รายงานวิจัยฉบับสมบูรณ์

โครงการ พอลิเมอร์ย่อยสลายได้จากเทอร์โมพลาสติกสตาร์ชและพอลิเอทิลีนโดยมีเส้นใยธรรมชาติเป็นสารเสริมแรง

โดย รศ.ดร.จุฑารัตน์ ปรัชญาวรากร

กุมภาพันธ์ 2555

สัญญาเลขที่ **RMU5180012**

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คณะผู้วิจัย	สังกัด
1. รศ.ดร.จุฑารัตน์ ปรัชญาวรากร	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
2. นส. เพียงฤทัย บุญประสิทธิ์	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
3. นส. พิมพ์ชนก แสงนิติเดช	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
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5. นส.ดารินทร์ โพธิ์ศรี	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
6. นส. ปาริชาติ จิรภัคเสถียร	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
7. นส. พรพิมล รัตนบุตร	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
8. นส. พิมวิไล บุญสม	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
9. นส. นิสานาถ หลิมสิริวงษ์	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
10 .นส. รัญชนา คงจินดามุนี	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
11. นส. สุภาวรัตน์ สุระกิจ	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง
12. นส. วัลลดา หวานเสนาะ	สถาบันเทคโนโลยีพระจอมเกล้า ฯ ลาดกระบัง

**สนับสนุนโดยสำนักงานคณะกรรมการอุดมศึกษา
และสำนักงานกองทุนสนับสนุนการวิจัย**

กิตติกรรมประกาศ

งานวิจัยเรื่อง พอลิเมอร์ย่อยสลายได้จากเทอร์โมพลาสติกสตาร์ชและพอลิเอทิลีนโดยมีเส้นใยธรรมชาติเป็นสารเสริมแรงดำเนินงานได้เป็นอย่างดี โดยได้รับทุนสนับสนุนการวิจัยตลอดระยะเวลา 3 ปี จากสำนักงานกองทุนสนับสนุนการวิจัย (สกว.) และสำนักงานคณะกรรมการอุดมศึกษา (สกอ.)

ขอขอบพระคุณสถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบังสำหรับเครื่องมือและสถานที่สำหรับงานวิจัยนี้

ขอขอบพระคุณ รศ.ดร.สมศักดิ์ วรมงคลชัย รศ.ดร มาลินี ชัยศุภกิจสินธ์ และ ผศ.ดร.สุปราณี แก้วภิรมย์ ที่กรุณาให้คำแนะนำต่าง ๆ ซึ่งเป็นประโยชน์สำหรับงานวิจัยนี้

รศ.ดร.จุฑารัตน์ ปรัชญาวรากร

บทคัดย่อ

งานวิจัยนี้เป็นการปรับปรุงสมบัติของเทอร์โมพลาสติกสตาร์ช (Thermoplastic starch, TPS) โดยการใช้แป้งข้าวเจ้ามาเป็นส่วนผสมหลัก ใช้กลีเซอรอลเป็นพลาสติไซเซอร์ในอัตราส่วนผสมกลีเซอรอลกับแป้งเป็น 1:1 ทำการเตรียมด้วยเครื่องผสมความเร็วสูง (High speed mixer) จากนั้นนำไปผสมด้วยเครื่องผสมระบบปิด (Internal mixer) ที่อุณหภูมิและความเร็วรอบ 170 องศาเซลเซียส และ 40 รอบต่อนาที แล้วนำไปขึ้นรูปโดยใช้เครื่องอัดขึ้นรูป (Compression molding) ทำการปรับปรุงสมบัติด้วยพอลิเอทิลีนชนิดความหนาแน่นต่ำและเติมสารช่วยผสมมาลิอิกแอนไฮไดรด์กราฟท์พอลิเอทิลีนและไวนิลไตรเมทอกซีไซเลน พบว่ามาลิอิกแอนไฮไดรด์กราฟท์พอลิเอทิลีนช่วยเพิ่มสมบัติเชิงกลดีกว่าการใช้ไวนิลไตรเมทอกซีไซเลน แต่การใช้มาลิอิกแอนไฮไดรด์กราฟท์พอลิเอทิลีนและไวนิลไตรเมทอกซีไซเลนทำให้การย่อยสลายของเทอร์โมพลาสติกสตาร์ชมีแนวโน้มลดลง ส่วนการปรับปรุงสมบัติของเทอร์โมพลาสติกสตาร์ชด้วยเส้นใยฝ้าย เส้นใยตาล เส้นใยไหม เส้นใยพอลิเอสเทอร์ และเส้นใยไนลอน พบว่า เทอร์โมพลาสติกสตาร์ช แสดงให้เห็นว่าสมบัติเชิงกลเพิ่มขึ้นตามปริมาณเส้นใย โดยที่ปริมาณ เส้นใย 10% ของน้ำหนักแป้งให้สมบัติเชิงกลดีที่สุด ส่วนการดูดซับความชื้นเทอร์โมพลาสติกสตาร์ชที่ผสมเส้นใยชนิดต่าง ๆ ทำให้ความสามารถในการดูดซับความชื้นลดลง และเมื่อศึกษาด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) แสดงให้เห็นว่าเส้นใยมีการกระจายตัวที่ดีและสามารถเข้ากับเมทริกซ์แป้งได้ นอกจากนี้พบว่าเสถียรภาพทางความร้อนมีค่าสูงขึ้น เมื่อเปรียบเทียบกับเทอร์โมพลาติกสตาร์ช สำหรับการย่อยสลายทางชีวภาพด้วยการฝังดิน เทอร์โมพลาสติกสตาร์ชมีแนวโน้มลดลงเมื่อผสมเส้นใยชนิดต่าง ๆ และจากการศึกษานี้เทอร์โมพลาสติกสตาร์ชที่มีสมบัติโดยรวมดีที่สุด คือ เทอร์โมพลาสติกสตาร์ชที่ผสมด้วยเส้นใยฝ้าย

