



Reactive blending of thermoplastic starch and polyethylene-graft-maleic anhydride with chitosan as compatibilizer

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ABSTRACT

Cassava starch was melt-blended with glycerol (70/30 wt%/wt%) at 140 °C to prepare thermoplastic starch (TPS). Chitosan (CTS) was premixed with starch and glycerol, in acidified water (lactic acid 2 wt%), at 1, 5 and 10 wt%/wt%. TPS/CTS was then melt-blended (160 °C) with polyethylene-graft-maleic anhydride (PE-MAH). Phase determination and scanning electron microscopy indicated TPS/PE-MAH/CTS had a co-continuous morphology and CTS-induced phase inversion to give dispersed PE-MAH particles in a TPS matrix. Tensile strength at break and elongation, melt viscosity, fracture toughness and water contact angle of TPS/PE-MAH were improved by CTS incorporation. TPS/PE-MAH/CTS blends decreased the melting temperature of TPS and PE-MAH compared to the neat polymers. FTIR confirmed a reaction had occurred between amino groups (–NH₂) of CTS and the MAH groups of PE-MAH. This reaction and the enhanced miscibility between TPS and CTS improved the mechanical properties of the TPS/PE-MAH/CTS blend, particularly at 5 wt%/wt% CTS.

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1. Introduction

Synthetic polymer materials have been widely used in many industries. However, the polymers usually originate from a petroleum source and are non-biodegradable. Petroleum resources are limited and their use negatively impacts the environment. Hence, there is a growing demand for environmentally-friendly, bio-based polymers that can compete or even surpass the existing petroleum-based materials on a cost-performance basis.

Starch is a natural polymer that is regenerated from carbon dioxide and water by photosynthesis in plants (Teramoto, Motoyama, Tosomiya, & Shibata, 2003). Due to its complete biodegradability, low cost and renewability, starch is considered a promising environmentally-friendly candidate to replace petroleum polymers. Thermoplastic starch (TPS) is a renewable, low-cost, biodegradable polymer, which is prepared by blending starch with a plasticizer, such as glycerol or sorbitol (Yu et al., 1999). Starch is inherently a brittle material at room temperature (Huleman, Janssen, & Feil, 1998). The addition of the plasticizer lowers the glass transition temperature of starch and improves

its chain flexibility. Many researchers have improved the properties of TPS (Lopez et al., 2014; Soares, Yamashita, Müller, & Pires 2013; Zeng et al., 2011). Blending a plasticizer with starch at high temperature and shear forces induces the formation of an amorphous structure (Mościcki et al., 2012). The interaction between the hydroxyl groups (–OH) of starch and plasticizer forms petroleum-like TPS polymers with melt-processing ability (Teramoto et al., 2003). Many plasticizers have been employed to prepare TPS, such as water (Bhatnagar & Hanna, 1995; Forssell, Mikkilä, Moates, & Parker, 1997; Leblanc et al., 2008) acetamide (Ma & Yu, 2004), formamide (Ma & Yu, 2004), glucose (Teixeira, Róz, Carvalho, & Curvelo, 2007), sorbitol (Ma & Yu, 2004; Róz, Carvalho, Gandini, & Curvelo, 2006), ethylene glycol (Róz et al. 2006), citric acid (Shi et al., 2007), and glycerol (Forssell et al., 1997; Leblanc et al., 2008; Ma & Yu, 2004; Shi et al., 2007; Teixeira et al., 2007). However, the TPS has poor long-term thermal stability and water absorption, which limits its applications. The addition of polymers is a common strategy to improve these inherent limitations. Some polymers that have been blended with TPS to improve its properties include: polypropylene (Rosa, Guedes, & Carvalho, 2007), polyethylene (PE) (Ning, Jiugao, Xiaofei, & Ying, 2007; Peres, Pires, & Oréfice, 2016; Prachayawarakorn, & Pombage, 2014; Rosa et al., 2007), poly(lactic acid) (Huneault & Li, 2007; Iovino, Zullo, Rao, Cassar, & Gianfreda, 2008; Martin & Avérous 2001; Schwach, Six, &

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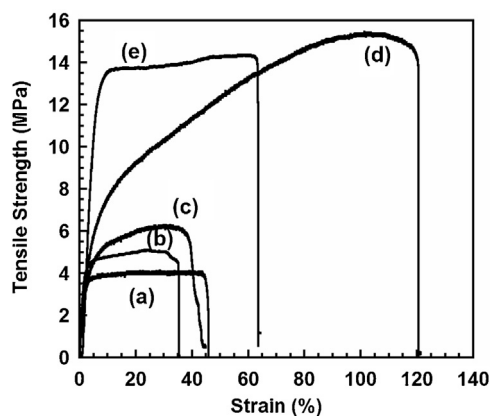


Fig. 1. Tensile strength of thermoplastic starch (TPS) melt-blended with polyethylene-graft-maleic anhydride (PE-MAH) and chitosan (CTS): (a) TPS; (b) TPS/PE-MAH, 70/30; (c) TPS/PE-MAH/CTS1, 69/30/1; (d) TPS/PE-MAH/CTS5, 65/30/5; (e) TPS/PE-MAH/CTS10, 60/30/10.

