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Maleated thermoplastic starch by reactive extrusion

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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.

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 CO_2. 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 *destructurize* 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.

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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 plasticized 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 dispersable 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, ^{1}H–^{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

^{1}H and ^{13}C 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 $K_{\alpha 1}$ radiation and a θ compensating slit. Data were acquired in 0.02° 2θ, at the rate of 1°/min. The spacing of crystals, d, was calculated using the Bragg's equation, $\lambda = 2d\sin\theta(\lambda(\mathrm{CuK}_{\alpha 1}) = 0.15406\ \mathrm{nm})$. 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 ([η]) and the recovery yield for the resulting maleated TPS (MTPS) after Soxhlet extraction. For the sake of comparison, the recovery yield and [η] for TPS, together with [η] 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 ([η]) for the resulting MTPS. For

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

Entry	Nature	Recovery yield (%)[a]	[η][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, [η] of MTPS prepared with 2.5 and 8 wt% MA were of 0.27 and 0.18 dL/g, respectively. This reduction in [η], 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 [η] of corn starch, unmodified starch underwent some partial depolymerization reactions (reducing the molecular weight of starch) after its plasticization (Stepto, 2003) as attested by the slight decrease in [η] (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 (–*C*HOH–; C7) and 63.5 ppm (–*C*H_2–OH; C8/8′); ^1H NMR: 3.5 ppm (–C*H*OH–; H7) and 3.1 and 3.8 ppm (–CH_2–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 (–C*H*=C*H*–)). 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

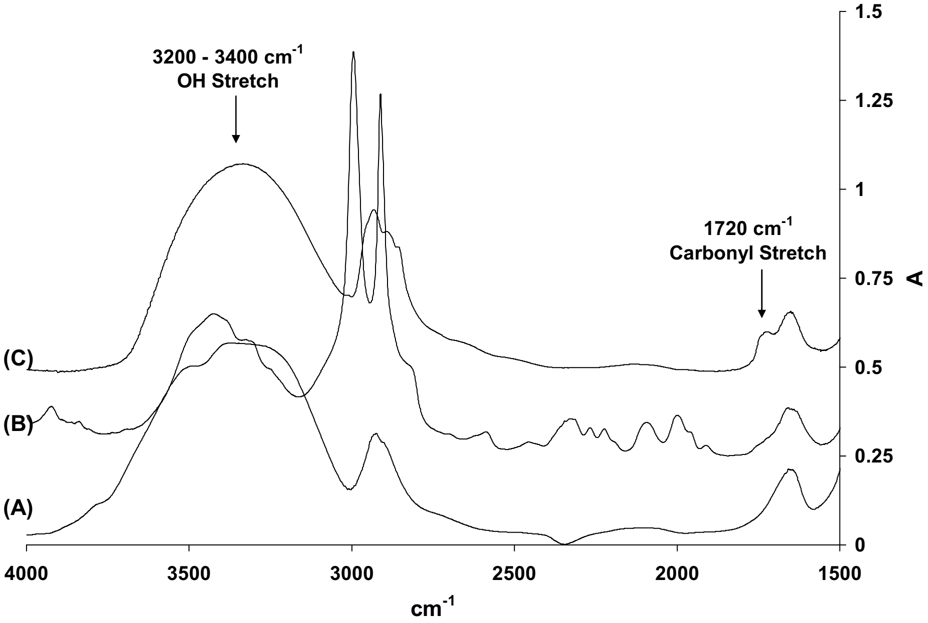


Fig. 1. Expanded FTIR spectra of extracted MTPS (C) modified with 8 wt% MA, TPS (B) and corn starch (A) (see Table 1).

