Melt-processing, moisture-resistance and strength retention properties of supercritical CO₂-processed thermoplastic starch resins

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Received 18 October 2017; accepted in revised form 11 January 2018

Abstract. This paper represents the first report of thermoplastic starch (scCO₂TPS) and glutaraldehyde (GA) modified TPS resins (scCO₂TPS₁₀₀GA_x), gelatinized and/or modified with the aid of supercritical carbon dioxide (scCO₂). The melt flow rate, initial and retention values of tensile strength (σ_f) of TPS and GA-modified TPS prepared using scCO₂ fluid were considerably higher than those of TPS and TPS₁₀₀GA_x materials prepared in the conventional way. After conditioning at 20 °C/50% RH for 56 days, the σ_f of properly prepared scCO₂TPS₁₀₀GA_{0.1} still remained at 17.5 MPa, which is around 3.5 times of that of the corresponding conditioned TPS₁₀₀GA_{0.1}. The moisture contents of conditioned scCO₂TPS and scCO₂TPS₁₀₀GA_x were considerably lower than those of the corresponding TPS and TPS₁₀₀GA_x aged for the same amounts of time. Conditioned scCO₂TPS and scCO₂TPS₁₀₀GA_x exhibited only V_h -type crystals with melting temperatures ~ 20 °C lower than those of corresponding conditioned TPS and TPS₁₀₀GA_x. In comparison to TPS and TPS₁₀₀GA_x, more dissociated amylopectin chains with loosely hydrogen-bonded –OH groups and significantly less retrogradation was found for conditioned scCO₂TPS and scCO₂TPS₁₀₀GA_x.

Keywords: biodegradable polymers, supercritical carbon dioxide, thermoplastic starch, moisture resistance, strength retention

1. Introduction

Polymeric products are indispensable to our modern life, but in a short time, the after-use fates of these products have led to a waste disposal problem [1]. Environment-friendly materials developed from natural and renewable resources have been arising as the most attractive and popular approach to overcome this problem [2]. Among natural and renewable resources, polysaccharide materials are generally considered as good candidates to replace synthetic polymers and

their applications [3–5]. For example, starch has great potential in packaging, food, paper, pharmaceuticals, cosmetics and other industries, because it can be easily obtained from renewable sources and is inexpensive [6]. However, starch, like all other natural-based polymers, is water sensitive and has very strong intra- and inter-molecular hydrogen bonding [7], which leads to the melt processing temperature being close to its decomposition temperature, and making processing difficult for most applications [8, 9].

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Melt-blending bio-renewable aliphatic polyesters, such as poly(lactic acid) (PLA) [10], poly(butylene succinate) (PBS) [11] or poly(3-hydroxyalkanoates) (PHA) [12] with starch granules could significantly overcome the water sensitivities and melt-processing difficulty of starch alone without negatively influencing biodegradability. Starch and aliphatic polyesters are usually thermodynamically immiscible, since starch is hydrophilic and aliphatic polyesters are hydrophobic polymers. This leads to poor interfacial characteristics between the two macrophase separated components in blends and, hence, poor mechanical performance [13]. Chemical modification, such as, substitution and crosslinking on hydroxyl groups in starch molecules has been conducted to modify the physical and chemical properties of native starches [14–30]. However, chemically modified and/or crosslinked starch-based blends often are difficult to process and exhibit poor mechanical properties (e.g. brittleness) [29–31]. In order to improve the melt-processing capability of native starches, thermoplastic starches (TPS) are generally prepared by the application of heat, pressure, mechanical work or by addition of plasticizers (e.g. glycerol, polyols or water [32–34]) in native starches. Thermoplastic starch processing typically involves an irreversible order-disorder transition termed gelatinization. Starch gelatinization is a combined process consisting of the hydration of the amorphous regions and subsequent melting of crystalline chain segments [35–41]. However, the resistance of TPS to shock or moisture is still relatively poor in comparison with many other commodity resins [42–46], which make it unsatisfactory for many applications.

In recent years, a great deal of attention has been paid to the use of sub- and/or supercritical fluids for the mild thermal processing of polysaccharides such as chitin, alginate, pectin, cellulose and starch [47–51]. Supercritical fluids (SCF) exhibit features with both gas-like diffusivities and liquid-like densities [52]. In the vicinity of the fluid's critical point, thermodynamic and transport properties of SCF can be easily tuned by adjusting the pressure or temperature [52]. High SCF diffusivities and low viscosities have important implications in polymerization kinetics and in polymer processing. One of the most commonly used supercritical fluids is supercritical carbon dioxide (scCO₂), since it is known for its high abundance, inexpensive cost, mild supercritical conditions ($T_c = 31.1\text{ }^\circ\text{C}$, $P_c = 7.38\text{ MPa}$) [53], chemically inert nature