ABSTRACT

This research aimed to study on modification of thermoplastic starch (TPS) prepared from rice starch using glycerol as a plasticizer at the ratio of starch:glycerol; 1:1. Starch and glycerol were mixed using a high-speed mixer,then compounded using an internal mixer at temperature of 170˚C and the rotor speed of 40 rpm. The specimens were shaped with compression molding. Properties of TPS were modified using low-density polyethylene with the addition of compatibilizers, i.e. maleic anhydride and vinyltrimethoxysilane. It was found that mechanical properties of TPS and low-density polyethylene were better improved by maleic anhydride. In addition, biodegradability of the TPS and low-density polyethylene was lower by the incorporation of maleic anhydride and vinyltrimethoxysilane. Properties of the TPS were also improved by reinforcing the TPS with cotton fibers, palmyra palm fibers, silk fibers, polyester fibers and nylon fibers. It was found that the mechanical properties of TPS increased with increasing fiber contents. The incorporation of the fibers at 10% wt fibers into the TPS matrix resulted in the best mechanical properties. Besides, water absorption of the TPS samples was clearly reduced by the addition of the fibers. For morphology, obtained from Scanning Electron Microscope (SEM), the results illustrated that the fibers were well distributed and compatible with the TPS matrix. In addition, thermal stability and biodegradability were improved by using the fibers. From this study, the best overall properties were obtained from the TPS reinforced by cotton fiber.

Executive Summary

งานวิจัยนี้มีวัตถุประสงค์เพื่อเตรียมพอลิเมอร์ที่ย่อยสลายได้ทางชีวภาพจากเทอร์โมพลาสติกสตาร์ช โดยแป้งที่ใช้ คือ แป้งข้าวเจ้าโดยมีกลีเซอรอลเป็นพลาสติไซเซอร์ ทำการผสมโดยใช้เครื่องผสมระบบปิดและขึ้นรูปโดยวิธีอัดขึ้นรูป จากนั้นจึงทำการทดสอบสมบัติต่าง ๆ จากการศึกษาพบว่าเทอร์โมพลาสติกสตาร์ชที่เตรียมได้มีสมบัติเชิงกลที่ต่ำและมีปัญหาการดูดซับน้ำที่สูง ดังนั้นจึงทำการแก้ไขปัญหานี้โดยการเติมพอลิเอทิลีนชนิดความหนาแน่นต่ำ เส้นใยฝ้าย เส้นใยตาลและเส้นใยไหมลงไปในปริมาณต่างๆ จากการทดสอบพบว่าการเติมเส้นใยฝ้าย เส้นใยตาล เส้นใยไหมหรือ พอลิเอทิลีนชนิดความหนาแน่นต่ำลงไปช่วยให้เทอร์โมพลาสติกสตาร์ชจากแป้งข้าวเจ้ามีสมบัติเชิงกลที่ดีขึ้นอย่างเห็นได้ชัด นอกจากนี้ยังช่วยให้สมบัติการดูดซับน้ำลดลง จากการทดสอบสมบัติทางความร้อนพบว่าเทอร์โมพลาสติกสตาร์ชจากแป้งข้าวเจ้ามีอุณหภูมิการเริ่มสลายตัวและเปอร์เซ็นต์การลดลงของน้ำหนักที่ลดลงซึ่งแสดงให้เห็นว่าการใช้เส้นใยฝ้าย เส้นใยตาล เส้นใยไหมหรือพอลิเอทิลีนชนิดความหนาแน่นต่ำช่วยให้เทอร์โมพลาสติกสตาร์ชจากแป้งข้าวเจ้ามีเสถียรภาพทางความร้อนที่เพิ่มขึ้น นอกจากนี้ได้ทำการศึกษาถึงผลของชนิดของเส้นใยสังเคราะห์ ได้แก่ เส้นใยพอลิ เอสเทอร์และเส้นใยไนลอนที่มีต่อสมบัติต่าง ๆ ของเทอร์โมพลาสติกสตาร์ชจากแป้งข้าวเจ้า จากการศึกษาพบว่าเส้นใยไนลอนสามารถปรับปรุงสมบัติเชิงกลของเทอร์โมพลาสติกสตาร์ชจากแป้งข้าวเจ้าได้ ส่วนการดูดซับน้ำและเสถียรภาพทางความร้อนของเทอร์โมพลาสติกสตาร์ชจากแป้งข้าวเจ้าสามารถปรับปรุงได้โดยการใช้เส้นใยพอลิเอสเทอร์และเส้นใยไนลอน

Output ที่ได้จากโครงการ

1. ผลงานวิจัยตีพิมพ์ในวารสารวิชาการนานาชาติ

มีผลงานวิจัยตีพิมพ์ในวารสารวิชาการนานาชาติจำนวน 5 เรื่อง ได้แก่

1. J. Prachayawarakorn, P. Sangnitidej and P. Boonpasith, “Properties of thermoplastic rice starch composites reinforced by cotton fibers or low-density polyethylene”, Carbohydrate Polymers, 81 (2010) 425-433. (IF = 3.167)
2. J. Prachayawarakorn, L. Hommanee, D. Phosee and P. Chairapaksatien, “Property improvement of thermoplastic mung bean starch using cotton fiber and low-density polyethylene”, Starch/Stärke, 62 (2010) 435-443. (IF = 1.000)
3. J. Prachayawarakorn, P. Ruttanabus and P. Boonsom, Effect of cotton fiber contents and lengths on properties of thermoplastic starch composites prepared from rice and waxy rice starches”, Journal of Polymers and the Environment, 19 (2011) 274-282 (IF = 1.571).
4. J. Prachayawarakorn, N. Limsiriwong, R. Kongjindamunee and S. Surakit, “Effect of agar and cotton fibers on properties of thermoplastic waxy rice starch composites, Journal of Polymers and the Environment, In press (IF = 1.507)
5. J. Prachayawarakorn and W. Wansanoet, “Effect of silk protein fibers on properties of thermoplastic rice starch”, Fibers and Polymers, Accepted for publication.

