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Effect of Starch and Plasticizer Types and Fiber Content on Properties of Polylactic Acid/Thermoplastic Starch Blend

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***Abstract*—**Polylactic acid (PLA) is the most commercially available bio-based and biodegradable plastic at present. PLA has been used in plastic related industries including single-used containers, disposable and environmentally friendly packaging owing to its renewability, compostability, biodegradability, and safety. Although PLA demonstrates reasonably good optical, physical, mechanical and barrier properties comparable to the existing petroleum-based plastics, its brittleness and mold shrinkage as well as its price are the points to be concerned for the production of rigid and semi-rigid packaging. Blending PLA with other bio-based polymers including thermoplastic starch (TPS) is an alternative not only to achieve a complete bio-based plastic, but also to reduce the brittleness, shrinkage during molding and production cost of the PLA-based products. TPS is a material produced mainly from starch which is cheap, renewable, biodegradable, compostable, and non-toxic. It is commonly prepared by a plasticization of starch under applying heat and shear force. Although glycerol has been reported as one of the most plasticizers used for preparing TPS, its migration caused the surface stickiness of the TPS products. In some cases, mixed plasticizers or natural fibers have been applied to impede the retrogradation of starch or reduce the migration of glycerol. The introduction of fibers into TPS-based materials could reinforce the polymer matrix as well. Therefore, the objective of the present research is to study the effect of starch type (i.e. native starch and phosphate starch), plasticizer type (i.e. glycerol and xylitol with a weight ratio of glycerol to xylitol of 100:0, 75:25, 50:50, 25:75 and 0:100) and fiber content (i.e. in the range of 1-25 %wt) on properties of PLA/TPS blend and composite. PLA/TPS blends and composites were prepared using a twin-screw extruder and then converted into dumbbell-shaped specimens using an injection molding machine. The PLA/TPS blends prepared by using phosphate starch showed higher tensile strength and stiffness than the blends prepared by using native one. In contrast, the blends from native starch exhibited higher extensibility and heat distortion temperature (HDT) than those from the modified starch. Increasing xylitol content resulted in enhanced tensile strength, stiffness and water resistance, but decreased extensibility and HDT of the PLA/TPS blend. Tensile properties and hydrophobicity of the blend could be improved by incorporating silane treated-jute fibers.

***Keywords*—**Polylactic acid, Thermoplastic starch, Jute fiber, Composite, Blend.

I. INTRODUCTION

RECENTLY, biodegradable bio-based plastics have received much attention in many developed countries due to the campaign from their government to reduce the environmental impact from using petroleum-based plastics. Bio-based plastics are derived from renewable resources such as starch, cellulose, proteins, etc., which are harmless to environment and life.

Polylactic acid (PLA) and thermoplastic starch (TPS) are two potentially biodegradable bio-based plastics, which can be processed using the same technologies as conventional plastics and converted into various kinds of products (e.g. cups, thermoformed trays and flexible films, etc.). TPS is a hydrophilic material obtained from the plasticization of starch under applying heat and high shear force. PLA is relatively hydrophobic polymer produced from the polymerization of lactic acid or lactide and possesses good mechanical properties, easy processability, water resistance, and transparency comparable to petroleum-based plastics [1]-[4]. However, PLA has brittleness and low heat distortion temperature (HDT), while TPS exhibits high moisture/water sensitivity resulting in poor mechanical and barrier properties. In addition, TPS-based products are always sticky at the surface after storing for a period of time due to the re-crystallization of starch molecules (retrogradation) which promotes the migration of small plasticizer, e.g. glycerol [5].

Utilization of chemically modified starch and incorporation of natural fibers have been reported as effective methods to reduce water absorption and retrogradation of TPS [6], [7]. Likewise, using mixed plasticizers (e.g. formamide/urea, sorbital/glycerol, glycerol/xylitol, etc.) could improve water resistance, and reduce retrogradation or migration of plasticizers [8]-[10]. In addition, natural fibers such as flax, kenaf, jute or bamboo was incorporated in PLA or TPS matrices to improve their mechanical properties via reinforcing effect [7], [11]-[13] and enhance their HDT via nucleating effect [14], [15]. Jute fiber is one of the most popular fibers incorporated in composite materials because it is cheap and has high tensile strength (393-773 MPa) and Young's modulus (26.5 GPa) [16].

