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Effect of amphiphilic molecules on characteristics and tensile properties of thermoplastic starch and its blends with poly(lactic acid)

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ABSTRACT

Three different types of amphiphilic molecules — Tween 60, linoleic acid, and zein were used as additives for the production of thermoplastic starch (TPS). The addition of those amphiphiles resulted in: (i) improved plasticization and processability, (ii) enhanced extensibility, (iii) increased crystallinity, and (iv) decreased stiffness, strength and rigidity of the TPS materials. Zein facilitated more effective plasticization, melting and processability of TPS material than did linoleic acid and Tween 60, respectively. However, Tween 60 allowed greater reduction of T_g and produced softer TPS material than did linoleic acid and zein, respectively. Binary blends of those TPS materials and poly(lactic acid) (PLA) were also fabricated by varying PLA content, i.e. 30, 50 and 70% (w/w). The melt flow index, tensile strength and elastic modulus of the TPF-PLA blends increased significantly with increasing PLA content. In addition, amphiphiles facilitated processability, flowability and extensibility of the blends. Linoleic acid was a more effective additive to enhance flowability of the TPS–PLA blends than were Tween 60 and zein, respectively.

1. Introduction

Recently, the environmental impacts caused by an excessive quantity of petroleum-based plastic wastes have received much attention. It is well-known that petroleum-based plastics are not biodegradable or compostable. The disposal of these plastic wastes causes not only air pollution and underground water contamination, but also adds to global warming or the “greenhouse effect,” all of which are harmful to human and animal life. Owing to the high consumption of plastics and the fluctuating cost of petroleum-based materials based on oil prices, biodegradable and renewable plastics such as poly(lactic acid) (PLA) (Anderson & Shive, 1997; Itavaara, Karjomaa, & Selin, 2002), poly(hydroxyalkanoates) (PHAs) (Pais et al., 2009), and thermoplastic starch (TPS) (Avella et al., 2005; Bhatnagar & Hanna, 1995; Leblanc et al., 2008; Mugnozza et al., 2006), etc., have been developed and have partially or completely replaced conventional plastics. Thermoplastics made of starch are one of the cheapest and most potentially useful materials in the single-use and/or non-durable plastic-related industries, especially in food packaging (Avella et al., 2005; Lorcks, 1998) and horticultural and agricultural films (Mugnozza et al., 2006).

Starch is a polysaccharide derived from the extraction of flour by alkali diluents and protease. It consists of amylose, which is a linear (1,4)-linked α-D-glucan, and amylopectin, which is a highly (1,6)-branched α-D-glucan. Starch has been used in a variety of applications – including food (De vlieger, 2003), coatings (Pareta & Edirisinghe, 2006), textiles (Meshram, Patil, Mhaske, & Thorat, 2005), pharmaceuticals (Atichokudomchai & Varavinit, 2003), packaging (Avella et al., 2005; Bhatnagar & Hanna, 1995) and plastics (Avella et al., 2005; Bhatnagar & Hanna, 1995; Mugnozza et al., 2006) – owing to its natural abundance, non-toxicity, low cost, renewability, biodegradability (Iovino, Zullo, Rao, Cassar, & Gianfreda, 2008) and compostability (Lorcks, 1998). In general, a starch granule degrades before it melts under applied heat because its molecular structure possesses strong inter- and intra-molecular hydrogen bonds (Trommsdorff & Tomka, 1995), which result in high glass transition (215–238 °C) (Singh, Okadome, Toyoshima, Isobe, & Ohtsubo, 2000) and melting temperatures (267–277 °C) (Singh et al., 2000). Many efforts have been made to fabricate TPS by methods based on a thermo-mechanical transformation of semi-crystalline starch granules to homogenous amorphous polymeric materials (De vlieger, 2003). The transformation has been performed by a single screw extruder (Leblanc et al., 2008; Ma, Yu, & Wan, 2006; Ma & Yu, 2004; Yang, Yu, & Ma, 2006), a twin screw extruder (Avella et al., 2005), or a Brabender Plasti-Corder (Forssell, Mikkila, Moates, & Parker, 1997) using temperatures ranging from 30 °C to 220 °C, pressures in the range of 25–150 bar, and high shear forces (e.g., screw speed in the range of 20 rpm to 210 rpm). A variety of plasticizers such as ethanolamine (Ma et al., 2006), urea

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(Ma et al., 2006; Ma & Yu, 2004), formamide (Ma & Yu, 2004), acetamide (Ma & Yu, 2004), ethylenebisformamide (Yang et al., 2006), glucose (Teixeira, Da Róz, Carvalho, & Curvelo, 2007), fructose (Teixeira et al., 2007), sucrose (Teixeira et al., 2007), sorbitol (Da Róz, Carvalho, Gandini, & Curvelo, 2006; Yang et al., 2006), ethylene glycol (Da Róz et al., 2006), propylene glycol (Da Róz et al., 2006), citric acid (Shi et al., 2007), water (Bhatnagar & Hanna, 1995; Forssell et al., 1997; Leblanc et al., 2008), and glycerol (Forssell et al., 1997; Leblanc et al., 2008; Ma et al., 2006; Ma & Yu, 2004; Shi et al., 2007; Teixeira et al., 2007) have been used to plasticize starch. Although TPS exhibits good oxygen barrier properties (Dole, Joly, Espuche, Alric, & Gontard, 2004), biodegradability (Iovino et al., 2008) and compostability (Lorcks, 1998), its strong water absorption (Teixeira et al., 2009), poor mechanical properties (Teixeira et al., 2009) and thermal stability (Liu, Misra, Askeland, Drzal, & Mohanty, 2005) limit its uses. Blending of TPS with other polymers is a simple, rapid and cheap method to overcome those drawbacks. Not only petroleum-based plastics such as polyethylene (Rosa et al., 2007), polypropylene (Rosa et al., 2007), etc., but also bio-based and biodegradable polymers (e.g. poly(hydroxybutyrate)) (PHB) (Godbole, Gote, Latkar, & Chakrabarti, 2003), poly(butylenes adipate-*co*-terephthalate) (PBAT) (Ren, Fu, Ren, & Yuan, 2009), PLA (Huneault & Li, 2007; Iovino et al., 2008; Martin & Averous, 2001; Ren et al., 2009; Schwach, Six, & Averous, 2008; Wang, Yu, & Ma, 2007), etc., have been blended with TPS.

PLA is a linear polyester produced from ring-opening polymerization of lactides or polycondensation of lactic acids in which the starting monomers are derived from renewable resources such as starch and sugar. PLA is biocompatible (Anderson & Shive, 1997), biodegradable (Anderson & Shive, 1997; Itavaara et al., 2002), compostable (Itavaara et al., 2002), low toxic (Conn et al., 1995) and rigid (Pillin, Montrelay, & Grohens, 2006). It has been used for many purposes including medical (Guptaa, Revagadea, & Hilbornb, 2007), textiles (Guptaa et al., 2007) and packaging (Holm, Mortensen, & Risbo, 2006).

Recently, the blending of TPS and PLA has been demonstrated (Huneault & Li, 2007; Iovino et al., 2008; Martin & Averous, 2001; Ren et al., 2009; Schwach et al., 2008; Wang et al., 2007); however, many researchers have mentioned the incompatibility between the hydrophilic TPS and hydrophobic PLA phases (Huneault & Li, 2007; Iovino et al., 2008; Martin & Averous, 2001; Schwach et al., 2008; Wang et al., 2007). Hence, reactive compatibilizers or coupling agents, such as maleic anhydride (Huneault & Li, 2007; Iovino et al., 2008; Wang et al., 2007) and methylenediphenyl diisocyanate (Schwach et al., 2008), have been added to improve the compatibility of TPS and PLA. Those compatibilizers are nevertheless synthetic substances which might be toxic when the blends are used in contact with foods and human tissues.