2. งานประชุมวิชาการนานาชาติ

มีผลงานนำเสนอในงานประชุมวิชาการนานาชาติ จำนวน 3 เรื่อง ได้แก่

1. L. Hommannee and J. Prachayawarakorn, “Modification of thermoplastic mung bean starch/low-density polyethylene blend using gelatin”, 2nd Polymer Conference, October 20-21, 2011, Chulabhorn Research Institute, Bangkok.
2. T. Kawinfrungfukul and J. Prachayawarakorn, “Properties of thermoplastic taro starch modified by cotton fiber and chitosan”, 2nd Polymer Conference, October 20-21, 2011, Chulabhorn Research Institute, Bangkok.
3. W. Hwansanoet and J. Prachayawarakorn, “Properties of thermoplastic rice starch reinforced by palm fibers”, 6th Thailand Materials Science and Technology Conference (MSAT) 26-27 August, 2010, Miracle Grand Convention Hotel Bangkok, Thailand.

3. ผลิตบัณฑิตในระดับปริญญาโทและปริญญาตรี

1. ผลิตบัณฑิตในระดับปริญญาโท

   สำเร็จการศึกษาแล้ว จำนวน 1 คน

   กำลังศึกษาอยู่ จำนวน 4 คน

2. ผลิตบัณฑิตในระดับปริญญาตรี

   สำเร็จการศึกษาแล้ว จำนวน 31 คน

   กำลังศึกษาอยู่ จำนวน 12 คน

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Properties of thermoplastic rice starch composites reinforced by cotton fiber or low-density polyethylene

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ABSTRACT

Biodegradable polymer was prepared from thermoplastic rice starch (TPRS) plasticized by glycerol. In order to improve poor tensile properties and high water absorption of the TPRS, cotton fiber or low-density polyethylene (LDPE) were added into the TPRS matrix. The effect of maleic anhydride-grafted-polyethylene (MAPE) and vinyltrimethoxy silane (VTMS) compatibilizers on properties of the TPRS/LDPE specimens were also studied. The TPRS/cotton fiber, TPRS/LDPE, TPRS/LDPE/MAPE and TPRS/LDPE/VTMS samples were analyzed for tensile and morphological properties. The results showed that the incorporation of either cotton fiber or LDPE into the TPRS matrix caused the considerable improvement of tensile strength and Young's modulus. Moreover, water absorption of the TPRS samples was clearly reduced by the inclusion of cotton fiber or LDPE. In addition, phase morphology, thermal stability and biodegradability were carried out for different TPRS samples.

1. Introduction

Many efforts have been made to develop biodegradable materials based on starch due to environmental problems resulting from petroleum-derived plastics. Starch is an important productive polysaccharide in plants. Due to its low cost, availability as a renewable resource, biodegradable and innocuous degradation products, it has already been widely researched as an important raw material for packaging, agricultural and biomedical applications.

The possibility of transforming native starch into a thermoplastic starch (TPS) has gained considerable interest (Curvelo, Carvalho, & Agnelli, 2001; Córdoba, Cuéllar, González, & Medina, 2008; Ma, Yu, & Kennedy, 2005; Yang, Yu, & Ma, 2006). Starch is not a true thermoplastic but in the presence of plasticizers at high temperature and under shear, it can readily melt and flow, allowing for its use as extruded or injected material, similar to most conventional synthetic thermoplastic polymers (Forssell, Mikkilä, Moates, & Parker, 1997). Thermoplastic process involves the transformation of the semi-crystalline starch granule into homogenous materials with the destruction of hydrogen bonds between the macromolecules under shear and pressure. In this process, plasticizer is added to the native starch and blended thoroughly and then plasticized, new hydrogen bonds between plasticizer and starch are formed synchronously with the destruction of hydrogen bonds between starch molecules; thus the starch is plasticized (Hulleman, Janssen, & Feil, 1998). Plasticizers increase starch flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular space. Traditional plasticizers are polyols such as glycerol, glycol, sorbitol, sugars and ethanolamine (Huang, Yu, & Ma, 2005; Ma, Yu, & Wan, 2006; Róz, Carvalho, Gandini, & Curvelo, 2006; Teixeira, Róz, Carvalho, & Curvelo, 2007), but the main plasticizer used in thermoplastic starch is glycerol (Curvelo et al., 2001; Ma et al., 2005; Róz et al., 2006; Teixeira et al., 2007). The proportion of plasticizer and its chemical nature strongly influence physical properties of TPS (Róz et al., 2006; Ma et al., 2006; Huang et al., 2005).

Starch from various sources has been studied as TPS, including corn starch (Curvelo et al., 2001; Córdoba et al., 2008; Ma et al., 2005; Róz et al., 2006), potato starch (Thuwall, Boldizar, & Rigdahl, 2006), cassava starch (Müller, Laurindo, & Yamashita, 2009; Teixeira et al., 2007) and wheat starch (Rodriguez-Gonzalez, Ramsay, & Favis, 2004). However, thermoplastic starch prepared from rice starch (TPRS) has not yet been prepared. Rice is the most widely consumed basic food in the world. Each year over 500 million tons of rice is harvested, providing sustenance to many countries and people throughout the world. Rice starch and its major component, amylose and amylopectin, are biopolymers, which are attractive raw materials used in packaging materials.

Generally, TPS still has two main disadvantages, compared to most plastics currently in use, i.e. poor mechanical properties and high water solubility. One approach to increase mechanical properties and reduce water absorption is that the use of natural fibers to reinforce TPS (Curvelo et al., 2001; Ma et al., 2005; Müller et al., 2009). It was reported that (Curvelo et al., 2001) tensile strength and

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modulus of glycerol plasticized corn starch increased by the reinforcement of Eucalyptus pulp. Winceyette fibers were also used to reinforce corn starch plasticized by urea and formamide (Ma et al., 2005). Another way to overcome these drawbacks of TPS is to blend TPS with synthetic polymers (Pierre, Favis, Ramsay, Ramsay, & Verhoogt, 1997). However, TPS and synthetic polymers tend to separate from each other due to incompatible chemical structures.