and has proven to be a suitable reaction medium and processing aid [54–56]. Application of scCO₂ in polymerization reactions and polymer processing has been rapidly expanding in recent years [57–68]. Pioneering studies on the use of CO₂ for starch modification were reported by Harris *et al.* [69]. It was demonstrated that, among other examples, acetylation of high amylose starch (70% amylose content) is possible in scCO₂ and products with relatively high degrees of substitution can be obtained [69]. Muljana *et al.* [70] reported that the maximum solubility values for native potato starch (NPS) and potato starch acetate (PSA) were 31 mg CO₂/g_{sample} and 79.4 mg CO₂/g_{sample}, respectively, when they were tested at two different temperatures (50 and 120 °C) and various pressures (up to 25 MPa). The higher solubility of CO₂ in PSA compared with NPS was attributed to favorable interactions between CO₂ and the acetyl carbonyl groups. The CO₂ solubility data for NPS can be of use for starch modification reactions in scCO₂ in general. da Cruz Francisco and Sivik [71] found that both pressure and supercritical fluid affected the gelatinization temperatures of potato, cassava and wheat starches in their supercritical gelatinization processes. Cassava and potato starches showed a lowering of their gelatinization temperatures at 8 MPa and an increase at 30 MPa, compared with the gelatinization at atmospheric pressure. On the other hand, the replacement of CO₂ by N₂ at 8 MPa increased the gelatinization temperature for all starches studied compared with atmospheric conditions. Muljana *et al.* [72] investigated the degree of gelatinization (DG) of potato starch after treatment with scCO₂. Quantification of the DG by DSC measurements indicated that starch gelatinization is induced by both temperature and pressure. A maximum DG of 14% was achieved at the highest pressure (25 MPa) and the highest temperature (90 °C) in the range studied. It is likely that scCO₂ acts as a plasticizer for the amorphous regions of starch and induces swelling. This will favor water penetration in such swollen regions and lead to gelatinization. Zaidul *et al.* [68] also found a significant reduction (10–18 °C) in the gelatinization temperatures for various starches and their blends when exposed to scCO₂ during their gelatinization processes. The significant reduction in the gelatinization temperatures of the above starches and their blends was attributed to the pH changes that occur when water is in contact with CO₂, along with plasticization of the amorphous

regions caused by pressurized CO₂. Most of the above-mentioned studies demonstrated that the starch gelatinization temperature could be lowered or gelatinization degree could be improved significantly by treatment with scCO₂. In other words, modification of starch molecules, gelatinization and/or complete disruption of molecular organization within the starch granules are facilitated with the aid of scCO₂ in processing. However, to the best of our knowledge, none of the above investigations (or other investigations) have reported the moisture resistance, mechanical properties or molecular interactions in scCO₂-assisted TPS resins, compared with those of TPS processed in the conventional manner using atmospheric pressure conditions.

This is the first paper to study the moisture-resistance and tensile retention properties of TPS and glutaraldehyde (GA) modified TPS resins prepared with the aid of scCO₂ in the gelatinization processes. The ease of melt-processing, moisture-resistance, initial and retention tensile mechanical properties of scCO₂-assisted TPS (scCO₂TPS) and GA modified scCO₂TPS resins were found to improve considerably compared to those of TPS or GA modified TPS resins prepared in the conventional way. In order to understand these improvements, Fourier transform infrared spectroscopy, thermal and wide-angle X-ray diffraction analyses of initial and conditioned TPS, GA modified TPS, scCO₂TPS and GA modified scCO₂TPS resins prepared in this investigation were performed. Possible reasons accounting for the significant improvement in ease of melt-processing, moisture-resistant properties, initial and retention values of tensile strength and elongation at break of scCO₂TPS and GA modified scCO₂TPS resins are proposed.

2. Experimental

2.1. Materials

Tapioca starch powder (containing 83% of amylopectin) was purchased from Eiamheng Tapioca Starch Industry Corporation (Samutprakarn, Thailand). Its initial moisture content was 11.2 wt%. Glutaraldehyde (GA) (25 wt% aqueous solution) and glycerol used in this study were purchased from Sinopharm Chemical Reagent Corporation, (Shanghai, China). Common purity CO₂ (≥90.0%) purchased from Wuhan Xiangyun Industry Corporation (Wuhan, China) was used without further purification.

2.2. Processing

2.2.1. Sample preparation and supercritical CO₂ treatment

Tapioca starch, glycerol and distilled water were mixed in a 5:2:3 mass ratio and fed into a Shanghai Yuanhuai ZCF-2 batch autoclave (Shanghai Yuanhuai Chemical Technology Corporation, (Shanghai, China)). A schematic drawing of the autoclave is provided in Figure 1. GA solutions at various parts per hundred parts of tapioca starch (PHR) were added and mixed with the compound prepared above. The autoclave was flushed with CO₂ to remove trapped air, pressurized to 9 MPa and then heated to the desired temperatures (ranging from 75 to 100 °C) with an oil bath. The compounds were gelatinized in supercritical carbon dioxide (scCO₂) and magnetic stirring condition at 190 rpm for 20 minutes to prepare the thermoplastic starches with scCO₂ as a processing aid. For comparison purposes, TPS resins were also prepared using conventional techniques by mixing tapioca starch, glycerol and distilled water in a mass proportion of 5:2:3 at 25 °C and then gelatinized at 100 °C for 20 minutes in an air environment under magnetic stirring (190 rpm) in the aforementioned autoclave. Furthermore, GA solutions at various contents were added and mixed with the basic media prepared above to prepare GA modified thermoplastic starch (TPS₁₀₀GA_x) resins. The above-prepared resins were dried in an infrared drying oven and then in a vacuum dry oven, both at 80 °C for 8 hours, to achieve a water content ≤0.5 wt%. The dried resins were then stored in a vacuum desiccator before further processing. Sample codes and compositions of the resins investigated herein are provided in Table 1.