From this point of view, we thus study the effect of starch type (i.e. native starch and phosphate starch), plasticizer type

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(i.e. glycerol and xylitol with a weight ratio of glycerol to xylitol of 100:0, 75:25, 50:50, 25:75 and 0:100) and fiber content (i.e. in the range of 1–25 %wt) on properties of PLA/TPS blend and composite.

II. MATERIALS

Cassava starch was supplied by Tongchan Co., Ltd. (Thailand). Phosphate starch (EHTEX 103) was provided by Eiamheng Tapioca Starch Industry Co., Ltd. (Thailand). Jute fibers were provided by Park Chong Jute Mill Co., Ltd. (Thailand). Glycerol used was a commercial grade product. Xylitol was purchased from Chemipan Corporation, Co., Ltd. (Thailand).

III. METHODS

A. Preparation of Thermoplastic Starch Resins

Native cassava starch or phosphate starch was premixed with plasticizer(s) (i.e., glycerol and xylitol) in a mechanical mixer. The weight ratio of starch to plasticizer(s) was fixed at 100:35, while the weight ratio of glycerol to xylitol was varied as 100:0, 25:75, 50:50, 75:25 and 0:100. The extrusion was then performed using a twin-screw extruder with an L/D ratio of 40 (LTE-20-40, Labtech Engineering, Thailand) using a barrel temperature in the range of 95–180 ºC, a screw speed range of 180–260 rpm and a material feed rate range of 6–30 rpm. The thermoplastic starch (TPS) extrudates were cut into pellets using a pelletizer (LZ-120, Labtech Engineering, Thailand). Two groups of TPS, i.e. TPS from native cassava starch (TPSN) and TPS from phosphate starch (TPSP) were prepared.

B. Preparation of Polylactic Acid/Thermoplastic Starch Blend Resins

The obtained TPS resins were subsequently compounded with a commercial polylactic acid (PLA) in a twin-screw extruder using a barrel temperature profile ranged from 95ºC to 150 ºC, a screw speed of 175 and a material feed rate of 8.5 rpm. The weight ratio of PLA to TPS was fixed at 60:40. After extrusion, PLA/TPS blend was pelletized into 2.5 mm-length resins using a pelletizer.

C. Preparation of Polylactic Acid/Thermoplastic Starch/Silane Treated Jute Fiber Composite Resins

The PLA/TPS blend with good processability, mechanical properties and water resistance was selected for further study, i.e. compounding with silane treated jute fibers (SJF) to prepare PLA/TPS/SJF composites. TPS was prepared using the same method as described in *A*, and subsequently compounded with PLA and SJF in a twin screw extruder. The weight ratio of PLA to TPS was fixed at 60:40, while the amount of JF was varied in the range of 1–25 wt% of the blend. The extrusion was carried out using the barrel temperature ranging from 95°C to 160°C, a screw speed range of 180–280 rpm, a feed rate range of PLA and TPS mixture of 4.3-8.5 rpm and a feed rate range of SJF of 10–35 rpm. The extruded composite was then pelletized into 2.5 mm-length resins.

D. Preparation of Dumbbell-Shaped Specimens

PLA/TPS blends and PLA/TPS/JF composites were converted into dumbbell-shaped specimens by a Battenfeld BA 250 CDC injection molding machine (Germany) using a temperature range of 140–185°C, a screw speed of 170–180 rpm, an injection speed of 12–45%, a maximum injection pressure of 65–120 bar and a cooling time of 25–30 s.

E. Tensile Testing

The dumbbell-shaped specimens were conditioned in desiccators containing a saturated solution of magnesium nitrate at 25°C (52% RH) for 2 days prior to testing. Tensile testing was carried out according to ASTM D638-03 using a tensile testing machine (B1-type, Cometech, Taiwan) with a crosshead speed of 50 mm/min, a load cell of 10 kN, a grip separation of 115 mm and a gage length of 100 mm. Three specimens were tested for each sample.