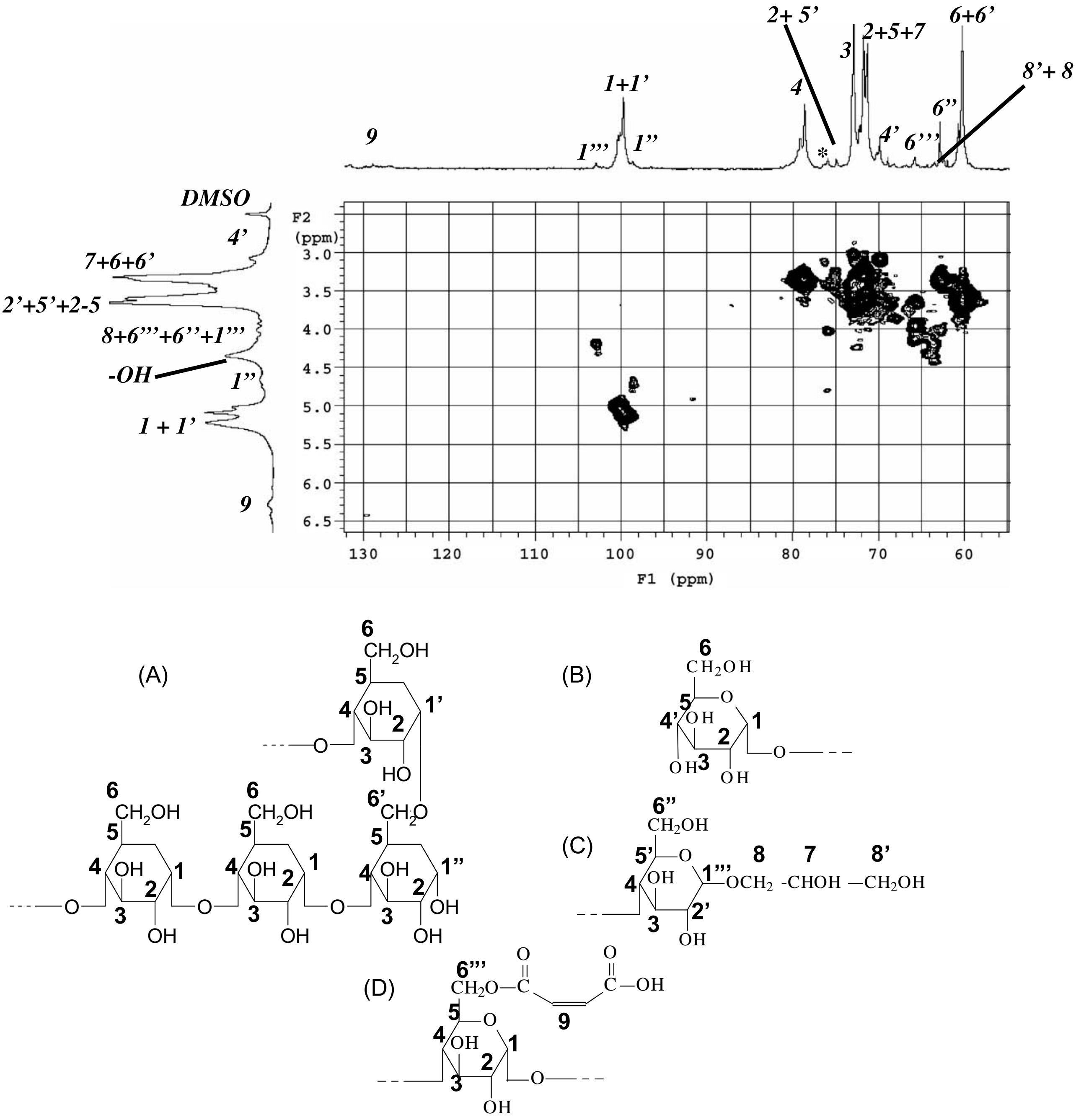
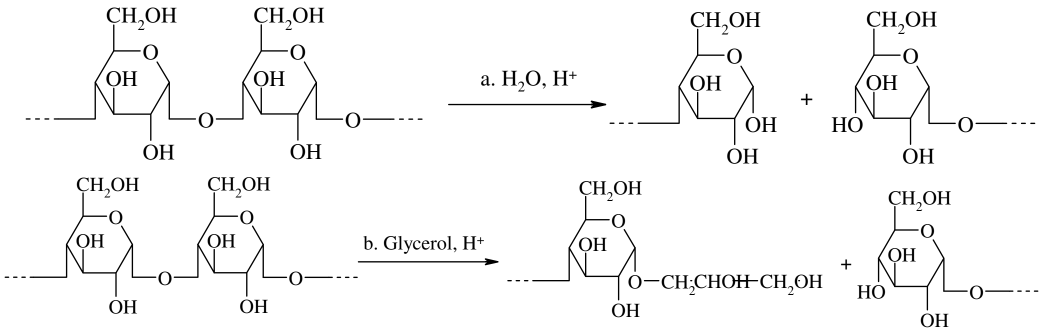