Figure 1. Schematic drawing of the high-pressure CO₂ reactor setup.

Table 1. Sample codes and compositions of TPS, TPS₁₀₀GA_x, scCO₂TPS and scCO₂TPS₁₀₀GA_x specimens.

Sample codes	Starch content(parts)	Glycerol content(parts)	Water content(parts)	Glutaraldehyde content(parts)
TPS	100	40	60	–
scCO ₂ TPS	100	40	60	–
TPS ₁₀₀ GA _{0.05}	100	40	60	0.05
TPS ₁₀₀ GA _{0.1}	100	40	60	0.10
TPS ₁₀₀ GA _{0.2}	100	40	60	0.20
TPS ₁₀₀ GA _{0.4}	100	40	60	0.40
TPS ₁₀₀ GA _{0.8}	100	40	60	0.80
scCO ₂ TPS ₁₀₀ GA _{0.05}	100	40	60	0.05
scCO ₂ TPS ₁₀₀ GA _{0.1}	100	40	60	0.10
scCO ₂ TPS ₁₀₀ GA _{0.2}	100	40	60	0.20
scCO ₂ TPS ₁₀₀ GA _{0.4}	100	40	60	0.40
scCO ₂ TPS ₁₀₀ GA _{0.8}	100	40	60	0.80

2.2.2. Injection molding

The aged properties (e.g. tensile, moisture absorption) of the dried resins were determined on injection-molded specimens prepared in accordance with ASTM D638 type IV. The specimens were prepared by injection molding at 210 °C using a Wuhan Reiming SZ-05 mini-injection machine and then cooled in the mold to 100 °C for 30 seconds. The injection-molded samples were conditioned at 20 °C/50% RH for specified time periods. The subscript *x* utilized in the sample code denotes the part of GA solution per hundred parts of TPS resin that was used during the conventional and scCO₂-assisted modification processes of TPS and scCO₂TPS resins.

2.3. Melt-processing and aged tensile and moisture-resistance properties

2.3.1. Melt flow rate

The melt flow rates (MFR) of TPS, TPS₁₀₀GA_x, scCO₂TPS and scCO₂TPS₁₀₀GA_x were measured using a GT-7100-MIR Melt Flow Indexer (Gotech Testing Machine Inc.) equipped with a capillary die at 210 °C and a driving weight of 2.16 kg. Before any MFR measurement, the resins were dried in an infrared drying oven and then in a vacuum drying oven, both at 80 °C for 8 hours, to maintain water content ≤0.5wt%.

2.3.2. Aged moisture-resistance properties

In order to analyze the effect of storage conditions on retrogradation, moisture resistance of conditioned TPS, TPS₁₀₀GA_x, scCO₂TPS and scCO₂TPS₁₀₀GA_x specimens, moisture contents of all specimens were determined gravimetrically using a Shanghai Jingke DHS16-A infrared moisture meter at temperatures

ranging from 25 to 120 °C for 30 minutes. Prior to moisture content measurement, the resins were dried to have a water content ≤0.5 wt% by preheating in an infrared drying oven and then in a vacuum oven, both at 80 °C for 8 hours. The reported moisture contents were obtained based on the average results of at least five measured specimens.

2.3.3. Aged tensile properties

The initial and aged tensile properties of injection-molded TPS, TPS₁₀₀GA_x, scCO₂TPS and scCO₂TPS₁₀₀GA_x specimens were performed on a Hung-Ta HT-9112 tension testing machine. All tensile tests were carried out at 25 °C, using a crosshead speed of 50 mm/min and a 35 mm gauge length. Reported values of initial and aged tensile properties are the average of the results for at least five specimens.

2.4. Characterization

2.4.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of all specimens were recorded on a Nicolet Avatar 370 Fourier transform infrared spectrometer. Data were collected at 25 °C from 500 to 4000 cm⁻¹, wherein 32 scans with a spectral resolution 1 cm⁻¹ were collected and signal averaged. Infrared spectra of the film specimens were determined using the conventional KBr disk method. All the specimens were ground, mixed and pressed with KBr disk at a ratio of 1:100 and then dried at 60 °C for 30 minutes to remove the absorbed water before the test. The film specimens prepared above were sufficiently thin so that the absorbances are within the range of the Beer-Lambert law.

2.4.2. Differential scanning calorimetry (DSC)

The differential scanning calorimetry experiments of initial and conditioned specimens were determined using a TA Instruments Q100 differential scanning calorimetry calibrated with indium to characterize the melting temperature (T_m). About 0.5 mg of samples were placed in standard sealed aluminum sample pans for determination of the T_m values and an empty aluminum pan was used as a reference. All DSC analyses were performed under flowing nitrogen (25 mL/min) and at a heating rate of 20 °C/min from 25 to 250 °C.

2.4.3. Wide-angle X-ray diffraction (WAXD)

The wide-angle X-ray diffraction experiments were performed on a Shimadzu XRD-6000 diffractometer, using Ni-filtered CuK α radiation. Each specimen with 2 mm thickness was maintained stationary and scanned through from 5 to 30° (2 θ) at 25 °C, using a target voltage and current of 40 kV and 100 mA and a scanning rate of 5° (2 θ) per minute.