In this present article, we prepared TPS from rice starch and modified the TPRS matrix by reinforcing either with natural cellulose fibers, i.e. cotton fiber or with synthetic polymer, i.e. LDPE. In the latter case, two different compatibilizers, i.e. maleic anhydride-grafted-polyethylene (MAPE) and vinyltrimethoxy silane (VTMS) were introduced into the TPRS/LDPE samples in order to improve phase compatibility. The effect of cotton fiber, LDPE, MAPE and VTMS contents on mechanical properties, determined from tensile testing, of the TPRS was investigated. In addition, water absorption, morphology, thermal stability and biodegradability of different TPRS samples were examined using percentage weight change, Scanning Electron Microscope (SEM), TG (Thermogravimetric Analyzer) and soil burial test, respectively.

2. Experimental

2.1. Materials

Rice starch (11.5–13.0% moisture) was obtained from Bangkok Interfood (Bangkok, Thailand), containing 17 wt% amylose and 83 wt% amylopectin. Glycerol (plasticizer) and stearic acid (processing aid) were purchased from Lab System Co. Ltd. (Thailand). Cotton fiber with the aspect ratio of 500:1 were obtained locally and used as-received. Low-density polyethylene (LDPE, LD1905F) with MFI of 5.2 g/10 min (tested at 21.6 N and 190 °C) was obtained from Thai Polyethylene, Co. Ltd. (Bangkok, Thailand). MAPE (MB 100D) and VTMS (A-171) compatibilizers were purchased from Chemical Innovation, Co. Ltd. (Thailand) and Momentive Performance Materials, Co. Ltd. (Thailand), respectively.

2.2. Sample preparation

Rice starch and glycerol were pre-mixed in polyethylene bags overnight. The weight ratio of rice starch and glycerol was maintained at 1:1. Each TPRS sample contained 2 wt% of stearic acid by weight of starch. Blending was carried out using a high-speed mixer (Lab-Tech Engineering, Thailand) at the temperature of 170 °C at the speed of 40 rpm for 5 min. in order to obtain a homogeneous material. The processed samples were compressed at 170 °C into 2 mm thick plates. Preliminary results showed that the TPRS could be mixed and processed at the 1:1 rice starch: glycerol ratio and at the processing condition (Patthanaponganun, Gatesuda, & Thammiga, 2007).

The property modification of the TPRS was carried out as followed:

1. By the addition of cotton fiber, the cotton fiber was added into the TPRS at 5 wt%, 10 wt% and 15 wt% by weight of starch and glycerol.
2. By the addition of LDPE, the LDPE was added into the TPRS at 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt% and 30 wt% by weight of starch and glycerol.
3. By the addition of compatibilizers, the MAPE or VTMS compatibilizer was added into the TPRS/LDPE at 1 wt%, 3 wt% and 5 wt% by weight of LDPE.

2.3. IR spectroscopic study

FTIR spectra of different TPRS samples were recorded on a Spectrum 2000 GX spectrometer (PerkinElmer, USA) using KBr disk technique with a resolution of 4 cm^{-1} in a spectral range of 4000–600 cm^{-1} using 16 scans per sample.

2.4. Tensile properties

Tensile tests were conducted according to ASTM D-638 at the temperature of 23 ± 1 °C and relative humidity of 60 ± 5%. The tensile measurements from dumbell specimens were carried out using Universal Testing Machine (LLOYD Instrument, LR 5K, UK) operated by WINDAP software with 100 N load cell and a crosshead speed of 40 mm/min. It should be noted that the mechanical property results of the TPRS samples were obtained by averaging from ten independent tested specimens.

2.5. Morphology

A LEO 1455 VP scanning electron microscopy (Carlzeiss, Germany) was employed to study the morphology of the TPRS with and without the modification by cotton fiber or LDPE. The samples were immersed in a nitrogen liquid before fractured. After that the samples were sputter-coated with a thin layer of gold to prevent electrical charging during the observation.

2.6. Water absorption

Newly prepared samples were dried at 105 °C for 12 h and then stored at 50% relative humidity at the temperature of 30 ± 2 °C. The 50% relative humidity was obtained using a saturated solution of $CaCl_2$ in a closed vessel. The amount of water absorbed by the samples was measured until the constant weight was reached. The percentage water absorption was calculated as followed:

$$\text{water absorption} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

where W_2 and W_1 were the final weight and the dried weight of the sample, respectively.

2.7. Thermal property

TG thermograms were recorded by Thermogravimetric analyzer (PerkinElmer, Pyris 1, USA). The TPRS samples were tested under nitrogen atmosphere using a temperature range of 50–600 °C and a heating rate of 10 °C/min. Thermal degradation temperature (T_d) was reported by the onset degradation temperature where the weight loss started to occur. Percentage weight loss was obtained from the onset decomposition temperature determined only for the starch decomposition.

2.8. Soil burial test

The TPRS samples with the dimension of 20 mm × 50 mm were burial under soil surface of approximately 10 cm. The pH and temperature of the soil were maintained at 7 and 32 ± 2 °C, respectively. The water content of the soil was in the range of 10–20% and the weight change was recorded for 21 days. Average percentage weight change was recorded from three independently tested samples.