Fig. 2. ^1H–^{13}C HMQC NMR spectrum of extracted MTPS prepared with 8 wt% MA (entry 5, Table 1) determined in DMSO-d_6 at 60 °C (see depictions hereafter for assignment; *ester carbon derived from maleated-starch ring).

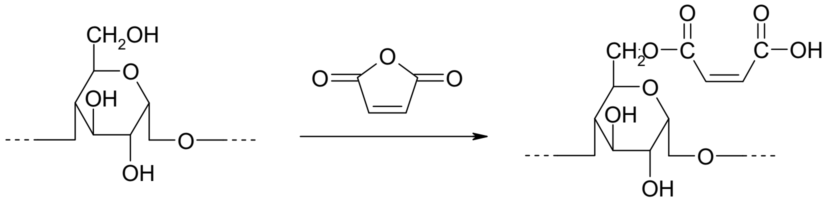
starch with glycol/glycerol at elevated temperature yields glucosides with chemical properties of acetal functions.

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 (C6‴/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 (C9/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 C=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).

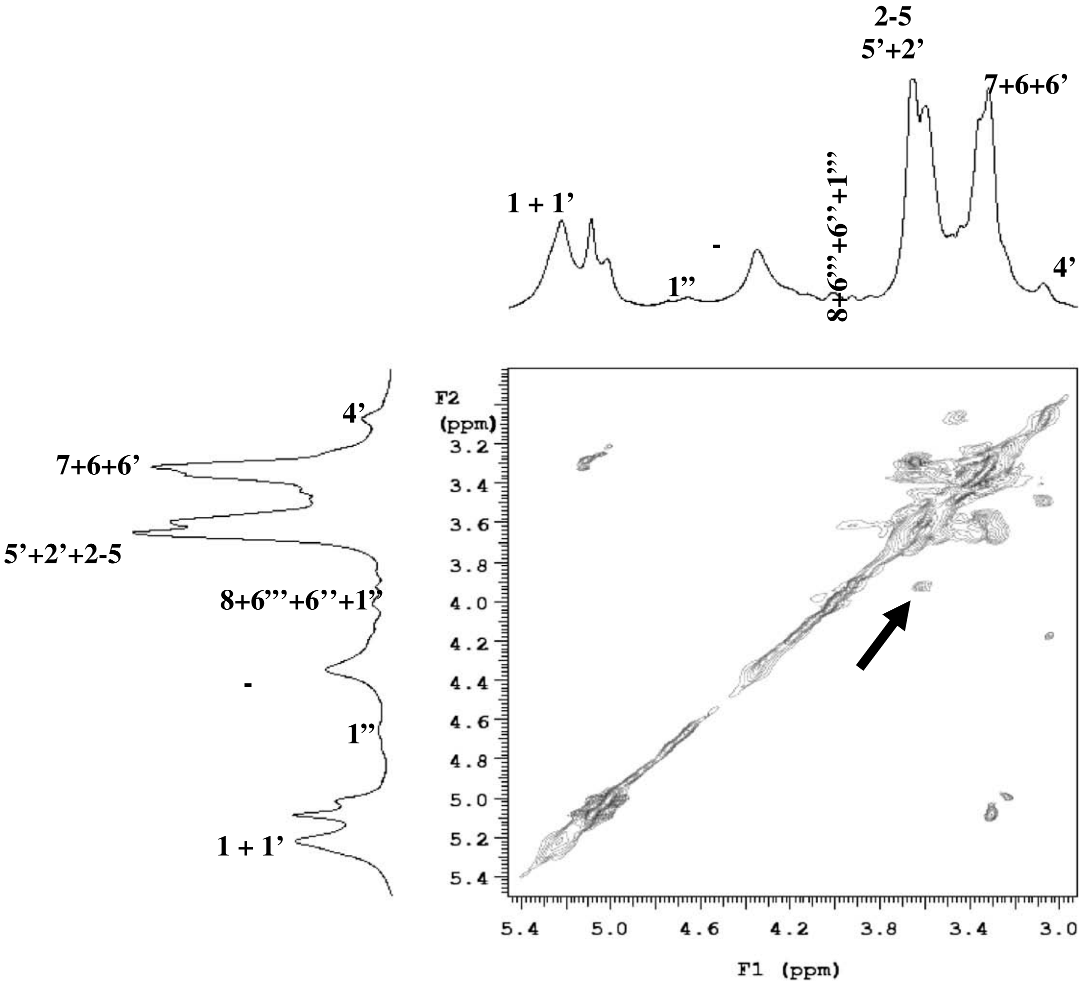


Fig. 3. ^1H–^1H g-COSY NMR spectrum of extracted MTPS prepared with 8 wt% MA (entry 5, Table 1) determined in DMSO-d_6 at 60 °C (see depictions for assignment; arrow represents ester proton of maleated-starch ring).

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 chemically 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