3. Results and discussion

3.1. Melt-processing and aged tensile and moisture-resistance properties

3.1.1. Melt flow rate

A MFR value at ~8.7 g/10 min was found for TPS prepared in the conventional way using atmospheric pressure conditions; while a considerably higher MFR value = 14.1 g/10 min was determined for scCO₂TPS prepared in the presence of scCO₂ (see Figure 2). After modification by glutaraldehyde, the MFR values of TPS₁₀₀GA_x were reduced significantly from 8.7 to 0.7 g/10 min, as GA content increased from 0 to 0.8 PHR. Similarly, MFR values for scCO₂TPS₁₀₀GA_x reduced from 14.1, to 11.9, 9.0 and 8.1 g/10 min, as GA content increased from 0 to 0.1, 0.4 and 0.8 PHR, respectively. As evidenced by FTIR analysis later in this manuscript, reaction of the hydroxyl groups of starch with the aldehyde groups of glutaraldehyde molecules did occur during the modification processes of TPS₁₀₀GA_x and scCO₂TPS₁₀₀GA_x. It is highly likely that crosslinking reaction between glutaraldehyde and starch molecules can carry out to some extent. As a consequence, MFR values of TPS₁₀₀GA_x and scCO₂TPS₁₀₀GA_x specimens reduced considerably with increasing GA contents of TPS₁₀₀GA_x and scCO₂TPS₁₀₀GA_x specimens. It is worth emphasizing that MFR values of scCO₂TPS and scCO₂TPS₁₀₀GA_x are considerably higher than

Figure 2. The melt flow rate values of TPS (●), TPS₁₀₀GA_{0.05} (◐), TPS₁₀₀GA_{0.1} (◑), TPS₁₀₀GA_{0.2} (◒), TPS₁₀₀GA_{0.4} (◓), TPS₁₀₀GA_{0.8} (◔), scCO₂TPS (▲), scCO₂TPS₁₀₀GA_{0.05} (△), scCO₂TPS₁₀₀GA_{0.1} (△), scCO₂TPS₁₀₀GA_{0.2} (△), scCO₂TPS₁₀₀GA_{0.4} (△) and scCO₂TPS₁₀₀GA_{0.8} (△) specimens.

those of the corresponding TPS and TPS₁₀₀GA_x specimens prepared with the same compositions but using atmospheric pressure during their gelatinization and modification processes. Gelatinization, complete disruption of molecular organization and/or modification within the starch granules is enhanced with the aid of scCO₂ in processing of scCO₂TPS and scCO₂TPS₁₀₀GA_x specimens.

3.1.2. Aged moisture-resistance properties

The moisture-resistance of TPS, TPS₁₀₀GA_x, scCO₂TPS and scCO₂TPS₁₀₀GA_x specimens was evaluated by measuring the moisture contents absorbed in specimens conditioned at 20 °C/50% RH for specified time periods (see Figure 3). The initial moisture content of all specimens was intentionally ~0.5%. In comparison, considerably lower moisture content of 7.6% was found for scCO₂TPS specimens at a conditioning time of 56 days. After modification with varying amounts of GA, the moisture contents of all conditioned TPS₁₀₀GA_x and scCO₂TPS₁₀₀GA_x specimens were significantly lower than those of the corresponding aged TPS and scCO₂TPS (see Figure 3). Aged scCO₂TPS₁₀₀GA_x exhibited considerably lower moisture contents than the corresponding aged TPS₁₀₀GA_x specimens, and conditioned scCO₂TPS₁₀₀GA_{0.1} displayed much lower moisture contents than other aged scCO₂TPS₁₀₀GA_x modified with GA contents other than 0.1 parts per hundred parts of TPS resin (PHR). It is worth emphasizing that the moisture content of scCO₂TPS₁₀₀GA_{0.1} reached

Figure 3. The moisture contents of initial and conditioned TPS (•), TPS₁₀₀GA_{0.05} (○), TPS₁₀₀GA_{0.1} (○), TPS₁₀₀GA_{0.2} (○), TPS₁₀₀GA_{0.4} (○), TPS₁₀₀GA_{0.8} (○), scCO₂TPS (▲), scCO₂TPS₁₀₀GA_{0.05} (△), scCO₂TPS₁₀₀GA_{0.1} (△), scCO₂TPS₁₀₀GA_{0.2} (△), scCO₂TPS₁₀₀GA_{0.4} (△) and scCO₂TPS₁₀₀GA_{0.8} (△) specimens.

4.7% when the specimen was aged at 20 °C/50% RH for 56 days. This value is only about one half of that of the corresponding conditioned TPS₁₀₀GA_{0.1}.