F. Determination of Heat Distortion Temperature

The dumbbell-shaped specimens were cut into a rectangular shape with a dimension of 13 mm × 125 mm × 4 mm and then conditioned at 50±5% RH and 23±2 °C about 3–4 days before testing. Heat distortion temperature (HDT) of each sample was tested according to ASTM D648-01 by a 148 HPDC heat distortion tester (Japan) using a load cell of 455 kPa and a heating rate of 2±0.2°C/min. HDT was recorded as a temperature, at which the specimen deflection was 0.254 mm. Three specimens were tested for each sample.

G. Water Contact Angle Measurement

Water contact angle was measured using an OCA 15EC contact angle analyzer (DataPhysics Instruments GmbH, Germany) with SCA 20 software to analyze the data. Contact angle was recorded as a function of time within the first 15 min after a drop of distilled water (3 μL) was placed on the sample surface. Three specimens were measured for each sample.

IV. RESULTS AND DISCUSSION

A. Tensile Properties

Tensile properties of PLA/TPS blends and PLA/TPS/JF composites were shown in Fig. 1.

PLA/TPSN blend is prepared by using glycerol as a plasticizer exhibited tensile strength, modulus and elongation at break of 40.9 MPa, 281 MPa and 20.6%, respectively, while the blends prepared by using a mixed plasticizer of glycerol and xylitol showed tensile strength, modulus and elongation at break in the ranges of 44.7–50.7 MPa, 299–370 MPa and 3.6–20%, respectively (Fig. 1). Tensile strength and modulus of the blend tended to increase with increasing xylitol content, while elongation at break decreased. The results indicated that PLA/TPSN blend became stronger and stiffer, but less extensible when glycerol to xylitol weight ratio was reduced. This might be due to the reduction of glycerol concentration in the blend. Glycerol is a good plasticizer for this blend system as compared with xylitol because it has smaller size, which can be well intervene into starch molecules to hinder H-bond formation among starch chains [17]. Similarly, tensile strength and modulus of PLA/TPSP blend also increased, while elongation at break decreased, when mixed plasticizer of glycerol and xylitol was used (Fig. 1). However, the reduction of glycerol to xylitol weight ratio did not significantly affect tensile properties of the PLA/TPSP blend. Moreover, PLA/TPSP blends possessed higher strength and stiffness but lower extensibility than the corresponding PLA/TPSN blends (Fig. 1).

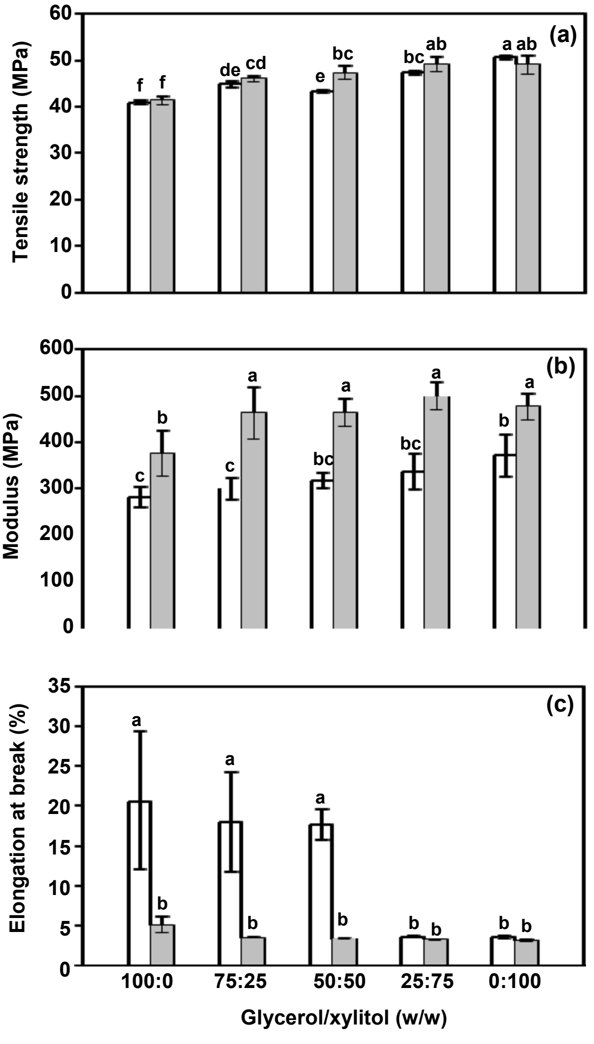

Fig. 1 (a) Tensile strength, (b) modulus and (c) elongation at break as a function of glycerol to xylitol weight ratio of PLA/TPSN blends (☐) and PLA/TPSP blends (▨)