Amphiphilic molecules, or amphiphiles, are compounds consisting of two parts of hydrophobic hydrocarbon moiety and hydrophilic polar groups such as carboxylates (CO_2^-), sulfates (SO_4^-), sulfonates (SO_3^-), and amines (NH_3^+) (Merianos, 2001). These two parts provide a compound with interfacial activity and give rise to a wide range of surface chemistry functions, such as wetting, emulsifying, softening, solubilizing, foaming/defoaming, rheology-modifying, and surface conditioning (Benvegnu, Plusquellec, & Lemiegre, 2008). Amphiphiles have been frequently used in the food (Thanatuksorn, Kawai, Hayakawa, Hayashi, & Kajiwara, 2009), agricultural (Lu & Zhu, 2009) and plastics industries (Corradini, de Carvalho, da Silva Curvelo, Agnelli, & Mattoso, 2007; Habeych, Dekkers, van der Goot, & Boom, 2008; Huang, Chang, & Jane, 1999; Pushpadass & Hanna, 2009). Fatty acids and proteins are good examples of natural amphiphiles which have been used in the production of starch-based plastics. The incorporation of a fatty acid such as stearic acid has decreased the detrimental effect on barrier properties of aged products due to the interference of stearic acid on crystallization of starch chains (Pushpadass & Hanna, 2009). Soy protein (Huang et al., 1999) and zein (Corradini et al., 2007; Habeych et al., 2008) have been used to produce starch/protein-based plastics. Huang et al. reported that soy protein imparted rigidity and strength to TPS when its content was lower than 60% (w/w) (Huang et al., 1999). The addition of zein facilitated plasticization of starch, reduced the equilibrium of water uptake, and enhanced extensibility of plastics (Corradini et al., 2007; Habeych et al., 2008). Tween 60 is an emulsifier for the food industry approved by the U.S. FDA, and has the potential use as an additive for the production of thermoplastics for food packaging. To our knowledge, studies on the use of linoleic acid and Tween 60 as additives for the production of TPS materials, as well as the effect of those amphiphiles and zein on binary blends of TPS–PLA have not yet been elucidated.

The present research thus aims to prepare TPS using three types of amphiphiles: i.e. Tween 60, linoleic acid and zein as additives. The effects of amphiphile type on processability, crystallinity, thermal characteristics and tensile properties of TPS materials were also investigated. In addition, we studied the blending of TPS materials and PLA, including the effect of PLA content and amphiphile type on processability, flow ability and tensile properties of the TPS–PLA blends.

2. Experimental

2.1. Materials

Cassava starch was supplied by Tongchan Co., Ltd., Thailand. Mung bean starch was purchased from Sitthinan Co., Ltd., Thailand. Poly(lactic acid) (Ingeo^{TM} 4042D) was obtained from Nature Works LLC, USA. Tween 60 was purchased from Acros Organics, Belgium. Linoleic acid (60–74% purity) was provided by Fluka Analytical, Germany. Zein was supplied by Sigma–Aldrich, USA. The glycerol used was a commercial grade product. All materials and chemicals were used as received.

2.2. Preparation of thermoplastic starch (TPS)

Cassava starch and mung bean starch with a weight ratio of 70:30 were mixed in a ribbon mixer (Reliance Tech-Service, Thailand). The starch mixture and mixed plasticizer containing glycerol and distilled water with a weight ratio of 3:1 were then fed into a twin screw extruder (LTE-20-40, Labtech Engineering Co., Ltd., Thailand, L/D = 40). The temperature profile along the extruder barrel was set in a range from 70 °C to 120 °C. The extrudates were cut by a pelletizer (LZ-120, Labtech Engineering Co., Ltd., Thailand) to obtain 3-mm length pellets. The pellets were dried at 50 °C overnight and kept in desiccators containing silica gel at an ambient temperature. The obtained product was named TPFN.

Three other different types of TPS materials, i.e. TPSTW, TPSLA and TPSZE, were also prepared in the same manner as TPSN; however, different amphiphiles, i.e. Tween 60, linoleic acid and zein, were added, respectively. The content of amphiphiles used was 1.55% (w/w).

2.3. Preparation of thermoplastic starch–poly(lactic acid) (TPS–PLA) blends

The obtained TPS pellets were physically mixed with PLA pellets using different TPS to PLA weight ratios (TPS:PLA) of 70:30, 50:50 and 30:70. The mixtures were subsequently fed into a twin screw extruder. The temperature profile along the extruder barrel ranged from 130 °C to 160 °C. The extrudates were cut into 3-mm length pellets. The obtained pellets were dried at 50 °C overnight and kept at an ambient temperature in desiccators containing silica gel.

2.4. Characterizations of TPS materials and TPS–PLA blends

X-ray diffraction (XRD) patterns were recorded by a JEOL JDX-3530 X-ray diffractomer (USA) over a 2θ range from 3° to 40° using a scan rate of 0.04° min^{-1}. Morphology of the samples was observed by a JEOL JSM-5600LV scanning electron microscope (USA) with an operating voltage of 10 kV. The samples were immersed in liquid nitrogen, broken and then mounted on a stub surface using two-sided carbon tape. The assemblies were dried under reduced pressure at an ambient temperature overnight, and then coated with a thin layer of gold prior to observation. Dynamic mechanical thermal analysis (DMTA) was carried out by a GABO Eplexor® qualimeter (Germany) in a compression mode using a scanning temperature ranging from −100 °C to 120 °C with a heating rate of 5 K/min and a frequency of 1 Hz. Differential scanning calorimetry (DSC) analysis was performed by a Mettler Toledo DSC822 (Switzerland) from −50 °C to 250 °C with a heating rate of 20 °C min^{-1} for a first heating scan. The samples were then cooled down to −50 °C at a cooling rate of 20 °C min^{-1}, held at −50 °C for 5 min, and reheated from −50 °C to 250 °C at a heating rate of 20 °C min^{-1}. A nitrogen

Fig. 1. Appearances of different TPS extrudates (left) and pellets (right): (A) TPSN, (B) TPSTW, (C) TPSLA and (D) TPSZE.

flow rate of 60 mL min^{-1} was maintained throughout the test. Thermogravimetric analysis (TGA) was performed by a Mettler Toledo TGA/DSC1 (Switzerland) under nitrogen atmosphere with a flow rate of 50 mL min^{-1}; the temperature used ranged from 30 °C to 600 °C, with a heating rate of 10 °C min^{-1}. The melt flow index (MFI) was measured according to ASTM 1238 by a Custom Scientific Instruments MFI2-203 (USA) using a temperature of 190 °C, load cell of 2.16 kg, and preheating time of 6 min. Sample pellets were dried at 50 °C overnight before testing.

2.5. Tensile testing of TPS materials and TPS–PLA blends

TPS materials and TPS–PLA blends were converted into dumbbell-shaped specimens by a Battenfeld BA 250 CDC injection molding machine (Germany) using temperature profiles of 140–185 °C; injection speeds of 18–25%; maximum injection pressures of 20–65 bar; and cooling times of 25–45 s. The obtained specimens were stored in a closed chamber containing sodium nitrite solution at 25 °C (65% RH) for 2 days. The preconditioned specimens were tested according to ASTM D638 by an H50K-S (Hounsfield Test Equipment, UK) equipped with a load cell of 500 kN. The test was performed using a crosshead speed of 50 mm min^{-1}, grip separation of 115 mm, and gage length of 50 mm.

3. Results and discussion

3.1. Appearances and characteristics of TPS materials

Four types of thermoplastic starches (TPS), i.e. TPSN, TPSTW, TPSLA and TPSZE, were prepared from cassava starch and mung bean starch by a twin screw extruder, using glycerol and water as plasticizers and Tween 60, linoleic acid and zein as additives for TPSTW, TPSLA and TPSZE, respectively. The appearances of the obtained TPS extrudates and pellets are illustrated in Fig. 1. TPSN was semitransparent, pale gray, and rigid (Fig. 1A). The TPS materials became more flexible, softer, and more easily processable when small amounts (1.55% (w/w)) of amphiphilic molecules (Tween 60, linoleic acid and zein) were added (Fig. 1B–D). The color of the products depended on amphiphile types. Evidently, zein gave TPSZE a pale yellow color (Fig. 1D). The plasticization of TPSZE was more easily performed than that of TPSLA, TPSTW and TPSN, respectively.