3. Results and discussions

3.1. IR spectroscopic study

The modification of the TPRS matrix with cotton fiber and LDPE reinforcing agents including MAPE and VTMS compatibilizers can be examined using IR technique. It can be seen in Fig. 1(a) that the pure TPRS exhibits IR main peak positions in the range of 3500–3250 cm^{-1}, 3000–2800 cm^{-1}, 1475–1450 cm^{-1}, 1275–1070 cm^{-1}, and 1200–1000 cm^{-1}, representing O–H stretching, C–H asymmetric stretching of –CH$_2$–, –CH$_2$– deformation, C–O–C stretching and C–O–H stretching, respectively (Bower & Maddams, 1989). As expected, both the TPRS and cotton fiber composed of the same cellulose chemical structures displayed these overlapped IR wave numbers. Furthermore, the peak position in the range of 1950–1600 cm^{-1} (assigned to C=O stretching) obtained from stearic acid component. The difference in IR spectra between the TPRS and TPRS/cotton fiber is that the O–H stretching peak is narrower in the TPRS/cotton fiber, possibly due to the rearrangement of hydrogen bonds between the TPRS and cotton fiber. The wave number in the range of 1000–850 cm^{-1} in the TPRS was attributed to C–C stretching; whereas, the 722 cm^{-1} in the TPRS/cotton fiber was assigned to –CH$_2$– rocking (Bower & Maddams, 1989).

Fig. 1(b) shows IR spectra of the TPRS/LDPE, TPRS/LDPE/MAPE and TPRS/LDPE/VTMS. The peak position of 1646 cm^{-1}, assigned

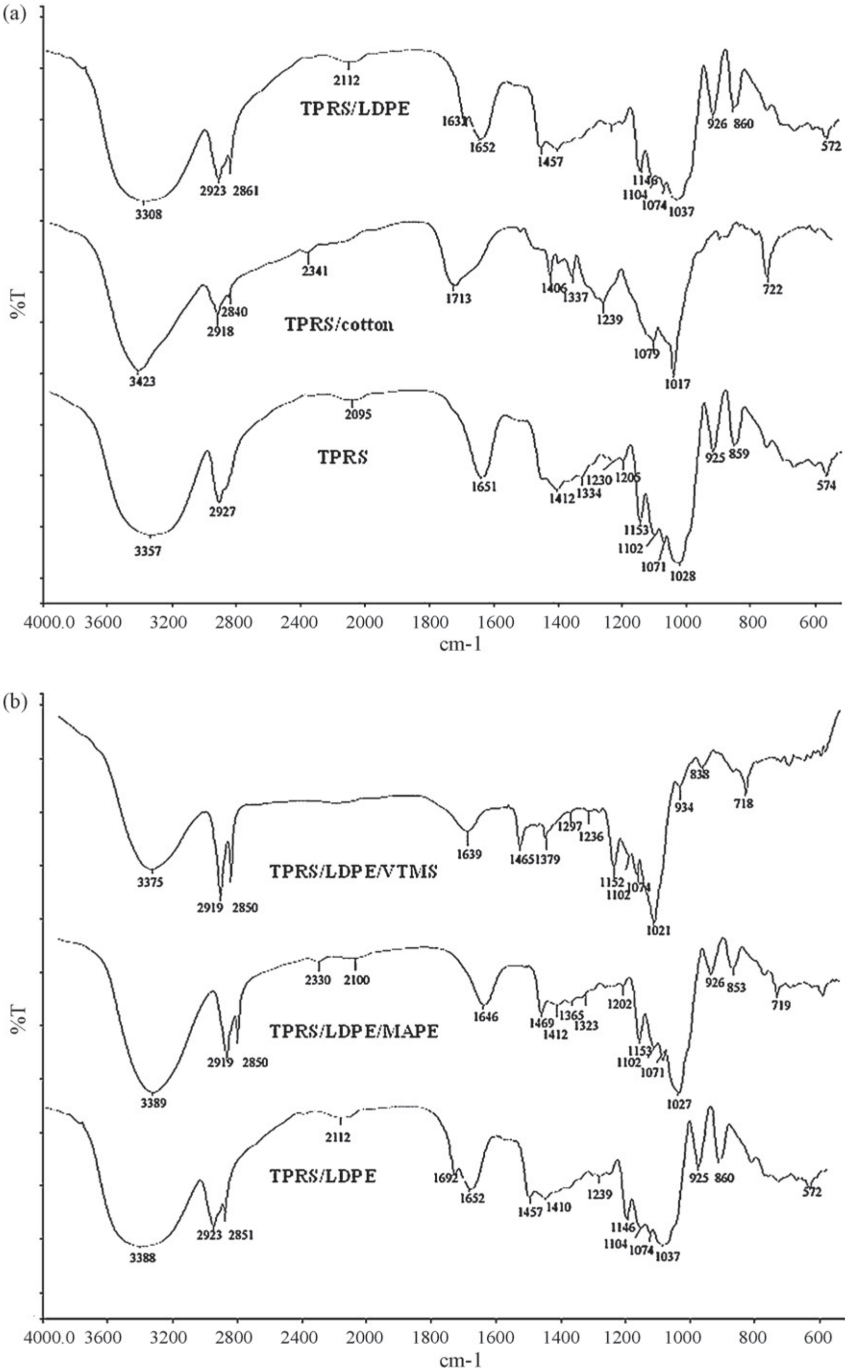

Fig. 1. (a) IR spectra of TPRS, TPRS/cotton fiber and TPRS/LDPE samples. (b) IR spectra of TPRS/LDPE, TPRS/LPDE/MAPE and TPRS/LDPE/VTMS samples.

for C=O stretching and appeared from not only stearic acid but also ester group formation between the TPRS and MAPE, was overlapped. Nevertheless, the ester bond formation could be identified by the wave number at 1027 cm^{-1} represented C–O stretching from ester group (Bower & Maddams, 1989). In the case of VTMS compatibilizer, new peak position at 1021 cm^{-1}, indicating of Si–O–C stretching (Bower & Maddams, 1989) was found, demonstrating of new chemical bond formed by the addition of VTMS compatibilizer.

3.2. Tensile properties

3.2.1. Effect of cotton fiber and LDPE

A biodegradable polymer must withstand normal stress encountered during its application. It is expected that the TPRS and cotton fiber are compatible due to the similarity of the main cellulose structures composed of hydroxyl functional groups; however, LDPE chemical structure is clearly different from those of starch and cotton fiber.