3.1.3 Aged tensile properties

Figure 4 displays tensile strength (σ_f) and elongation at break (ϵ_f) of all specimens conditioned at 20 °C/50% RH for specified time periods. The σ_f retention values of TPS specimens were reduced dramatically from 20.3 to 2.9 MPa, as the conditioning time increased from 0 to 56 days. While ϵ_f values for TPS specimens correspondingly increased ~2 fold, with increasing conditioning time. In comparison, scCO₂TPS displayed considerably higher σ_f of 23.1 MPa, and their σ_f retention values reduced more slowly on aging: from 23.1 to 16.3 MPa, 9.1 and to 7.2 MPa. Their ϵ_f values increased more slowly than those of the corresponding conditioned TPS: from 13.4 to 14.5, 16.9 and to 18.5%, as conditioning time increased from 0 to 7, 28 and to 56 days, respectively. After modification with varying amounts of GA, the initial σ_f values of TPS₁₀₀GA_x/scCO₂TPS₁₀₀GA_x were reduced significantly from 20.3/23.1 MPa, to 17.4/21.6 MPa and 14.4/14.6 MPa, respectively, as

Figure 4. Tensile strength and elongation at break of initial and conditioned TPS (•, ▴), TPS₁₀₀GA_{0.05} (○, □), TPS₁₀₀GA_{0.05} (○, □), TPS₁₀₀GA_{0.2} (○□), TPS₁₀₀GA_{0.4} (○, □), TPS₁₀₀GA_{0.8} (○□), scCO₂TPS (▲, ▴), scCO₂TPS₁₀₀GA_{0.05} (△, ▴), scCO₂TPS₁₀₀GA_{0.1} (△, ▴), scCO₂TPS₁₀₀GA_{0.2} (△, ▴), scCO₂TPS₁₀₀GA_{0.4} (△, ▴) and scCO₂TPS₁₀₀GA_{0.8} (△, ▴) specimens conditioned at 20 °C/50% RH for varying amounts of time.

GA contents increased from 0 to 0.1 and 0.8 PHR. The corresponding initial ϵ_f values of TPS₁₀₀GA_x/scCO₂TPS₁₀₀GA_x specimens were nearly the same with increasing GA content. It is interesting to note that conditioned scCO₂TPS₁₀₀GA_x specimens exhibited considerably higher σ_f but lower ϵ_f retention than those of the corresponding aged TPS₁₀₀GA_x specimens (see Figure 4). In addition, scCO₂TPS₁₀₀GA_{0.1} exhibited

considerably higher σ_f but lower ε_f retention values than other corresponding conditioned $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ specimens modified with GA contents other than 0.1 PHR. For example, after conditioning at 20 °C/50% RH for 56 days, the σ_f and ε_f retention values of $\text{scCO}_2\text{TPS}_{100}\text{GA}_{0.1}$ remained at 17.5 MPa and 15.6%, respectively. The above values are equivalent to 81 and 125% of its initial σ_f and ε_f values, respectively, and around 3.5 times and 80% of those of the corresponding conditioned $\text{TPS}_{100}\text{GA}_{0.1}$ specimens, respectively.

3.2. Characterization

3.2.1. Fourier transform infrared spectroscopy

Distinctive C=O and C–H stretching absorption bands centered at 1713 and 2751 cm^{-1} [73] were found in the FTIR spectrum of GA (see Figure 5 curves (a)). Similar distinctive C–O stretching, O–H bending, H–O–H, C–H and O–H stretching absorption bands centered at 1043, 1403, 1638, 2943 and

3434 cm^{-1} , respectively [74] were observed in the FTIR spectra of TPS and scCO_2TPS specimens. However, the intensities of the O–H stretching and bending vibration bands of scCO_2TPS were considerably larger than those of the TPS.

After modification with various contents of GA, a new ether (–C–O–C–) stretching absorption band centered at 1156 cm^{-1} and gradually weaken O–H stretching band was found in spectra of $\text{TPS}_{100}\text{GA}_x$ and $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$, as their GA contents increased (see Figure 5 curves (c)–(e) and (g)–(i)). However, the C=O and C–H stretching bands of aldehyde groups in GA disappeared nearly completely in spectra of $\text{TPS}_{100}\text{GA}_x$ and $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ specimens. It is interesting to note that the intensities of the newly formed ether stretching bands for $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ were significantly larger than those of $\text{TPS}_{100}\text{GA}_x$ prepared with the same compositions but using atmospheric pressure during their modification processes. Similar to those found for scCO_2TPS , the

Figure 5. FTIR spectra of (a) GA, (b) TPS, (c) $\text{TPS}_{100}\text{GA}_{0.05}$, (d) $\text{TPS}_{100}\text{GA}_{0.1}$, (e) $\text{TPS}_{100}\text{GA}_{0.2}$, (f) scCO_2TPS , (g) $\text{scCO}_2\text{TPS}_{100}\text{GA}_{0.05}$, (h) $\text{scCO}_2\text{TPS}_{100}\text{GA}_{0.1}$ and (i) $\text{scCO}_2\text{TPS}_{100}\text{GA}_{0.2}$ specimens.

Figure 6. Schematic model of (a) backbone structure [after reference 90] and hydrogen bonds in the original starches; (b) backbone structure and hydrogen bonds in TPS and TPS₁₀₀GA_x prepared in the conventional way and (c) backbone structure and hydrogen bonds in scCO₂TPS and scCO₂TPS₁₀₀GA_x prepared in the presence of scCO₂.

intensities of O–H stretching and bending bands of $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ were also considerably larger than those of the corresponding $\text{TPS}_{100}\text{GA}_x$.