3.2. Microstructure of TPS materials

The changes in crystal structure type during the extrusion process, and crystallinity percentage of the TPS materials, were investigated by XRD analysis. Cassava starch and mung bean starch granules exhibited similar XRD patterns, with characteristic peaks at 2θ of 15°, 17°, 18° and 23° corresponding to A-type crystal structure (Fig. 2a and b) (Hoover, 2001; Ohwada, Ishibashi, Hironaka, & Yamamoto, 2003). The appearance of those peaks implied the crystalline portion of native starch granules. The crystallinities of cassava starch and mung bean starch were 35.6% and 34.2%, respectively, as determined from XRD patterns. After plasticization, the obtained materials showed significant reduction of peak intensities at 2θ of 15°, 17°, 18° and 23°, reflecting the partial destruction of A-type crystals (Fig. 2c–f), while exhibiting new diffraction peaks at 2θ of 13° and 20° attributed to V-type crystals (Da Róz et al., 2006; Shi et al., 2006). The V-type structure could be induced by the interaction between amylose helixes and small hydrophobic molecules (i.e. inclusion complex) during the cooling process. Shi et al. (2007) and Corradini et al. (2007) revealed the formation of V-type crystals from amylose–glycerol interaction induced after the compression molding process during aging (Corradini et al., 2007; Shi et al., 2006). For TPS materials containing amphiphiles, V-type crystals might also be a result of the amylose–amphiphile inclusion complex formation, e.g. amylose–linoleic acid complex (Bhatnagar & Hanna, 1994). The starch/zein V-complex could also be formed after compression during storage at 22 °C and 52% RH for 1 month, as reported by Corradini et al. (Corradini et al., 2007). All TPS materials showed reduced crystallinity as compared to native starch granules. The crystallinities of TPSN, TPSTW, TPSLA and TPSZE were 7.7%, 11.8%, 21.7% and 16.6%, respectively. The higher crystallinity of TPS materials containing amphiphiles might be caused by the additional V-type crystal formation of amylose–amphiphile inclusion complexes.

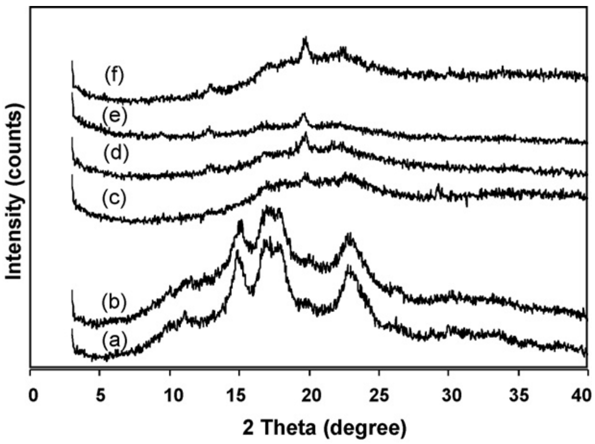

Fig. 2. X-ray diffraction patterns of: (a) cassava starch, (b) mung bean starch, (c) TPSN, (d) TPSTW, (e) TPSLA and (f) TPSZE.

The morphology of starch granules and TPS materials was observed by SEM. The granules of cassava starch were irregular in shape, with an average size of 5–18 μm (Fig. 3A), while mung bean starch granules exhibited an oval shape with an indentation in the middle and an approximate granule size of 10–25 μm (Fig. 3B). The plasticization of starch with glycerol and water under shear stress and heat caused destruction of starch granules and homogenously smooth surfaces, implying a predominantly amorphous phase (Fig. 3C) (Da Róz et al., 2006). This finding corresponded to the reduction in crystallinity of TPSN as compared to that of native granules (see XRD result). However, small pieces of starch granules were observed in the micrograph. This result suggested that the crystal structure of starch granules was partially disrupted during plasticization. By the addition of amphiphiles, the surface of TPS materials became rough, indicating a semicrystalline structure (Fig. 3D–F) (Teixeira et al., 2007). The surface roughness of TPSLA (Fig. 3E) was greater than those of TPSZE (Fig. 3F) and TPSTW (Fig. 3D), respectively, reflecting that TPSLA possessed higher crystallinity than TPSZE and TPSTW. This result was in agreement with the crystallinity percentage determined from XRD data (see XRD result).

3.3. Dynamic mechanical thermal analysis of TPS materials

Storage modulus (E') and loss factor or damping coefficient (tan δ) of TPS materials as a function of temperature were investigated by DMTA. TPS materials exhibited high storage modulus at temperatures ranging from −100 °C to −75 °C, implying that the molecules were in a glassy state (Fig. 4A). The storage modulus decreased with increasing temperature from −75 °C to 120 °C, indicating the relaxation of molecules. In other words, TPS materials exhibited rubbery characteristics at this region, and became softer. Considering the rubbery region, TPSN exhibited higher storage

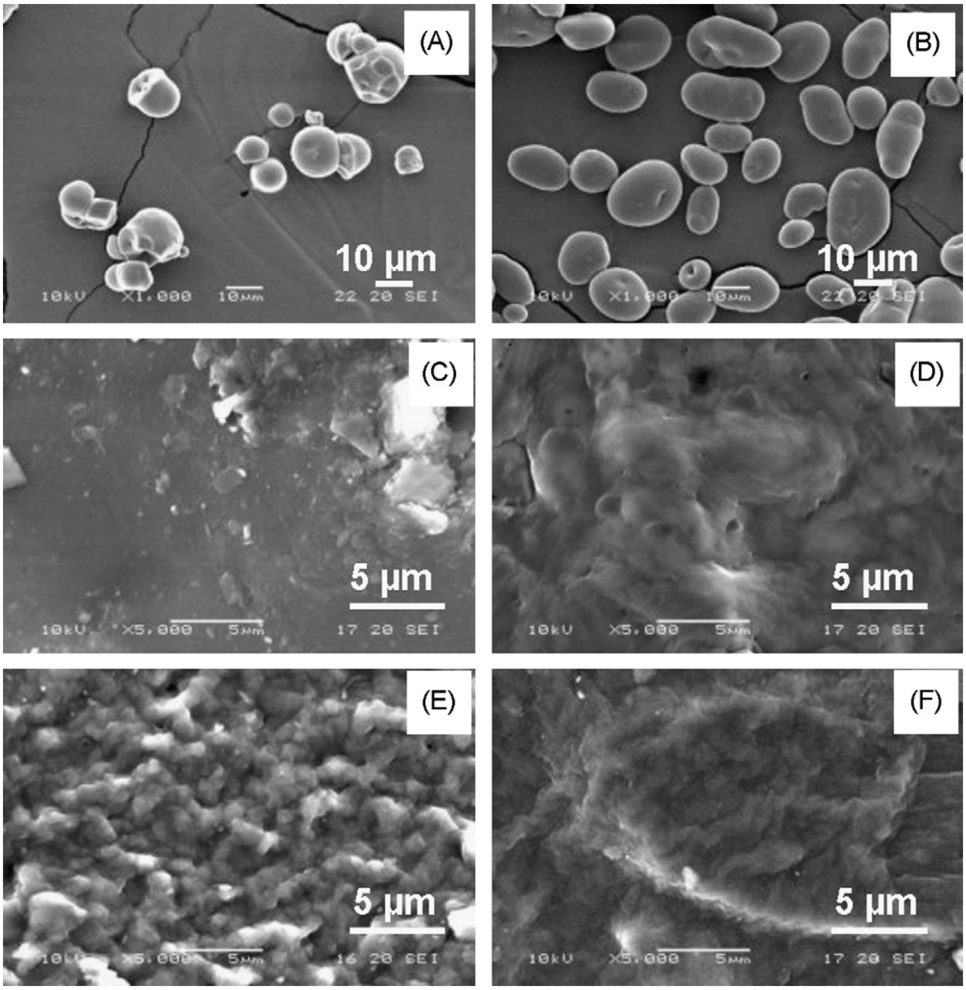

Fig. 3. SEM micrographs at 10 kV of: (A) cassava starch (1000×), (B) mung bean starch (1000×) and (C)–(F) fractured surface of different TPS materials (5000×): (C) TPSN, (D) TPSTW, (E) TPSLA and (F) TPSZE.

modulus than TPSZE, TPSLA and TPSTW, respectively. This result reflected that TPSN could store more energy or were stiffer than TPSZE, TPSLA and TPSTW.