The PLA/TPSP blend prepared by using a mixed plasticizer of glycerol and xylitol with an equal weight was chosen for further study. The effect of silane treated jute fibers (SJF) on tensile properties of PLA/TPSP blend was illustrated in Fig. 2. PLA/TPSP blend had tensile strength, modulus and elongation at break of 42.5 MPa, 404 MPa and 3.1%, respectively. Incorporating SJF with a content of 25% could improve tensile strength of PLA/TPSP blend (Fig. 2 (a)). Modulus of the PLA/TPSP blend increased (Fig. 2 (b)), while its elongation at break decreased by adding SJF (Fig. 2 (c)). The stiffness of PLA/TPSP blend increased with increasing SJF concentration (Fig. 2 (b)), or in other words its extensibility decreased (Fig. 2 (c)). These results suggested that SJF could act as reinforcement for the PLA/TPSP blend system.

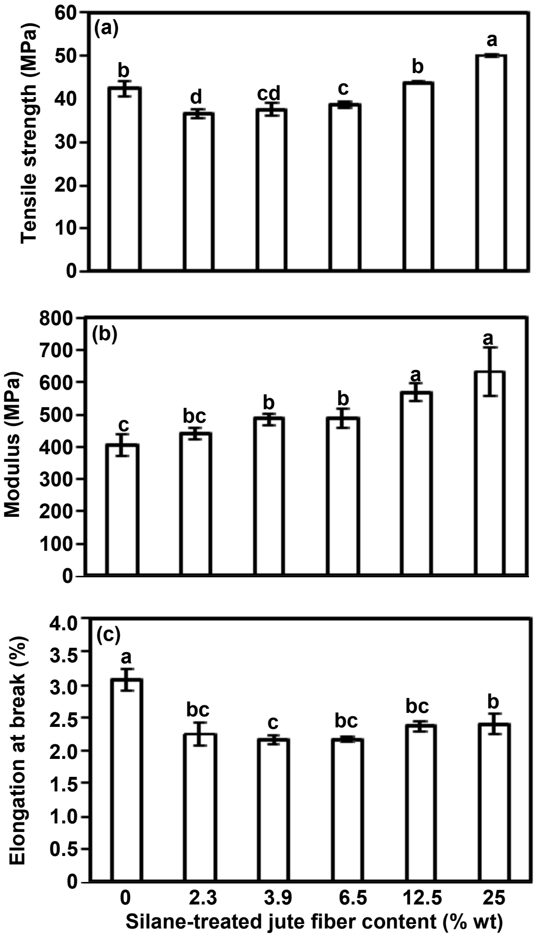

Fig. 2 (a) Tensile strength, (b) modulus and (c) elongation at break as a function of SFJ content of PLA/TPS/SJF composites

B. Heat Distortion Temperature

Heat distortion temperature (HDT) of PLA/TPSP blends and PLA/TPSP/SJF composites was measured at a load of 455 kPa and a heating rate of 2°C/min. The HDT value was recorded at a specimen deflection of 0.254 mm. HDT values of PLA/TPSN and PLA/TPSP blends were in the range of 52-57°C (Fig. 3 (a)), which were not much different from that of neat PLA (55.6°C). This might be due to the high content of PLA in the blends (~ 60% wt.) and low thermal stability of TPSP. The blends showed decreased HDT when mixed plasticizer was used (Fig. 3 (a)), implying that xylitol had negative effect to HDT of the blends. PLA/TPSP blends exhibited lower HDT than PLA/TPSN (Fig. 3 (a)), suggesting that phosphate starch gave the blends with lower thermal stability. This might be attributed to the reduction of H-bonds formed among phosphate starch molecules as compared with native starch because hydroxyl groups of starch were substituted with phosphate groups.