It is also worth noting that the absorption bands centered at 1043 cm^{-1} (C–O stretching) of TPS and $\text{TPS}_{100}\text{GA}_x$ specimens shifted to 1046 cm^{-1} for scCO_2TPS and $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ prepared with the aid of scCO_2 fluid. Similarly, the bands centered at $3434, 3424, 3436$ and 3442 cm^{-1} (O–H stretching) of TPS, $\text{TPS}_{100}\text{GA}_{0.05}$, $\text{TPS}_{100}\text{GA}_{0.1}$ and $\text{TPS}_{100}\text{GA}_{0.2}$ specimens shifted to $3443, 3432, 3449$ and 3444 cm^{-1} for those of scCO_2TPS , $\text{scCO}_2\text{TPS}_{100}\text{GA}_{0.05}$, $\text{scCO}_2\text{TPS}_{100}\text{GA}_{0.1}$ and $\text{scCO}_2\text{TPS}_{100}\text{GA}_{0.2}$, respectively. The shift of the C–O and O–H stretching bands to higher frequencies for scCO_2TPS and $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ were attributed to the lengthening or weakening of inter- or intramolecular hydrogen bonds [27, 75, 76] originally present in TPS and $\text{TPS}_{100}\text{GA}_x$ specimens. As reported by several investigators [51, 53, 72], the extremely high diffusivities and low viscosities of scCO_2 can lead to effective plasticization for the amorphous regions of starch granules, and favor water and glycerol penetration in the amorphous and crystalline regions of starch (see Figures 6). This creates free volume in the starch and increases the mobility of the starch molecules [77], which is beneficial to the enhancement of the gelatinization processes. In which, disruption of hydrogen bonds, particularly disruption of those hydrogen bonds linking adjacent double helices within original starch molecules, become much easier with the aid of scCO_2 in gelatinization processing (see Figures 6). These free hydroxyl groups obtained after disruption of those hydrogen bonds linking adjacent double helices could form hydrogen bonds much easier with the plasticizers (i.e. glycerol and water) during gelatinization processes (see Figure 6c). As a consequence, much more loosely starch hydrogen-bonded –OH groups were found in FTIR spectra of scCO_2TPS and $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ specimens compared with TPS and $\text{TPS}_{100}\text{GA}_x$. These loosely hydrogen-bonded –OH groups could then react with aldehyde groups of GA molecules to a higher extent during the modification process of $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ compared to $\text{TPS}_{100}\text{GA}_x$ gelatinized and modified under conventional atmospheric conditions.

3.2.2. Differential scanning calorimetry

Figure 7 illustrate DSC thermograms, melting temperature (T_m) and enthalpy values (ΔH) of melting

endotherms of TPS, $\text{TPS}_{100}\text{GA}_x$, scCO_2TPS and $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ specimens conditioned at $20^\circ\text{C}/50\%\text{ RH}$ for specified time periods. Thermograms without any feature were found for the TPS, $\text{TPS}_{100}\text{GA}_x$, scCO_2TPS and $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ specimens without any conditioning treatment (see Figures 7a curves (a), (f), (k), (p), 7b curves (a), (f), (k), (p)). A melting endotherm ($T_m = 180^\circ\text{C}$) gradually appeared in DSC thermograms of TPS specimens after conditioning at $20^\circ\text{C}/50\%\text{ RH}$ for ≥ 7 days. The magnitude of this melting endotherm increased considerably with increasing conditioning time. However, T_m s of conditioned TPS specimens reduced from around 183 to 175°C as the conditioning time increased from 7 to 56 days. In contrast, no melting endotherm was found in thermograms of scCO_2TPS conditioned at $20^\circ\text{C}/50\%\text{ RH}$ for less than 14 days (see Figures 7b curves (a), (b)). After aging for ≥ 14 days, the magnitudes of melting endotherms of conditioned scCO_2TPS were considerably smaller than those of the corresponding TPS specimens aged for the same amounts of time. The ΔH of melting endotherms of conditioned scCO_2TPS were about 15% smaller than those of the corresponding TPS specimens conditioned at $20^\circ\text{C}/50\%\text{ RH}$ for the same amounts of time. The melting temperatures of conditioned scCO_2TPS specimens reduced from around 163 to 153°C , as the conditioning time increased from 14 to 56 days. These melting temperatures of conditioned scCO_2TPS specimens are about 20°C lower than those of the corresponding conditioned TPS specimens maintained at $20^\circ\text{C}/50\%\text{ RH}$ for the same amounts of time.

After modification with GA, no melting endotherm was observed for $\text{TPS}_{100}\text{GA}_x$ and $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ specimens conditioned for less than 14 days (see Figures 7a curves (h)–(t) and 7b curves (h)–(t)). In comparison with aged TPS, endotherms with significantly smaller ΔH were observed for conditioned $\text{TPS}_{100}\text{GA}_x$ and $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ when maintained at $20^\circ\text{C}/50\%\text{ RH}$ for ≥ 14 days. In addition, the melting temperatures and ΔH of conditioned $\text{scCO}_2\text{TPS}_{100}\text{GA}_x$ were lower and significantly smaller than those of the corresponding conditioned $\text{TPS}_{100}\text{GA}_x$ specimens (see Figures 7a curves (h)–(t) and 7b curves (h)–(t)). For example, ΔH for conditioned $\text{scCO}_2\text{TPS}_{100}\text{GA}_{0.1}$ specimens were about 10–22% smaller than those of the corresponding $\text{TPS}_{100}\text{GA}_{0.1}$ aged for the same amounts of time. Similarly, the melting temperatures of the aged $\text{scCO}_2\text{TPS}_{100}\text{GA}_{0.1}$ reduced from

Figure 7. DSC thermograms of a) TPS, TPS₁₀₀GA_{0.05}, TPS₁₀₀GA_{0.1} and TPS₁₀₀GA_{0.2}, b) scCO₂TPS, scCO₂TPS₁₀₀GA_{0.05}, scCO₂TPS₁₀₀GA_{0.1} and scCO₂TPS₁₀₀GA_{0.2} specimens conditioned at 20 °C/50% RH for varying amounts of time.

around 173 to 168 °C and then to 166 °C as the conditioning time increased from 14 to 28 and 56 days, respectively. These peak melting temperatures are about 16–18 °C lower than those of the corresponding TPS₁₀₀GA_{0.1} specimens maintained at 20 °C/50% RH for the same amounts of time.