Glass transition temperature (T_g) of the materials could be determined from the highest transition (peak) of the loss factor-temperature curve (Fig. 4B). TPSN exhibited two transition temperatures at −55.2 and 59.4 °C, implying a partially miscible system with two main transitions (Fig. 4Ba). The former T_g was attributed to the relaxation of the glycerol-rich phase, while the latter corresponded to the relaxation of plasticized starch (Forssell et al., 1997). The addition of amphiphiles caused the reduction of T_g (Fig. 4Bb–d). The T_g of plasticized starch containing zein, linoleic acid and Tween 60 were 38.1 °C, 23.4 °C and 8.1 °C, respectively, lower than that of TPSN. This result suggested that TPS materials became softer when 1.55% (w/w) of amphiphiles were added. However, TPSTW was softer than TPSLA and TPSZE, respectively.

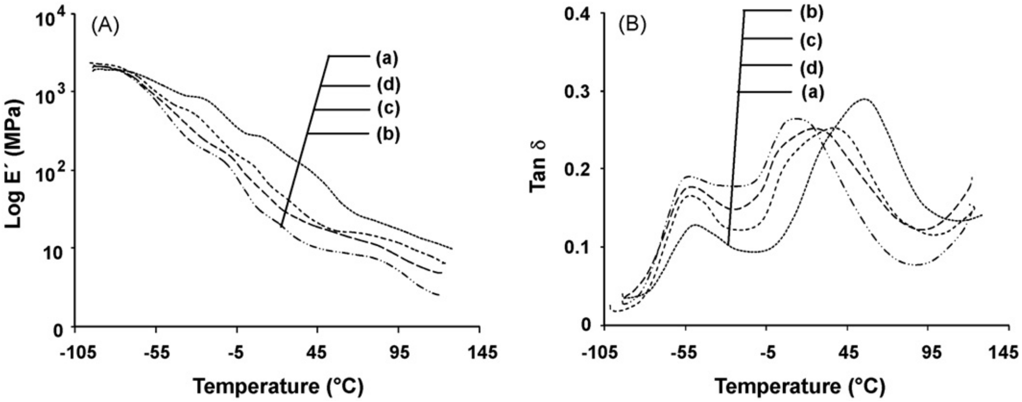

Fig. 4. (A) Storage modulus and (B) tan δ as a function of temperature of different TPS materials: (a) TPSN, (b) TPSTW, (c) TPSLA and (d) TPSZE.

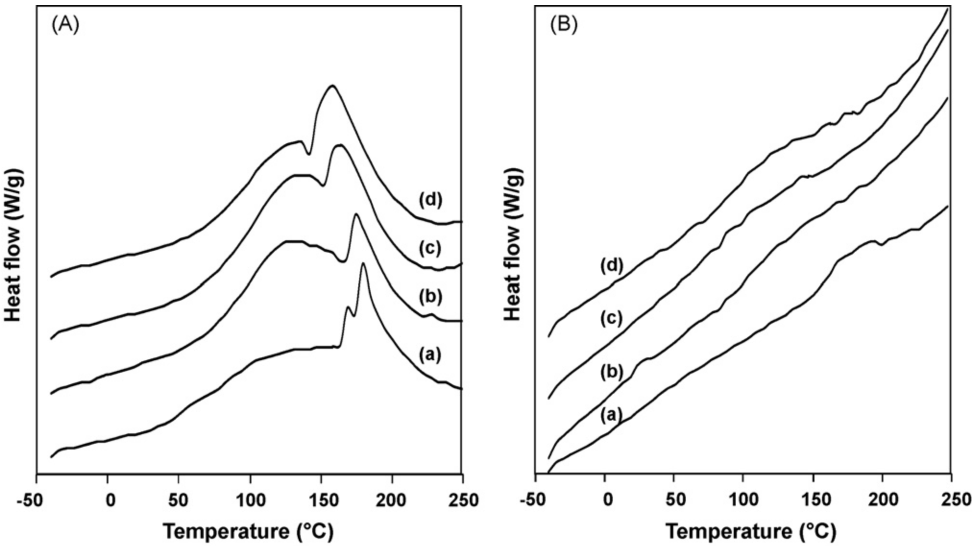

Fig. 5. DSC thermograms (endo up) for (A) first heating scan and (B) second heating scan of different TPS materials: (a) TPSN, (b) TPSTW, (c) TPSLA and (d) TPSZE.

3.4. *Thermal properties of TPS materials*

DSC was also applied to determine T_g and melting temperature (T_m) of TPS materials. The first heating scan was considered to obtain the information about thermal characteristics which is important for the further conversion process. Fig. 5A shows that T_g of TPS materials was hardly observed by DSC. However, TPSN revealed T_g at 56.7 °C (Fig. 5Aa), which was very close to the value observed by DMTA technique (see Section 3.3). In addition, TPSN exhibited two sharp endothermic peaks at 168.7 °C and 179.3 °C, implying T_m of the material possessing two main different crystal structures or sizes. The crystal melted at lower temperature might belong to plasticized starch derived from starch granules with higher disruption degree; while the one melted at higher temperature might result from plasticized starch obtained from slightly disrupted starch granules. This result was in agreement with that observed by SEM, i.e. small pieces of partially disrupted starch granules dispersed in highly amorphous plasticized starch. However, by the addition of amphiphiles, only a sharp endothermic peak was observed, reflecting that the obtained plasticized starch possessed sole-structured crystals or sole-sized crystals (Fig. 5Ab–d). The T_m of TPS materials containing amphiphiles was lower than that of TPSN. For example, TPSTW, TPSLA and TPSZE revealed T_m at 172.8 °C, 159.8 °C and 157.2 °C, respectively. The results suggested that the addition of amphiphiles enhanced starch granule disruption and facilitated melting of TPS materials, which is advantageous for the further conversion processes. However, the first heating scan is generally used to eliminate the thermal history of the materials; the second heating scan was thus performed (Fig. 5B). TPS materials showed a broad endothermic transition reflecting a uniform structured/sized crystal formation after quenching. However a broad transition might result from an entropic contribution to the melting behavior of starch at low plasticizer content (Soest, Bezemer, Wit, & Vliegenthart, 1996). TPSN showed T_m at 178 °C, while TPS materials containing amphiphiles gave lower T_m, i.e. in the range of 119–135 °C. TPSTW revealed higher T_m than TPSLA and TPSZE. The reduction of T_m by the addition of amphiphile corresponded to that observed from the first heating scan thermograms.