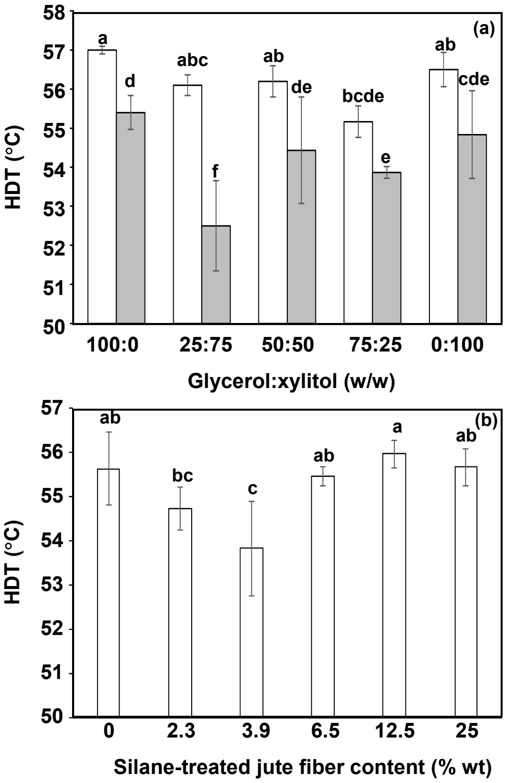

Fig. 3 Heat distortion temperature (HDT) (a) as a function of glycerol to xylitol weight ratio of PLA/TPSN blends (☐) and PLA/TPSP blends (▨) and (b) as a function of SFJ content of PLA/TPS/SJF composites

Fig. 3 (b) shows that HDT of PLA/TPSP/SJF composites prepared by using a mixed plasticizer of glycerol and xylitol with a weight ratio of 50:50, varied in the range of 53-56°C. Incorporating SJF with a low content (2.3-3.9% wt.) reduced HDT of the composites; while their HDT values were not different from that of the naked PLA/TPSP blend when high amount of SJF (6.5-25% wt) was added. This might be explained by the high interaction between SJF and matrix and/or reinforcing effect of the fibers [18].

C. Water Contact Angle

Wettability and hydrophobic characteristics of PLA/TPSP/SJF composites can be evaluated from the water contact angle. A lower water contact angle is generally observed for high hydrophilic materials or the materials with good water wettability. Water contact angle of the samples was measured for 15 min.

PLA/TPSP blend showed highest water contact angle (Fig. 4 (a)). The addition of SJF resulted in decreased water contact angle of the material (Figs. 4 (b)-(f)). This might be due to the void formation at the interfaces between matrices and fibers. Water contact angle of the PLA/TPSP/SJF composite increased with increasing SJF content. This phenomenon was attributed to the higher hydrophobicity of SJF. In addition, silane coupling agent could react with the hydroxyl groups of jute fibers and starch molecules to form stable covalent bond rendering less hydrophilicity.

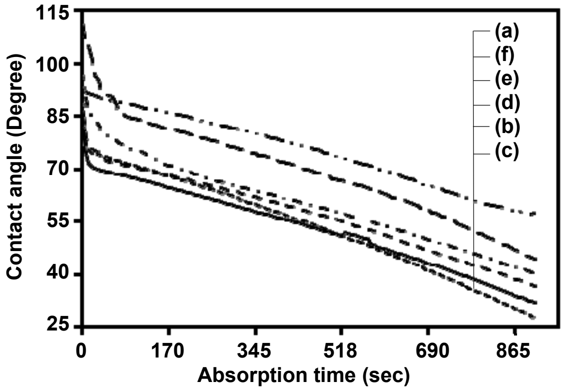

Fig. 4 Water contact angle of TPS/PLA/SJF composites with different SJF concentrations: (a) 0%, (b) 2.3%, (c) 3.9%, (d) 6.5%, (e) 12.5% and (f) 25%

V. CONCLUSION

Using starch phosphate and/or replacing glycerol plasticizer with xylitol in the TPS preparation step could enhance tensile strength and stiffness of the PLA/TPS blend, but decrease its extensibility. HDT of the blend decreased when starch phosphate was used to prepare TPS. The PLA/TPS blend became stronger and stiffer, while less extensible by incorporating SJF.

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