plasticization of barley starch with glycerol and water. *Journal of Macromolecular Science – Pure and Applied Chemistry*, A33, 703.
- Gidley, M. (1985). Quantification of the structural features of starch polysaccharides by n.m.r. spectroscopy. *Carbohydrate Research*, 139, 85.
- Gross, R. (2002). Biodegradable polymers for the environment. *Science*, 297, 803.
- Ho, R. M., Su, A. C., Wu, C. H., & Chen, S. I. (1993). Functionalization of polypropylene via melt mixing. *Polymer*, 34, 3264.
- Imberty, A., Buleon, A., Tran, V., & Perez, S. (1991). Recent advances in knowledge of starch structure. *Starch/Stärke*, 43, 375.
- Lai, L. S., & Kokini, J. L. (1991). Physicochemical changes and rheological properties of starch during extrusion. *Biotechnology Progress*, 7, 251.
- Mani, R., Battacharya, M., & Tang, J. (1999). Functionalization of polyesters with maleic anhydride by reactive extrusion. *Journal of Polymer Science Part A – Polymer Chemistry*, 37, 1693.
- Martin, O., Schwach, E., Averous, L., & Couturier, Y. (2001). Properties of biodegradable multi-layer films based on plasticized wheat starch. *Starch/Stärke*, 53, 372.
- Miladinov, V. D., & Hanna, M. A. (2000). Starch esterification by reactive extrusion. *Industrial Crops and Products*, 11, 51.
- Minoura, Y., Ueda, M., Mizunuma, S., & Oba, M. (1969). The reaction of polypropylene of maleic anhydride. *Journal of Applied Polymer Science*, 13, 1625.
- Mohanty, A. K., Misra, M., & Hinrichsen, G. (2000). Biofibres, biodegradable polymers and biocomposites: An overview. *Macromolecular Materials and Engineering*(276/277), 1.
- Muhrbeck, P. (1991). On crystallinity in cereal and tuber starches. *Starch/Stärke*, 43, 347.
- Nabar, Y., Draybuck, D., & Narayan, R. (2006). Physico-mechanical and hydrophobic properties of starch foams extruded with different biodegradable polymers. *Journal of Applied Polymer Science*, 102, 58.
- Nabar, Y., Raquez, J.-M., Dubois, P., & Narayan, R. (2005). Production of starch foams by twin-screw extrusion: Effect of maleated poly(butylene adipate-co-terephthalate) as a compatibilizer. *Biomacromolecules*, 6, 807.
- Narayan, R. (1994). Polymeric materials from agricultural feedstocks. In *Polymers from Agricultural Coproducts*. In M. L. Fishman, R. B. Friedman, & S. J. Huang (Eds.), *ACS Symposium Series* (p. 2) (Vol. 575).
- Nayak, P. (1999). Biodegradable polymers: Opportunities and challenges. *Journal of Macromolecular Science – Reviews in Macromolecular Chemistry and Physics*, C39(3), 481.
- Neumann, P. E., & Seib, P. A. (1993). US 5,208,267.

- Oliphant, K. E., Russel, K. E., & Baker, W. E. (1995). Melt grafting of a basic monomer on to polyethylene in a twin-screw extruder-reaction kinetics. *Polymer*, 36, 1597.
- Radley, J. (1976). *Industrial uses of starch and its derivatives*. London: Applied Science Publishers.
- Raquez, J.-M., Nabar, Y., Dubois, P., & Narayan, R. (2007). In situ compatibilization of maleated thermoplastic starch/polyester melt-blends by reactive extrusion. *Polymer Engineering and Science*, in press.
- Ratnayake, W. S., Hoover, R., & Warkentin, T. (2002). Pea starch: Composition, structure and properties – A review. *Starch/Stärke*, 54, 217.
- Reddy, C., Ghai, R., & Rashmi, V. (2003). Polyhydroxyalkanoates: An overview. *Bioresource Technology*, 87, 137.
- Rengarajan, R., Parameshwar, V. R., Lee, S., & Rinaldi, P. L. (1990). NMR analysis of polypropylene maleic-anhydride copolymer. *Polymer*, 31, 1703.
- Ruggeri, G., Aglietto, M., Petramani, A., & Ciardelli, F. (1983). Some aspects of polypropylene functionalization by free radical reactions. *European Polymer Journal*, 19, 863.
- Sarko, A., & Wu, H.-C. H. (1978). The crystal structures of A-, B- and C-polymorphs of amylose and starch. *Starch/Stärke*, 30, 73.
- Shi, D., Yang, J., Yao, Z., Wang, Y., Huang, H., Jing, W., et al. (2001). Functionalization of isotactic polypropylene with maleic anhydride by reactive extrusion: Mechanism of melt-grafting. *Polymer*, 42, 5549.
- Shogren, R. L. (1996). Preparation, thermal properties, extrusion of high-amylose starch acetates. *Carbohydrate Polymers*, 29(1), 57.
- Shogren, R. L., Fanta, G. F., & Doane, W. M. (1993). Development of starch-based plastics – A re-examination of selected polymer systems in historical perspective. *Starch/Stärke*, 45, 276.
- Singh, R. P. (1992). Surface grafting onto polypropylene – A survey of recent developments. *Progress in Polymer Science*, 17, 251.
- Souza, R., & Andrade, C. (2002). Investigation of the gelatinization and extrusion processes of corn starch. *Advances in Polymer Technology*, 21, 17.
- Stepito, R. (2003). The processing of starch as a thermoplastic. *Macromolecular Symposia*, 201, 203.
- Tomasik, P., Wang, P., & Jane, J. (1995). Facile route to anionic starches – Succinylation, maleination and phthalation of corn starch on extrusion. *Starch/Stärke*, 47, 96.
- Van Soest, J. (1996). Starch plastics: Structure–property relationships. PhD Thesis, University of Utrecht.
- Van Soest, J., Benes, K., & de Witt, D. (1996). The influence of starch molecular mass on the properties of extruded thermoplastic starch. *Polymer*, 37, 3543.
- Vermeulen, R., Goderis, B., Reynaers, H., & Delcour, J. A. (2004). Amylopectin molecular structure reflected in macromolecular organization of granular starch. *Biomacromolecules*, 5(5), 1775.
- Vijayakumar, M. T., Reddy, C. R., & Joseph, K. T. (1985). Grafting of poly(glycidyl methacrylate) onto alginic acid. *European Polymer Journal*, 21, 415.
- Wang, L., & Shogren, R. L. (1997). Proceedings 6th Annual Meeting of the Bio/Environmental Degradable Polymer Society. St. Paul, MN: The Society.
- Willett, J. L., & Shogren, R. L. (2002). Processing and properties of extruded starch polymer foams. *Polymer*, 43, 5935.
- Winter, W. T., & Sarko, A. (1974). Crystal and molecular structure of V-anhydrous amylase. *Biopolymers*, 13, 1447.
- Wu, J., Lee, W.-C., Kuo, W.-F., Kao, H.-C., Lee, M.-S., & Lin, J.-L. (1995). Effects of molecular-weights and compatibilizing agents on the morphology and property of blends containing polypropylene and nylon-8. *Advances in Polymer Technology*, 14(2), 47.
- Xie, F., Yu, L., Liu, H., & Chen, L. (2006). Starch modification using reactive extrusion. *Starch/Stärke*, 58, 131.
- Xu, W., & Doane, W. M. (1998). US 5,854,345.