Thermal stability and decomposition temperature (T_d) of the materials were examined by TGA technique, in which the mass loss was measured as a function of temperature. Fig. 6Aa illustrated that TPSN performed a three-step mass loss at temperatures below 100 °C, 160–234 °C and 287–336 °C, attributed to the loss of water, the volatilization of hydrolyzed glycerol (Leblanc et al., 2008; Ma et al., 2006) and the decomposition of TPSN, respectively. The maximum mass loss corresponding to T_d was easily observed as a peak in a derivative TG, or so-called DTG, thermogram (Fig. 6B). For example, T_d of TPSN was 317.3 °C. Similarly, TPS materials containing amphiphiles also showed a three-step mass loss (Fig. 6Ab–d). However, as compared to TPSN, TPSTW exhibited a slightly higher T_d (318.7 °C), while TPSLA (316.8 °C) and TPSZE (314.5 °C) exhibited a little lower (Fig. 6Bb–d). This shift of T_d was not markedly observable, implying that the addition of amphiphilic molecules with a

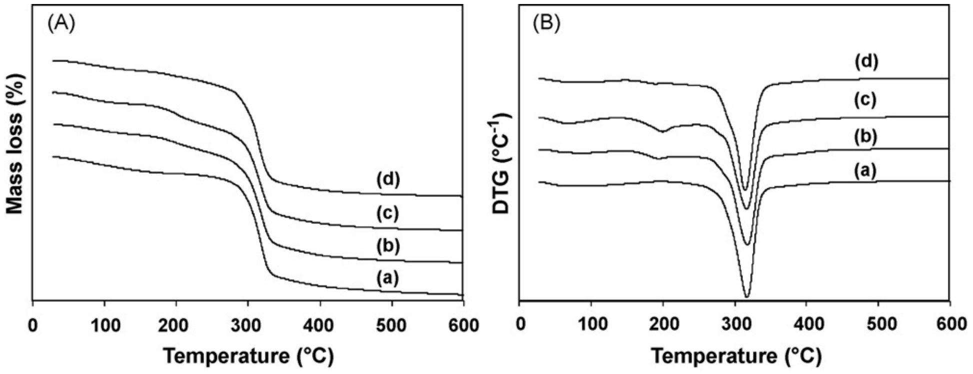

Fig. 6. (A) TG and (B) DTG thermograms of different TPS materials: (a) TPSN, (b) TPSTW, (c) TPSLA and (d) TPSZE.

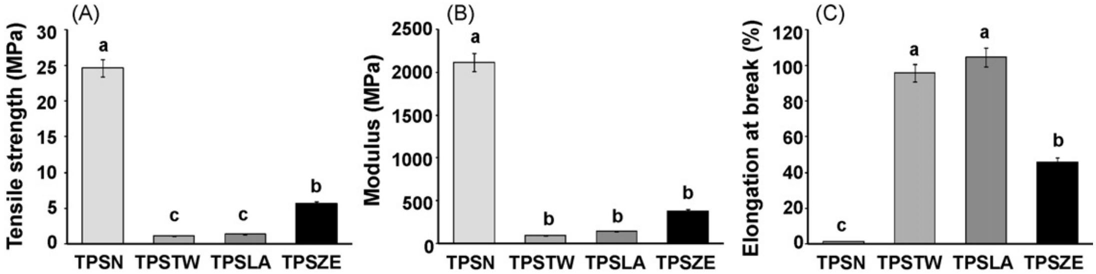

Fig. 7. (A) Tensile strength, (B) modulus and (C) elongation at break of different TPS materials. The data is reported as mean ± SD, $n = 3–5$. The different small letters indicate significant difference at $p < 0.05$ (Duncan's new multiple range test).

concentration of 1.55% (w/w) did not affect the thermal stability of TPS materials.

3.5. Tensile properties of TPS materials

Mechanical properties of TPS materials were determined in a tension mode. TPSN showed tensile strength (TS) and modulus of 25 MPa and 2117 MPa, respectively (Fig. 7A and B). By the addition of amphiphiles, TS and modulus significantly decreased to values ranging from 1 MPa to 6 MPa and from 94 MPa to 376 MPa, respectively. TPSZE exhibited TS 3- to 4-fold higher than TPSLA and TPSTW. The modulus of TPSZE was also higher than those of TPSLA and TPSTW, by about two to three times. In contrast, elongation at break (*E*) of TPSN was relatively low (1%) as compared to those of TPS materials containing amphiphiles (46–105%) (Fig. 7C). TPSZE gave lower *E* than TPSLA and TPSTW (about half). The results reflected that Tween 60, linoleic acid and zein significantly reduced the strength and rigidity, while improving the extensibility, of TPS materials. This might be explained by the reduction of T_g when those amphiphiles were added; as a result the materials were in a rubbery state (see Section 3.3). Considering the results by amphiphile type, zein produced a strong and rigid TPS material, while Tween 60 and linoleic acid provided extensible materials.

The morphology of TPS materials at the fractured surface after tensile testing was observed by SEM (Fig. 8). TPSN exhibited a homogeneously smooth surface, implying rigid material (Fig. 8A),

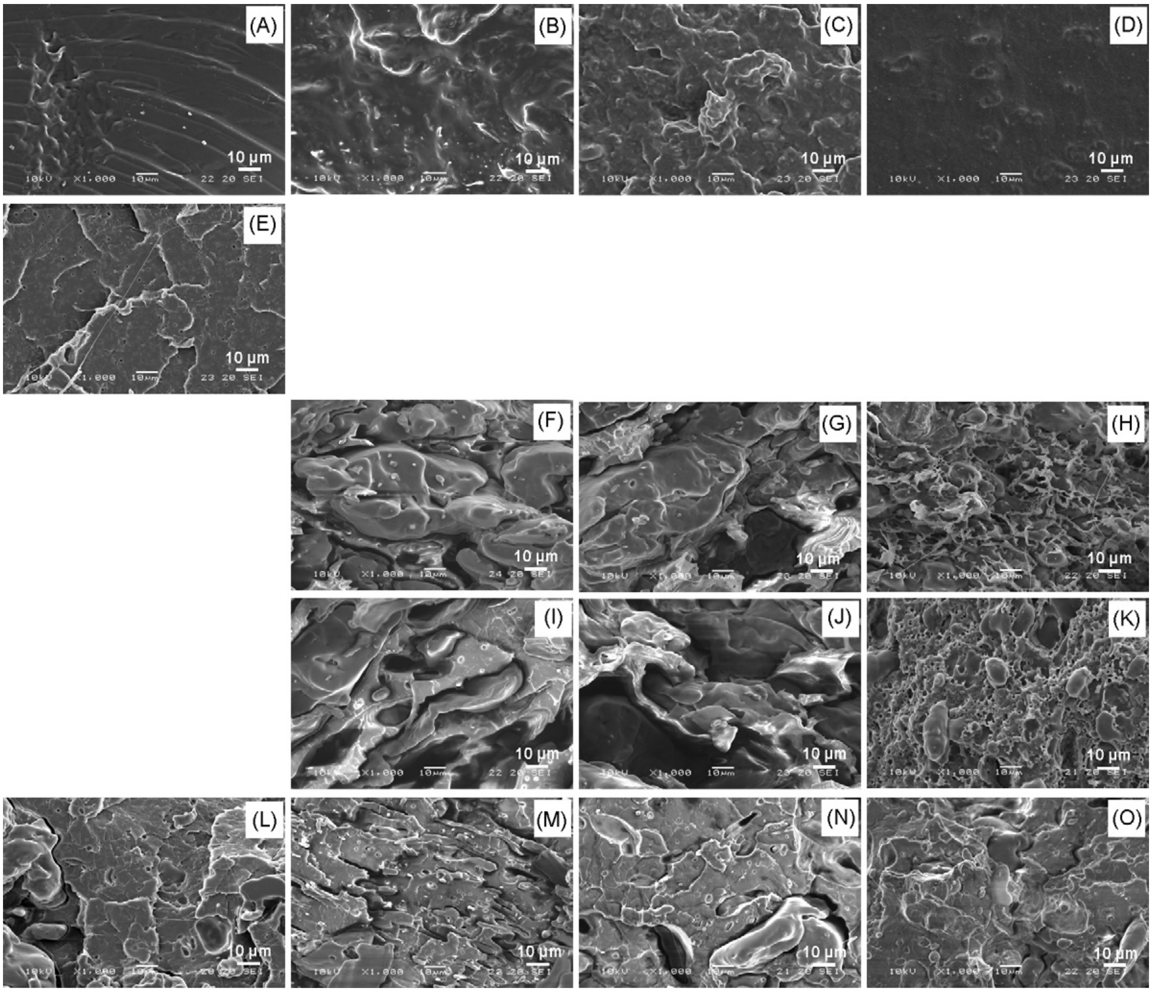

Fig. 8. SEM micrographs at 10 kV (1000×) of fractured surface after tensile testing of different samples: (A) TPSN, (B) TPSTW, (C) TPSLA, (D) TPSZE, (*E*) PLA, (F) TPSTW(70)-PLA(30), (G) TPSLA(70)-PLA(30), (H) TPSZE(70)-PLA(30), (I) TPSTW(50)-PLA(50), (J) TPSLA(50)-PLA(50), (K) TPSZE(50)-PLA(50), (L) TPSN(30)-PLA(70), (M) TPSTW(30)-PLA(70), (N) TPSLA(30)-PLA(70) and (O) TPSZE(30)-PLA(70).