It can be seen in Fig. 2(a) that tensile strength of the pure TPRS was approximately 0.3 MPa; however, tensile strength of the TPRS clearly increased twice by the incorporation of 10% cotton fiber. The results suggest that cotton fiber can reinforce the TPRS matrix due to the fiber structure and also the phase compatibility. On the other hand, greater weight % of cotton fiber (15%) resulted in the decline of tensile strength, possibly due to the discontinuity of the TPRS matrix. On the contrary, the gradual improvement of tensile strength was found when the contents of LDPE were in the range of 0–30%, possibly because LDPE can flow easier than the TPRS. The tensile strength of the TPRS/LDPE could probably resulted from more dominant property of LDPE since LDPE shows higher tensile strength than that of the TPRS.

Fig. 2(b) shows the relationship between strain at break of the TPRS with the addition of different amounts of cotton fiber or LDPE. It can be observed that cotton fiber caused the decrease in strain at break of the TPRS matrix gradually; however, LDPE continually increased strain at break of the TPRS. The former case could be due to the high crystallinity of the fibers; whereas, the rise of strain at break in TPRS/LDPE sample could be affected by the LDPE flexibility and toughness.

Young's modulus of the TPRS can also be improved by the incorporation of cotton fiber or LDPE as presented in Fig. 2(c). Similar to tensile strength, Young's modulus of the TPRS enlarged and it reached the maximum value at 10% cotton fiber; then, it tended to clearly drop. By the introduction of LDPE, Young's modulus enhanced greatly with the increased content of LDPE.

A considerable increase in tensile strength and Young's modulus of the TPRS/5% cotton fiber and TPRS/10% cotton fiber indicates that the TPRS is suited as the matrix for natural cellulose fibers. This is due to the remarkable adhesion of the fiber-matrix interface caused by the chemical similarity of rice starch and cotton fiber. The tensile results were in accordance with Curvelo et al. (2001) who studied the thermoplastic corn starch-cellulose composites. It was found that tensile strength and Young's modulus of the composites greatly increased with the addition of the Eucalyptus bleached wood pulp. It should be noted that the addition of 5% or 10% cotton fiber gives higher values of tensile strength and Young's modulus of the TPRS than those of 5% or 10% LDPE. This implies better reinforcement by cotton fiber in the TPRS matrix.

3.2.2. Effect of MAPE and VTMS compatibilizers

Due to the incompatibility between the hydrophilic rice starch and the hydrophobic LDPE, MAPE and VTMS compatibilizers were introduced into the TPRS/LDPE system. Fig. 3 shows the relationship between tensile properties of the TPRS/LDPE samples with different contents of MAPE. It can be seen in Fig. 3(a) that tensile strength of the TPRS/LDPE increases with the addition of MAPE compatibilizer. The maximum tensile strength could be obtained when 3% MAPE was used for different contents of LDPE. On the contrary, strain at break in Fig. 3(b) decreased when 1% of MAPE was added into the TPRS/LDPE samples; after that strain at break tended to be maintained by the use of 3% and 5% MAPE. Similar to tensile strength, Young's modulus of the TPRS enlarged with the increased amount of MAPE and the maximum value could be obtained with 3% MAPE as presented in Fig. 3(c). The improvement of tensile properties could be due to the chain entanglement between LDPE and polyethylene part of MAPE molecule as presented in Fig. 4. In addition, strong ester linkage could form between maleic anhydride part of MAPE and hydrophilic rice starch (as previously shown in Fig. 1(b)) so that the incompatible part between the hydrophilic rice starch and the hydrophobic LDPE could be linked and strengthened (Fig. 4).

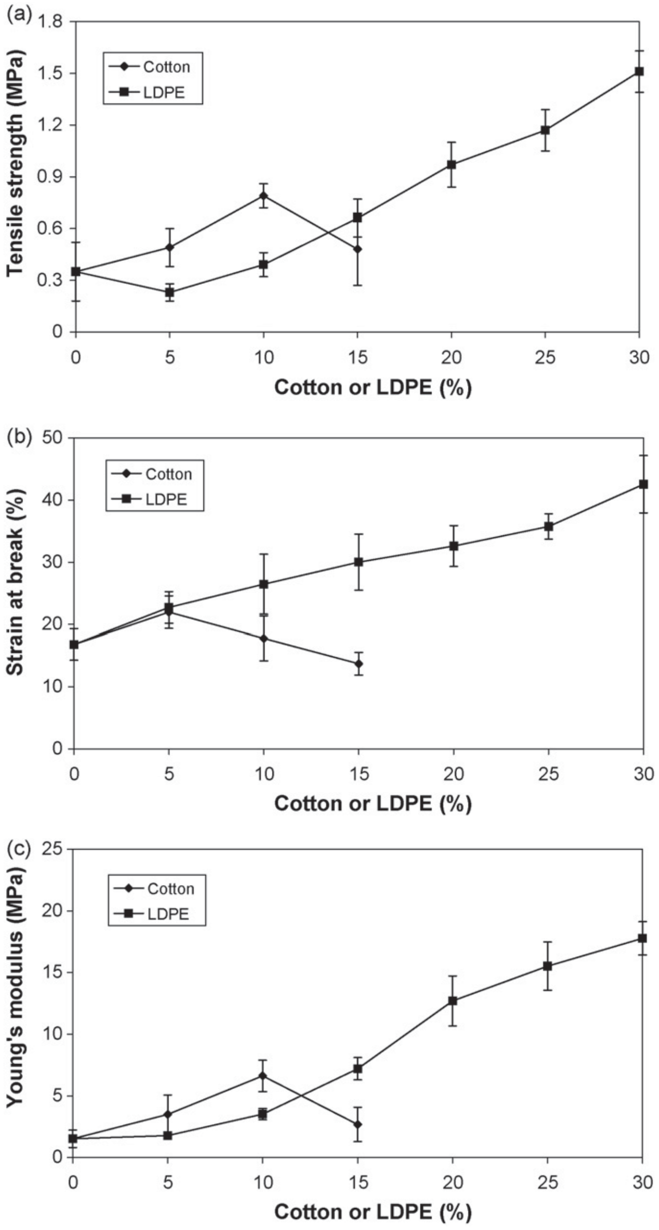

Fig. 2. Mechanical properties of TPRS/cotton fiber and TPRS/LDPE (a) Tensile strength (b) %Elongation at break and (c) Young's modulus.