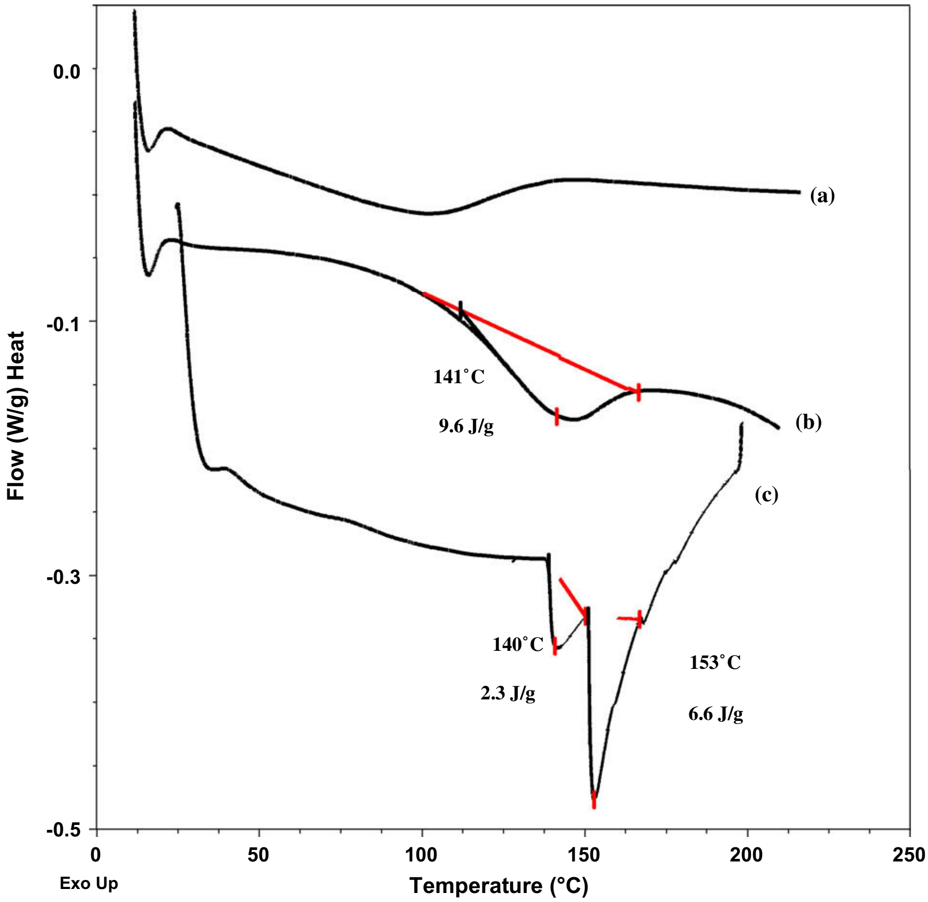


Fig. 4. DSC thermograms of starch (a), TPS (b) and MTPS modified with 2.5 wt% MA (c) (entries 1–3, Table 1; determined from −50 °C to 200 °C at a heating rate of 10 °C/min under nitrogen flow, second scan).