while TPS materials containing amphiphiles possessed rougher surfaces (Fig. 8B–D), especially TPSTW (Fig. 8B) and TPSLA (Fig. 8C), reflecting soft materials. This observation supported the results from tensile testing, i.e. TPSN illustrated high TS and modulus, while TPSTW, TPSLA and TPSZE gave high *E* (Fig. 7). It should be noted that TPSZE showed a homogeneously smoother surface than TPSTW and TPSLA (Fig. 8D); as a result TPSZE possessed superior TS and modulus, but inferior *E*, to TPSTW and TPSLA (Fig. 7).

3.6. Tensile properties of TPS–PLA blends

In order to improve the mechanical properties of TPS materials, PLA (a commercially available biodegradable polyester) was chosen to be blended with the starch-based thermoplastics because it is derived from naturally renewable resources and shows complete biodegradability. Four types of TPS materials, i.e. TPSN, TPSTW, TPSLA and TPSZE, were blended with PLA at different PLA contents: 0%, 30%, 50% and 70% (w/w). It was found that PLA enhanced the extrusion and injection molding processabilities of TPS materials. The processability of TPS–PLA blends improved as a function of PLA content. The obtained TPS–PLA blends were stiffer and more opaque than TPS materials.

The mechanical properties of TPS–PLA blends were determined in a tension mode. Fig. 9A and B shows that TS and modulus of the blends are in the range of 8–38 MPa and 505–4014 MPa, respectively, which are higher than those of TPS materials (see Fig. 7A and B). TS and modulus increased significantly with increasing PLA content. The results suggested that PLA could impart strength and rigidity to the blends. This might be a result of relatively high TS (56 MPa) and modulus (3806 MPa) of neat PLA (data not shown). It should be pointed out that the preparation of TPSN-PLA blends containing low PLA content, i.e. $\leq$50% (w/w), could not be achieved; as a result the tensile testing data of those blends was not presented in Fig. 9. The limitation of compounding might result from low fluidity of the blend materials. However the blends containing amphiphiles, i.e. TPSTW-PLA, TPSLA-PLA and TPSZE-PLA blends, could be successfully prepared, though PLA content of $\leq$50% (w/w) was used. This suggested that amphiphiles facilitated processability of the TPS–PLA blends, especially when PLA content was $\leq$50% (w/w). On the other hand, *E* of the blends ranged from 1% to 16% (Fig. 9C), which was significantly lower than that of the TPS materials (see Fig. 7C). This might be due to the characteristics of PLA, e.g. rigidity, brittleness and very low extensibility ($E \sim 2\%$) (data not shown). PLA content did not significantly affect *E* of the blends. However, the TPSN-PLA blend containing PLA content of 70% (w/w) showed a similar *E* value as TPSN material, implying that the addition of PLA to the stiff and low-extensible TPS material could not influence the extensibility of the material. The results suggested that TPSN material and TPSN-PLA blends were stronger and more rigid, but less extensible than TPS materials and TPS–PLA blends containing amphiphiles. This finding pointed out that the addition of amphiphiles not only assisted the processability of TPS–PLA blends, but also improved their extensibility and/or flexibility. Considering the results by amphiphile type, zein gave a stronger and more rigid TPS–PLA blend than Tween 60 and linoleic acid, respectively, when PLA content was $\leq$50% (w/w). On the contrary, Tween 60 and linoleic acid provided more extensible blends than zein.

After tensile testing, the morphology of the fractured surfaces of the TPS–PLA blends was observed by SEM (Fig. 8F–O). In general, PLA showed a smooth crack propagation area on the fractured surface, reflecting brittleness and rigidity (Fig. 8E). The blending of TPS materials with PLA caused changes in the fractured surface morphology (Fig. 8F–O). The morphology of the blends containing 70% (w/w) of PLA was similar to that of neat PLA, in which a smooth crack propagation area was observed (Fig. 8L–O). However the blends showed a relatively higher degree of cracking, implying lower strength, rigidity and brittleness as compared to neat PLA. In contrast, the morphology of the blends containing PLA content of $\leq$50% (w/w) was different from those of neat TPS materials and PLA, and was influenced by amphiphile type (Fig. 8F–K). Although TPSTW-PLA and TPSLA-PLA blends with PLA contents of 30% and 50% (w/w) exhibited similar surface morphology (Fig. 8F–G and I and J), they possessed different morphology from TPSZE-PLA blends (Fig. 8H and K). The inhomogeneity and cavity existence on the fractured surface of TPSTW-PLA and TPSLA-PLA blends implied elongate materials, while the smooth crack surface of TPSZE-PLA blends suggested the brittleness and rigidity of these materials. However, the surface cracking degree of TPSZE-PLA blends containing PLA content of 30% and 50% (w/w) was higher than that of the blend with 70% (w/w) of PLA, implying lower strength, rigidity and brittleness. These findings supported the tensile testing results.

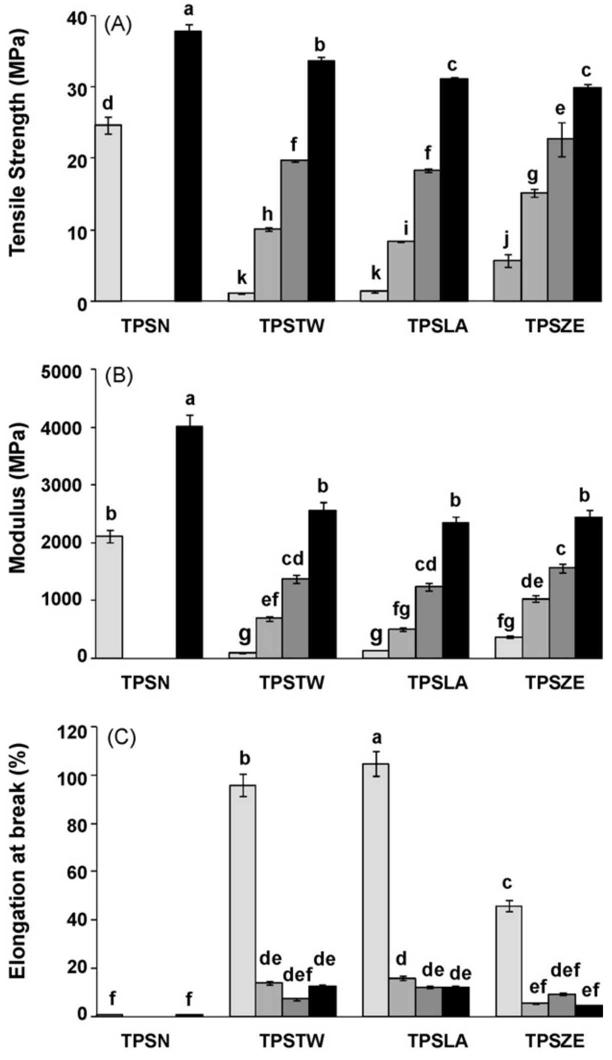

Fig. 9. (A) Tensile strength, (B) modulus and (C) elongation at break of different TPS–PLA blends with different PLA contents. TPS–PLA blends: TPSN-PLA, TPSTW-PLA, TPSLA-PLA and TPSZE-PLA. PLA content: (□) 0% (w/w), (▨) 30% (w/w), (▩) 50% (w/w) and (■) 70% (w/w). The data is reported as mean ± SD, $n = 3$–5. The different small letters indicate significant difference at $p < 0.05$ (Duncan's new multiple range test).