By the use of VTMS compatibilizer, it can be seen in Fig. 5 that tensile strength and Young's modulus of the TPRS/LDPE samples could be improved. However, strain at break tended to be constant with different amounts of the VTMS compatibilizer. Similar

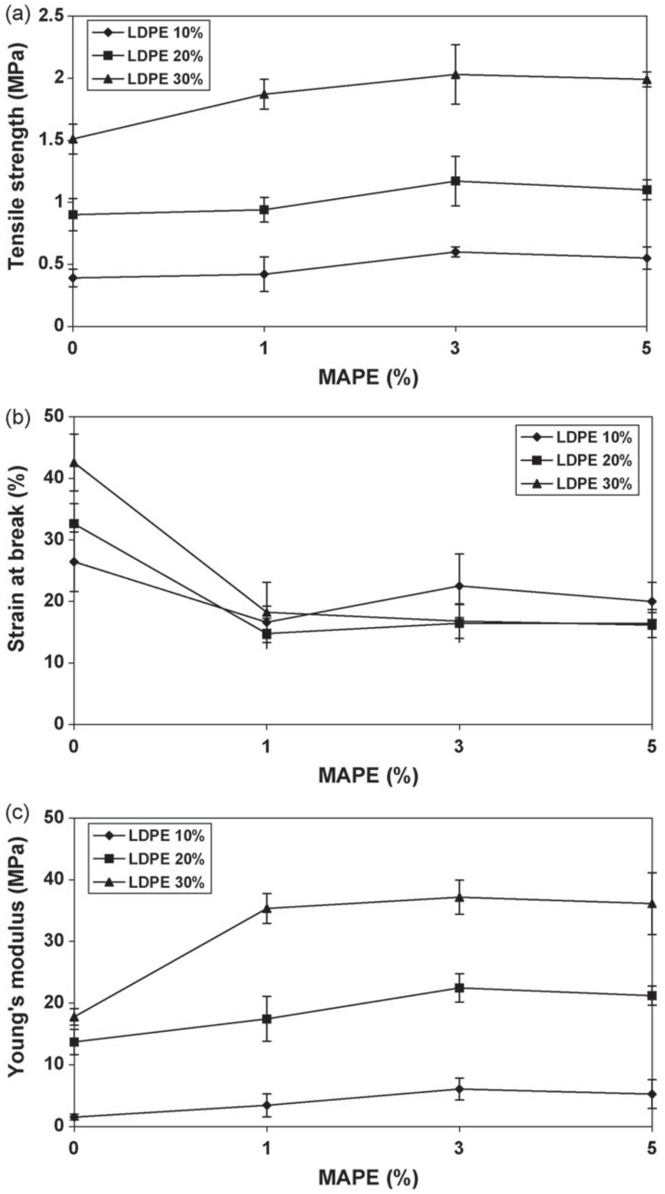

Fig. 3. Mechanical properties of TPRS/LDPE with different amounts of MAPE compatibilizer.

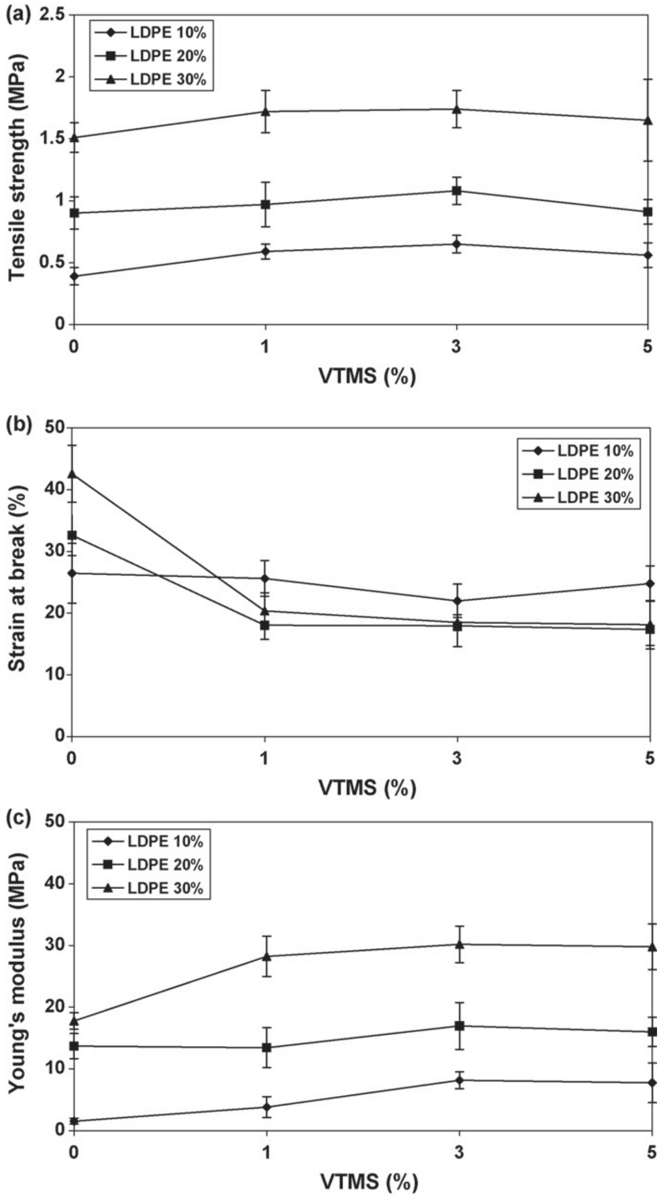

Fig. 5. Mechanical properties of TPRS/LDPE with different amounts of VTMS compatibilizer.