Avérous, 2008; Wang, Yu, & Ma 2007), and poly(butylensadipateco-terephthalate) (Ren, Fu, Ren, & Yuan 2009)

Chitosan (CTS) is derived from *N*-deacetylation to form a linear polymer of $\alpha(1 \rightarrow 4)$ -linked 2-amino-2-deoxy- β -D-glucopyranose (Dutta, Dutta, & Tripathi, 2004). CTS is a natural, non-toxic, biocompatible and biodegradable polymer with antimicrobial activity and good mechanical properties. The amino groups ($-\text{NH}_2$) of the molecule react readily with epoxy, maleic anhydride (MAH) and other reactive groups. CTS is highly hydrophobic but can be solubilized in acidified water. CTS has been widely used in food, pharmaceutical, textile, agricultural, biomedical, and cosmetic products (Dutta et al., 2004).

In this research, TPS was melt-blended with PE-MAH. CTS was then incorporated as a compatibilizer, facilitating an interaction between TPS and PE-MAH to improve the properties of the blend. The mechanical properties, morphology, wettability, thermal properties, rheological properties, and reaction mechanism of the blend were investigated.

2. Materials and methods

2.1. Materials

Cassava starch (Dragon Fish brand, amylose/amylopectin content 17%/83%, moisture content of 11% total weight and molecular weight of 1.34×10^8 g/mol) was purchased from Tong Chan registered ordinary partnership, Thailand. Glycerol (99%) and CTS (deacetylation degree of 85% and molecular weight of 5.0×10^5 g/mol) were purchased from Union Science Co., Ltd., Thailand. PE-MAH (DuPont (Thailand) Co., Ltd.) name of Fusabond (EMB226-D) with melt flow index of 1.75 g/10 min, and MAH content of 2%, was kindly supplied by Chemical Innovation Co., Ltd., Thailand. PE (Thai-ZEX 1600J) was kindly supplied by Polyethylene Public Co., Ltd., Thailand. Lactic acid (99%) was a product of Merck (Darmstadt, Germany).

2.2. Sample preparation

Starch was dried to remove the moisture at 60 °C for 24 h. TPS was prepared by melt-blending cassava starch with glycerol (70/30 wt%/wt%) using a Brabender internal mixer (Labo Plastomill, Toyo Seiki Co. Ltd., Japan). TPS and CTS (at 1, 5 and 10 wt%/wt%) were then premixed by overhead stirrer at 500 rpm in distilled water (100 mL/50 g starch) containing lactic acid (2% v/v lactic acid solution, 100 mL), using a water bath at 90 °C for 30 min. The premix

Table 1

The composition and codes of blends prepared from thermoplastic starch (TPS), polyethylene-graft-maleic anhydride (PE-MAH) and chitosan (CTS).

Sample	Composition (wt%)		
	TPS	PE-MAH	CTS
TPS/PE-MAH	70	30	–
TPS/PE-MAH/CTS1	69	30	1
TPS/PE-MAH/CTS5	65	30	5
TPS/PE-MAH/CTS10	60	30	10

was subsequently melt-blended using a two-roll mill (Pirom-Olarn Co. Ltd., Thailand, PI-140) at 140 °C for 10 min to form the TPS/CTS blend. TPS and the TPS/CTS blend were independently melt-mixed with PE-MAH at 160 °C for 5 min, using a Brabender internal mixer. The final compositions of the blends and their codes are shown in Table 1.

2.3. Tensile measurements

Tensile properties of the samples were measured using a tensile tester (Tensilion UTM-II-20; Orientec Co. Ltd., Japan) at 2 mm/min crosshead speed. The bone-shaped samples were prepared as sheets by compression molding at 160 °C for 3 min using a gauge length, width and thickness of 10 mm, 3 mm and 0.5 mm, respectively. Tensile samples were conditioned at 50% relative humidity (RH) for 48 h at 25 °C. At least five specimens were tested for each composition.

2.4. Scanning electron microscopy

Morphology of the samples was observed by scanning electron microscopy (SEM) (SM-200, Topcon Corp., Japan). The samples were shattered in liquid nitrogen, and then the fractured samples were treated with hot water (90 °C) for 1 h. The purpose of this water treatment was to selectively remove any water-soluble polymers near the surface of the samples, that were not intricately bound within the blend, thus revealing the structural morphology of the blend. The fractured surface of the samples was coated with a thin layer of gold, to induce electrical conductivity, and observed with an acceleration voltage of 10 kV.

2.5. Contact angle

Drop shape analysis (DSA30E, Krüss Co. Ltd., Germany) was used to observe water contact angle. The samples were prepared as sheets by hot-compression at 160 °C for 3 min. Water was dropped onto the surface of the sheets and images were taken automatically every min for 3 min. Samples were conditioned at least 48 h at 25 °C under relative humidity of 50%. The measurements were average from three samples for each composition.

2.6. Differential scanning calorimetry

Melting temperature of the samples was determined by differential scanning calorimetry (DSC) (Perkin Elmer Diamond DSC, USA). The sample (8–10 mg) was accurately weighed into aluminum pans and sealed. The procedure was as follow: heating from -10 °C to 200 °C at 10 °C min^{-1} , isotherm 5 min, cooling from 200 °C to -10 °C and heating from -10 °C to 200 °C at 10 °C min^{-1} . The second scan curve was used to determine the melting temperature (T_m) of the sample i.e. the maximum temperature (peak) of the endotherm. All of the experiments were performed under nitrogen atmosphere.

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