3.7. Melt flow index of TPS–PLA blends

The flow behavior of thermoplastic materials is generally determined by the value of the melt flow index (MFI). The MFI value also relates to the molecular mass, and is always used to measure

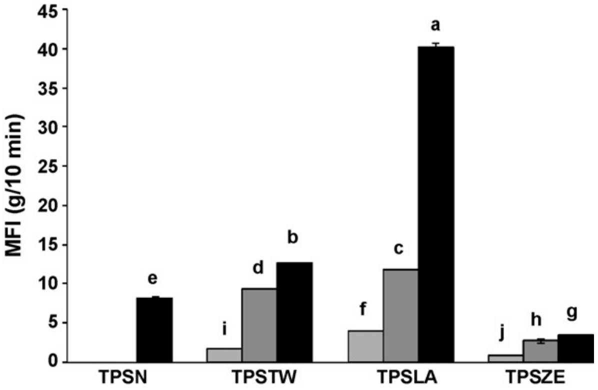

Fig. 10. MFI of different TPS–PLA blends with different PLA contents. TPS–PLA blends: TPSN-PLA, TPSTW-PLA, TPSLA-PLA and TPSZE-PLA. PLA content: (░) 30% (w/w), (▒) 50% (w/w) and ■ 70% (w/w). The data is reported as mean ± SD, $n = 3$. The different small letters indicate significant difference at $p < 0.05$ (Duncan's new multiple range test).

the melt viscosity of the materials. High MFI value indicates good flow, small molecules and low melt viscosity. Information about MFI can be used to predict the appropriate converting processes for each material and to determine an optimal condition for those processes. For example, materials with higher MFI are better converted to products by a blow molding process, while lower MFI materials are more easily shaped by injection molding or extrusion processes (Ren et al., 2009).

It should be pointed out that the MFI of TPS materials could not be determined according to the ASTM 1238 using a temperature of 190 °C and load of 2.16 kg; this might be due to an extremely high melt viscosity of TPS materials. This finding was in agreement with the result reported by Rosa et al. (2007). The MFI values of TPS–PLA blends are shown in Fig. 10. Values varied from 1 to 40 g/10 min, depending on PLA content as well as amphiphile type. MFI values of the blends increased significantly with increasing PLA content. This might be an effect of PLA flowability, i.e. MFI $\sim$33 g/10 min, due to the fact that the melt viscosity of PLA is lower than that of TPS materials. The results suggested that PLA improved the melt flow ability of TPS materials. Blends of TPS and PLA could thus be shaped by thermal processes. In other words, the processability of TPS–PLA blends improved as a function of PLA content, which might be a result of the reduced melt viscosity. Amphiphile or TPS types also affected the flow behavior of the blends. TPSLA gave a higher MFI value than TPSTW and TPSZE, respectively, for all PLA contents. This finding implied that linoleic acid was more effective in reducing the melt viscosity of TPS–PLA blends than Tween 60 and zein, respectively.

4. Conclusions

Four types of TPS materials — TPSN, TPSTW, TPSLA and TPSZE — were produced from cassava starch and mung bean starch by a twin screw extruder using glycerol and water as plasticizers. Amphiphilic molecules, i.e. Tween 60, linoleic acid and zein, were used as additives for the production of TPFSTW, TPSLA and TPSZE, respectively. The addition of amphiphiles facilitated melting and improved plasticization and processability of the TPS materials, owing to the reduction of $T_{\rm g}$ and $T_{\rm m}$, which is advantageous for further converting processes. TPSN showed $T_{\rm g}$ and $T_{\rm m}$ at 59.4 °C and 179.3 °C, respectively, while the plasticized starch containing zein, linoleic acid and Tween 60 gave $T_{\rm g}$ at 38.1 °C, 23.4 °C and 8.1 °C, respectively, and $T_{\rm m}$ at 157.2 °C, 159.8 °C and 172.8 °C, respectively. The plasticization of TPSZE was more easily carried out than those of TPSLA, TPSTW and TPSN, respectively. Thermal stability of TPS materials was not significantly influenced by the addition of 1.55% (w/w) of amphiphiles ($T_{\rm d}$ $\sim$315–319 °C). The crystallinity of TPS materials containing amphiphiles (11.8–21.7%) increased as compared to that of TPSN (7.7%) owing to the additional V-type crystal formation. The addition of amphiphiles decreased stiffness, tensile strength and rigidity of TPS materials, while imparting extensibility. TPSZE was five times stronger and two to three times more rigid than TPSLA and TPSTW, while TPSLA and TPSTW showed twice as great an extensibility as TPSZE. The tensile strength and rigidity of TPS materials were improved 1 to 30 times by blending with 30–70% (w/w) of PLA. TS and modulus of TPS–PLA blends increased significantly with increasing PLA content. The augmentation of PLA content caused more reduced melt viscosity, improved flowability and allowed easier processability. Amphiphiles also facilitated processability of the TPS–PLA blends, especially when PLA content was $\leq$50% (w/w), and enhanced extensibility of the blends. The type of amphiphile also affected tensile properties and rheology of the blends. Tween 60 and linoleic acid provided more extensible blends, while zein gave a stronger and more rigid blend, especially when PLA content was $\leq$50% (w/w). Linoleic acid and Tween 60 improved flowability of the blend, while zein depressed it.

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References

Anderson, J. M., & Shive, M. S. (1997). Biodegradation and biocompatibility of PLA and PLGA microspheres. *Advanced Drug Delivery Reviews*, *28*, 5–24.

Atichokudomchai, N., & Varavinit, S. (2003). Characterization and utilization of acid-modified cross-linked Tapioca starch in pharmaceutical tablets. *Carbohydrate Polymers*, *53*, 263–270.

Avella, M., De Vliegar, J. J., Errico, M. E., Fischer, S., Vacca, P., & Volpe, M. G. (2005). Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chemistry*, *93*, 467–474.

Benvegnu, T., Plusquellec, D., & Lemiegre, L. (2008). Chapter 7 — Surfactants from renewable sources: Synthesis and applications. In M. N. Belgacem, & A. Gandini (Eds.), *Monomers, polymers and composites from renewable resources* (pp. 153–178). UK/USA: Elsevier Ltd.

Bhatnagar, S., & Hanna, M. A. (1994). Amylose-lipid complex formation during single-screw extrusion of various corn starches. *Cereal Chemistry*, *71*, 582–587.

Bhatnagar, S., & Hanna, M. A. (1995). Properties of extruded starch-based plastic foam. *Industrial Crops and Products*, *4*, 71–77.

Conn, R. E., Kolstad, J. J., Borzelleca, J. F., Dixler, D. S., Filer, L. J., LaDu, B. N., et al. (1995). Safety assessment of polylactide (PLA) for use as a food-contact polymer. *Food and Chemical Toxicology*, *33*, 273–283.

Corradini, E., de Carvalho, A. J. F., da Silva Curvelo, A. A., Agnelli, J. A. M., & Mattoso, L. H. C. (2007). Preparation and characterization of thermoplastic starch/zein. *Materials Research*, *10*, 227–231.

Da Róz, A. L., Carvalho, A. J. F., Gandini, A., & Curvelo, A. A. S. (2006). The effect of plasticizers on thermoplastic starch compositions obtained by melt processing. *Carbohydrate Polymers*, *63*, 417–424.

De vlieger, J. J. (2003). Green plastics for food packaging. In R. Advenainen (Ed.), *Novel food packaging techniques* (pp. 519–534). England/USA: Woodhead Publishing Limited and CRC Press LLC.

Dole, P., Joly, C., Espuche, E., Alric, I., & Gontard, N. (2004). Gas transport properties of starch based films. *Carbohydrate Polymers*, *58*, 335–343.

Forssell, P. M., Mikkila, J. M., Moates, G. K., & Parker, R. (1997). Phase and glass transition behavior of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch. *Carbohydrate Polymers*, *34*, 275–282.