3.2.3. Wide-angle X-ray diffraction

As shown in Figure 8a curve (a), diffraction peaks centered at $2\theta = 10.6, 11.5, 15.0^\circ$, an unresolved doublet at $17.0, 17.9$, and 23.0° were observed for tapioca starch. These diffraction peaks mainly correspond to A-type starch crystals with strong reflections at 2θ around 14.8 , an unresolved doublet at

around 17 and 23° [78–80] (there are relatively minor reflections corresponding to B-type starch crystals at $2\theta \sim 10.6$ and 11.5° [81]). One can barely see these diffraction peaks in the diffraction patterns of the initial TPS and scCO₂TPS specimens (see Figure 8b curve (a) and 8c curve (a)). New diffraction peaks centered at $2\theta = 13.0, 19.8$ and 20.9° appeared gradually after TPS was conditioned for no less than 7 days. These new diffraction peaks grew in intensity with increasing the conditioning time (see Figures 8b curves (a)–(e)). The diffraction peaks in these locations have been reported and identified as V_h -type crystallinity [75, 80]. However, after conditioning for ≥ 14 days, additional diffraction peaks

Figure 8. Wide-angle X-ray diffraction patterns of (a) Tapioca, (b) TPS, TPS₁₀₀GA_{0.05}, TPS₁₀₀GA_{0.1} and TPS₁₀₀GA_{0.2}, and (c) scCO₂TPS, scCO₂TPS₁₀₀GA_{0.05}, scCO₂TPS₁₀₀GA_{0.1} and scCO₂TPS₁₀₀GA_{0.2} specimens conditioned at 20 °C/50% RH for varying amounts of time.

associated with B-type crystals (7.8, 22.4 and 24.7° [78, 81, 82–85]) were also observed. In contrast, no diffraction peaks were found for scCO₂TPS conditioned for less than 14 days (see Figures 8c curves (a), (b)). After ≥14 days, scCO₂TPS specimens exhibited only *V_h*-type diffraction peaks [75, 80]. In addition, the *V_h*-type diffraction peaks were considerably smaller than those of the corresponding TPS specimens conditioned for the same amounts of time.

Similar to aged TPS, new diffraction peaks at $2\theta = 7.8, 13.0, 19.8, 20.9$ and 22.4° appeared gradually after TPS₁₀₀GA_x specimens were conditioned for no less than 28 days. These arise from a combination of *V_h*-type (13.0, 19.8 and 20.9°) and B-type crystals ($2\theta = 7.8$ and 22.4°) [78, 81, 82–85] when maintained at 20 °C/50% RH for no less than 28 days (see Figures 8b curves (i), (j), (o) and (t)). In contrast, after conditioning for ≥14 days, scCO₂TPS₁₀₀GA_x specimens exhibited only a typical *V_h*-type diffraction pattern [75, 80] and the diffraction peaks corresponding to *V_h*-type crystals of conditioned scCO₂TPS₁₀₀GA_x were considerably smaller than those of the corresponding aged TPS₁₀₀GA_x specimens.

In summary, WAXD analyses revealed that A- and B-type crystals were completely disrupted during the gelatinization processes of tapioca starch granules. The appearance of diffraction peaks of *V_h*- and B-type crystals for aged TPS and TPS₁₀₀GA_x specimens, was ascribed to significant retrogradation of tapioca starch molecules occurring during their conditioning processes. *V_h*-type starch crystals have been reported as the main crystalline structures for single helical amylose molecules in starches [86, 87], while double helical amylopectin structures with an open packing of helices with 36 inter-helical water molecules in each hexagonal crystal unit [84, 85] were reported as the main crystal structure of B-type starch crystals [88]. During retrogradation, recrystallization of TPS specimens occurred considerably in the moisture rich environment, since TPS specimens easily absorb moisture after remaining at 20 °C/50% RH for specified time periods. Moreover, a higher moisture content environment would facilitate movement of double helices [85], which could promote the formation of B-type crystals among the branched chains of amylopectin during conditioning [79, 83–85, 89]. However, ΔH of the new melting endotherms and diffraction peaks of *V_h*- and B-type crystals for conditioned TPS₁₀₀GA_x specimens were considerably