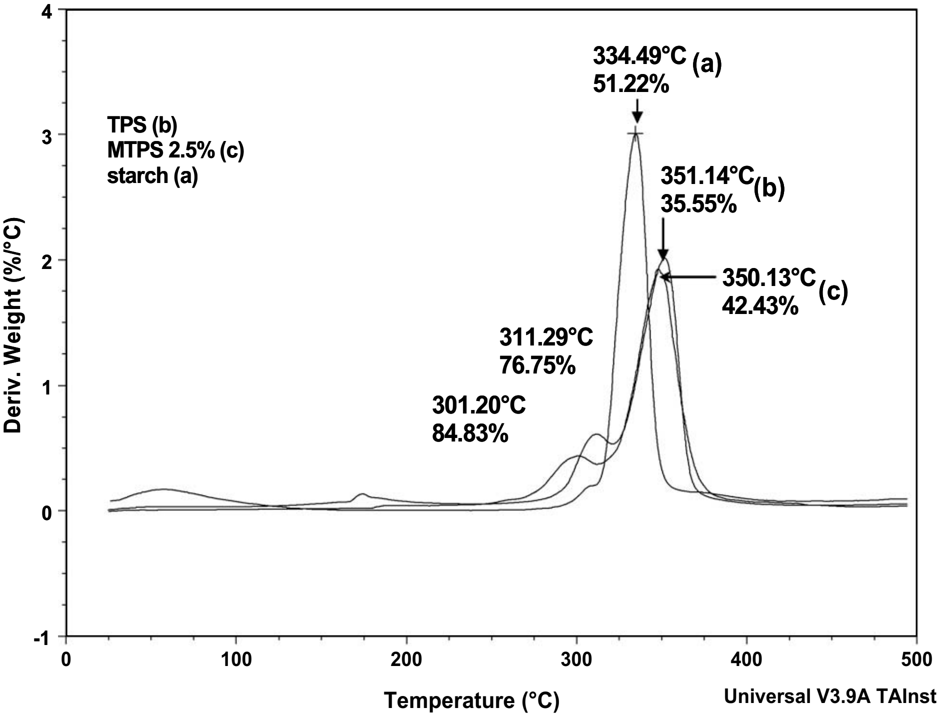


Fig. 5. TGA results of starch (a), TPS (b) and MTPS samples modified with 2.5 wt% MA (c) (entries 1–3, Table 1; from r.t. to 500 °C at a heating rate of 20 °C/min under helium flow).