Godbole, S., Gote, S., Latkar, M., & Chakrabarti, T. (2003). Preparation and characterization of biodegradable poly-3-hydroxybutyrate-starch blend film. *Bioresource Technology*, *86*, 33–37.

Guptaa, B., Revagadea, N., & Hilbornb, J. (2007). Poly(lactic acid) fiber: An overview. *Progress in Polymer Science*, *32*, 455–482.

Habeych, E., Dekkers B., van der Goot, A. J., & Boom, R. (2008). Starch-zein blends formed by shear flow. *Chemical Engineering Science*, *63*, 5229–5238.

Holm, V. K., Mortensen, G., & Risbo, J. (2006). Quality changes in semi-hard cheese packaged in a poly(lactic acid) material. *Food Chemistry*, *97*, 401–410.

Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches: A review. *Carbohydrate Polymers*, *45*, 253–267.

Huang, H. C., Chang, T. C., & Jane, J. (1999). Mechanical and physical properties of protein–starch based plastics produced by extrusion and injection molding. *Journal of the American Oil Chemists' Society*, *76*, 1101–1108.

Huneault, M. A., & Li, H. (2007). Morphology and properties of compatibilized polylactide/thermoplastic starch blends. *Polymer*, *48*, 270–280.

Iovino, R., Zullo, R., Rao, M. A., Cassar, L., & Gianfreda, L. (2008). Biodegradation of poly(lactic acid)/starch/coir biocomposites under controlled composting conditions. *Polymer Degradation and Stability*, *93*, 147–157.

Itavaara, M., Karjomaa, S., & Selin, J.-F. (2002). Biodegradation of polylactide in aerobic and anaerobic thermophilic conditions. *Chemosphere*, *46*, 879–885.

Leblanc, N., Saiah, R., Beucher, E., Gattin, R., Castandet, M., & Saiter, J. M. (2008). Structural investigation and thermal stability of new extruded wheat flour based polymeric materials. *Carbohydrate Polymers*, *73*, 548–557.

Liu, W., Misra, M., Askeland, P., Drzal, L. T., & Mohanty, A. K. (2005). 'Green' composites from soy based plastic and pineapple leaf fiber: Fabrication and properties evaluation. *Polymer*, *46*, 2710–2721.

Lorcks, J. (1998). Properties and applications of compostable starch-based plastic material. *Polymer Degradation and Stability*, *59*, 245–249.

Lu, L., & Zhu, L. (2009). Reducing plant uptake of PAHs by cationic surfactant-enhanced soil retention. *Environment Pollution*, *157*, 1794–1799.

Ma, X. F., Yu, J. G., & Wan, J. J. (2006). Urea and ethanolamine as a mixed plasticizer for thermoplastic starch. *Carbohydrate Polymers*, *64*, 267–273.

Ma, X., & Yu, J. (2004). The plasticizers containing amide groups for thermoplastic starch. *Carbohydrate Polymers*, *57*, 197–203.

Martin, O., & Averous, L. (2001). Poly(lactic acid): Plasticization and properties of biodegradable multiphase systems. *Polymer*, *42*, 6209–6219.

Merianos, J. J. (2001). Chapter 14 — Surface-active agents. In S. S. Block (Ed.), *Disinfection, sterilization, and preservation* (pp. 283–320). Lippincoti Williams & Wilkins Ltd: USA.

Meshram, M. W., Patil, V. V., Mhaske, S. T., & Thorat, B. N. (2005). Graft copolymer of starch and its application in textiles. *Carbohydrate Polymers*, *75*, 71–78.

Mugnozza, G. S., Schettini, E., Vox, G., Malinconico, M., Immirzi, B., & Pagliara, S. (2006). Mechanical properties decay and morphological behavior of biodegradable films for agricultural mulching in real scale experiment. *Polymer Degradation and Stability*, *91*, 2801–2808.

Ohwada, N., Ishibashi, K., Hironaka, K., & Yamamoto, K. (2003). Physicochemical properties of mung bean starch. *Journal of Applied Glycoscience*, *50*, 481–485.

Pais, J., Farinha, I., Serafim, L. S., Prieto, M. A., Arevalo-Rodriguez, M., & Reis, M. A. M. (2009). Bioplastic production from cheese whey by recombinant *E. coli*. *New Biotechnology*, *25*, S220.

Pareta, R., & Edirisinghe, M. J. (2006). A novel method for the preparation of starch films and coatings. *Carbohydrate Polymers*, *63*, 425–431.

Pillin, I., Montrelay, N., & Grohens, Y. (2006). Thermo-mechanical characterization of plasticized PLA: Is the miscibility the only significant factor? *Polymer*, *47*, 4676–4682.

Pushpadass, H. A., & Hanna, M. A. (2009). Age-Induced changes in the microstructure and selected starch films plasticized with glycerol and stearic acid. *Industrial and Engineering Chemistry Research*, *48*, 8457–8463.

Ren, J., Fu, H., Ren, T., & Yuan, W. (2009). Preparation, characterization and properties of binary and ternary blends with thermoplastic starch, poly(lactic acid) and poly(butylenes adipate-*co*-terephthalate). *Carbohydrate Polymers*, *77*, 576–582.

Rosa, D. S., Guedes, C. G. F., & Carvalho, C. L. (2007). Processing and thermal, mechanical characterization of post-consumer polyolefins/thermoplastic starch blends. *Journal of Material Science*, *42*, 551–557.

Schwach, E, Six, J.-L., & Averous, L. (2008). Biodegradable blends based on starch and poly(lactic acid): Comparison of different strategies and estimate of compatibilization. *Journal of Polymers and the Environmental*, *16*, 286–297.

Shi, R., Liu, Q., Ding, T., Han, Y., Zhang, L., Chen, D., et al. (2006). Ageing of soft thermoplastic starch with high glycerol content. *Journal of Applied Polymer Science*, *103*, 574–586.

Shi, R., Zhang, Z., Liu, Q., Han, Y., Zhang, L., Chen, D., et al. (2007). Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending. *Carbohydrate Polymers*, *69*, 748–755.

Singh, V., Okadome, H., Toyoshima, H., Isobe, S., & Ohtsubo, K. (2000). Thermal and Physicochemical Properties of Rice Grain, Flour and Starch. *Journal of Agricultural and Food Chemistry*, *48*, 2639–2647.

Soest, J. J. G., Bezemer, R. C., Wit, D., & Vliegenthart, J. F. G. (1996). Influence of glycerol on the melting of potato starch. *Industrial Crops and Products*, *5*, 1–9.

Teixeira, E. M., Da Róz, A. L., Carvalho, A. J. F., & Curvelo, A. A. S. (2007). The effect of glycerol/sugar/water and sugar/water mixtures on the plasticization of thermoplastic cassava starch. *Carbohydrate Polymers*, *69*, 619–624.

Teixeira, E. M., Pasquini, D., Curvelo, A. A. S., Corradini, E., Belgacem, M. N., & Dufresne, A. (2009). Cassava bagasses cellulose nanofibrils reinforced thermoplastic cassava starch. *Carbohydrate Polymers*, *78*, 422–431.

Thanatuksorn, P., Kawai, K., Hayakawa, M., Hayashi, M., & Kajiwara, K. (2009). Improvement of the oral bioavailability of coenzyme Q_{10} by emulsification with fats and emulsifiers used in the food industry. *Food Science and Technology*, *42*, 385–390.

Trommsdorff, U., & Tomka, I. (1995). Structural of amorphous starch 1. An atomistic model and X-ray scattering study. *Macromolecules*, *28*, 6128–6137.

Wang, N., Yu, J., & Ma, X. (2007). Preparation and characterization of thermoplastic starch/PLA blends by one-step reactive extrusion. *Polymer International*, *56*, 1440–1447.

Yang, J. H., Yu, J. G., & Ma, X. F. (2006). Study on the properties of ethylenebisformamide and sorbitol plasticized corn starch (ESPTPS). *Carbohydrate Polymer*, *66*, 110–116.