smaller than those of corresponding TPS specimens aged for the same amounts of time. This apparently is due to the significant improvement in moisture-resistance of TPS₁₀₀GA_x and less movement of double helices during retrogradation, since the moisture-absorbing starch hydroxyl groups were successfully reacted with GA aldehyde groups during the modification processes of TPS₁₀₀GA_x. On the other hand, as revealed by FTIR analyses, disruption of hydrogen bonds, particularly disruption of those hydrogen bonds linking adjacent double helices within starch molecules became much easier with the aid of scCO₂ in gelatinization processing. Gelatinization, complete disruption of molecular organization and/or modification within amylose or even amylopectin chains of the starch granules, became more favorable with the aid of scCO₂ in gelatinization and/or modification processing of scCO₂TPS and scCO₂TPS₁₀₀GA_x. This would imply that dissociated amylopectin chains have the possibility and time to entangle and form hydrogen bonds not only with themselves and the plasticizer (i.e. glycerol and water), but also with amylose molecules during the gelatinization process (see Figure 6c). The considerably higher MFR values and much more favorable melt-processing behavior found for dried scCO₂TPS and scCO₂TPS₁₀₀GA_x are most likely due to the remained glycerol molecules (plasticizers) linking adjacent double helices within starch molecules. Presumably, these stronger but dissociated amylopectin intermolecular interactions present in scCO₂TPS and scCO₂TPS₁₀₀GA_x improves their ease of melt-processing, tensile retention, and moisture-resistant properties and inhibit their recrystallization and/or retrogradation during their conditioning processes. As a consequence, conditioned scCO₂TPS and scCO₂TPS₁₀₀GA_x exhibited only *V_h*-type crystals with melting temperatures around 20 °C lower than those of the corresponding aged TPS and TPS₁₀₀GA_x specimens with both *V_h*- and B-type crystals.

4. Conclusions

The ease of melt-processing, moisture-resistance and tensile retention properties of thermoplastic starch (scCO₂TPS) and GA modified TPS (scCO₂TPS₁₀₀GA_x) resins were considerably improved with the aid of supercritical carbon dioxide (scCO₂) fluid during their gelatinization and/or modification processes. The MFR values of scCO₂TPS and scCO₂TPS₁₀₀GA_x specimens measured at

210 °C/2.16 kg were considerably higher than those of the corresponding TPS and TPS₁₀₀GA_x specimens. All conditioned scCO₂TPS and scCO₂TPS₁₀₀GA_x specimens exhibited significantly lower moisture contents than those of corresponding aged TPS and TPS₁₀₀GA_x specimens maintained at 20 °C/50% RH for the same amounts of time. Conditioned scCO₂TPS₁₀₀GA_{0.1} exhibited significantly lower moisture contents than other corresponding conditioned scCO₂TPS₁₀₀GA_x specimens modified with GA contents other than 0.1 PHR. Conditioned scCO₂TPS₁₀₀GA_{0.1} exhibited considerably higher σ_f but lower ε_f retention values than other corresponding conditioned scCO₂TPS₁₀₀GA_x modified with GA other than 0.1 PHR.

As evidenced by FTIR analyses, much more and loosely hydrogen-bonded –OH groups of starch molecules were observed in FTIR spectra of scCO₂TPS and scCO₂TPS₁₀₀GA_x compared to TPS and TPS₁₀₀GA_x specimens, respectively. These loosely hydrogen-bonded –OH groups could then react to a greater extent with GA aldehyde groups during the modification processes of scCO₂TPS₁₀₀GA_x compared to TPS₁₀₀GA_x gelatinized and modified under conventional atmospheric conditions. The enthalpies of the melting endotherms and the magnitudes of the diffraction peaks of V_h- and B-type crystals of conditioned TPS₁₀₀GA_x were considerably smaller than those of the corresponding conditioned TPS specimens. This is presumably due to the significant improvement in moisture-resistant properties of the TPS₁₀₀GA_x specimens and less movement of double helices during retrogradation, since the moisture-absorbing starch hydroxyl groups were successfully reacted with GA aldehyde molecules during the modification processes of TPS₁₀₀GA_x. However, conditioned scCO₂TPS and scCO₂TPS₁₀₀GA_x exhibited only V_h-type crystals with melting temperatures approximately 20 °C lower than those of corresponding conditioned TPS and TPS₁₀₀GA_x specimens. As revealed by FTIR analyses, gelatinization, complete disruption of molecular organization and/or modification within amylose or even amylopectin chains of the starch granules, became much easier with the aid of scCO₂ in the processing of scCO₂TPS and scCO₂TPS₁₀₀GA_x. This implies that the dissociated amylopectin chains have the possibility and time to entangle and form hydrogen bonds, not only with

themselves and the plasticizer (i.e. glycerol and water), but also with amylose molecules during the gelatinization process. The considerably higher MFR values and much more favorable melt-processing behavior found for dried scCO₂TPS and scCO₂TPS₁₀₀GA_x are most likely due to the remained glycerol molecules (plasticizers) linking adjacent double helices within starch molecules. Presumably, these stronger but dissociated amylopectin intermolecular interactions present in scCO₂TPS and scCO₂TPS₁₀₀GA_x would improve their moisture-resistance, ease of melt-processing, tensile retention properties and inhibit their recrystallization and/or retrogradation during their conditioning processes.

Acknowledgements

The authors would like to express their appreciation to GraceBio and Nytex Composites Corporation and Ministry of Science and Technology, Taiwan (MOST 104-2622-E-168-003 –CC, MOST 105-2622-E-168-003 –CC3 and MOST 106-2622-E-168-004-CC3) for support of this work. JR would like to thank the NSF Polymers Program for support through DMR-1505953.

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