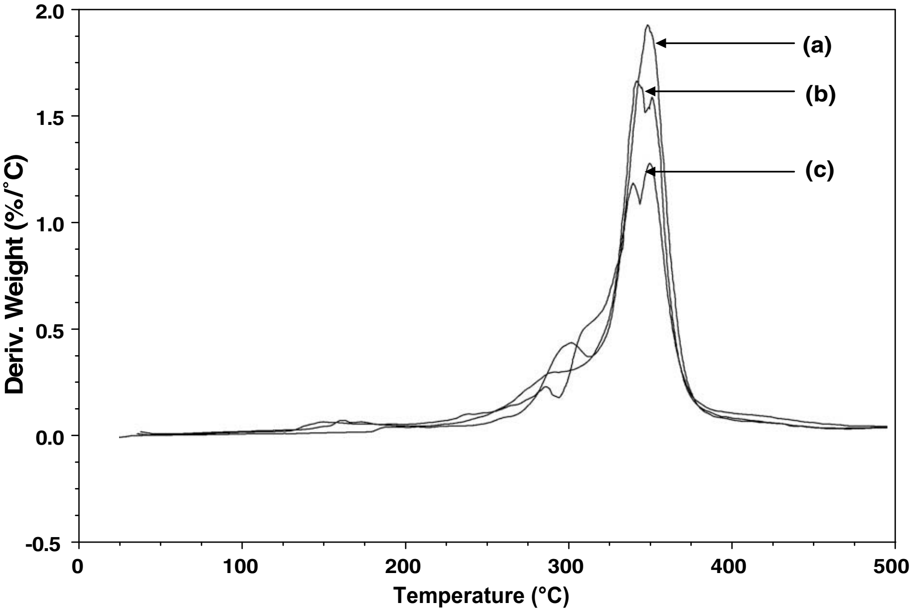


Fig. 6. TGA results of MTPS samples modified with 2.5 (a), 5 (b) and 8 wt% (c) MA (entries 3–5, Table 1; from r.t. to 500 °C at a heating rate of 20 °C/min under helium flow).

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 biosynthetically assembled as semi-crystalline granules. The type of native, crystalline structure, labeled as A-, B-, or

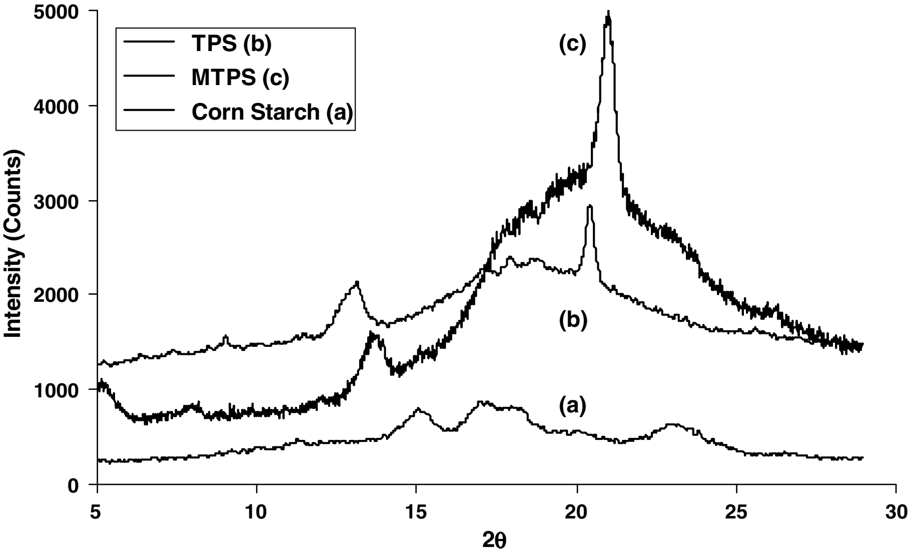


Fig. 7. WAXS diffraction patterns for granular starch (a), TPS (b), and MTPS modified with 8 wt% MA (c) (entries 1–2 and 5, Table 1).

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 recrystallization 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 (~17°) (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: $a = 13.0$, $b = 22.5$, $c = 7.9$ Å (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 ~17° 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).

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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, ^{13}C-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., Mikkila, J., Suortti, T., Seppala, 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.

Stepto, 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.

Vermeylen, 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.