to MAPE compatibilizer, 3% VTMS provided the maximum tensile properties of the TPRS/LDPE. The schematic diagram of the interactions between the TPRS and LDPE with the use of VTMS is presented in Fig. 6. The improvement of tensile properties of the TPRS/LDPE/VTMS samples was due to Si–O–Starch chemical bond formed between the silanol group of VTMS and hydroxyl group of rice starch (Fig. 1(b)). Besides, double bond in vinyl part in the VTMS molecule could probably be dissociated at high processing temperature so this possibly leaded to chemical bond between the vinyl part of the VTMS and LDPE molecule. Comparison

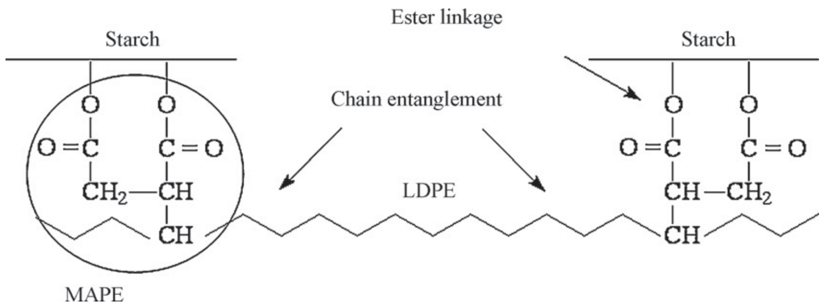

Fig. 4. Schematic diagram of interaction in TPRS/LDPE/MAPE.

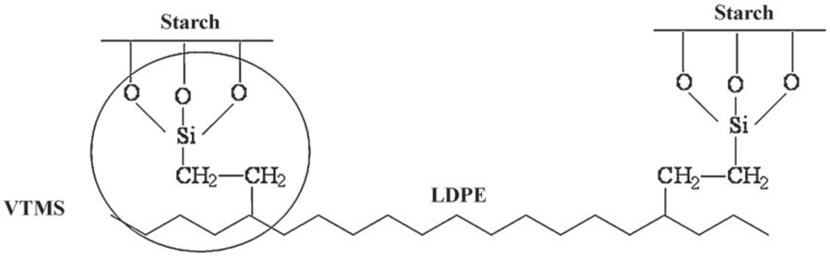

Fig. 6. Schematic diagram of interaction in TPRS/LDPE/VTMS.

between the TPRS/LDPE samples added with either MAPE or VTMS compatibilizer, it was found that the use of MAPE leaded to greater mechanical properties of the TPRS samples than those using VTMS and the best mechanical properties were obtained in the TPRS/30%LDPE/3%MAPE. However, when the modification of the TPRS with 10% cotton fiber or with 10%LDPE/3%MAPE was compared, it was found that the highest mechanical properties were obtained in the TPRS/10% cotton fiber (Figs. 2 and 3).

3.3. *Morphology*

Morphological structure of polymer is a very important characteristic because it ultimately determines many polymer properties. SEM micrographs of cryofractured surfaces of fragile test specimens are shown in Fig. 7. Rough surface of the glycerol plasticized TPRS could be observed as presented in Fig. 7(a). For the TPRS reinforced by cotton fiber, the SEM micrograph in Fig. 7(b) showed long cotton fiber embedded into the TPRS matrix and the fiber surface was wetted by the TPRS matrix.

On the contrary, the addition of LDPE into the TPRS matrix resulted in the poor phase distribution between TPRS and LDPE because of the differences in polarity. It can be seen in Fig. 7(c) that the hydrophilic TPRS phase tends to separate from the hydrophobic LDPE phase, representing by the smoother surface region in the micrograph.

Fig. 7(d) and (e) present the SEM micrographs of the TPRS/LDPE samples with MAPE and VTMS compatibilizers, respectively. It can be observed that similar phase morphology could be obtained with the use of either MAPE or VTMS compatibilizers. Phase separation between the TPRS and LDPE could not be observed as can be seen in the TPRS/LDPE specimen in Fig. 7(c). This phase morphology is the good evidence of phase compatibility of the TPRS and LDPE by the use of MAPE or VTMS compatibilizers.

3.4. *Water absorption*

Water sensitivity is another important criterion for many applications of starch products. The results of water absorption of different TPRS specimens performed at the temperature of 30 ± 2 °C and 50% RH are shown in Fig. 8. It can be seen that it took about 3 days for different TPRS samples with or without modification to reach absorption equilibrium. The equilibrium water contents for the pure TPRS, TPRS/10% cotton and TPRS/10% LDPE were approximately 380%, 305% and 225%, respectively.

It was found that water absorption of the TPRS was clearly reduced with the incorporation of cotton fiber because of the less hydrophilic character of the fibers in comparison to starch hydrophilic property (Fig. 8). Moisture absorption of cotton fiber is approximately 7.0–8.0%; whereas, it is in the range of 11.5–13.0% for the rice starch (Li, Shoemaker, Ma, Moon, & Zhong, 2008; Morton & Hearle, 1997).

As expected, the incorporation of LDPE into the TPRS matrix could dramatically restrain the water absorption of the TPRS matrix and reduced the water sensitivity of the TPRS due to the hydrophobic characteristic of LDPE. Greater content of LDPE caused the decline of water absorption of the TPRS/LDPE specimens. It should be noted that; although, cotton fiber shows more hydrophilic nature than LDPE, water absorption of the TPMBS can be decreased by the incorporation of cotton fiber.

When MAPE or VTMS compatibilizer were added into the TPRS/30% LDPE samples, it was found that water absorption tended to increase slightly due to the more hydrophilic nature of the MAPE and VTMS compatibilizers, compared with LDPE.

3.5. *Thermal properties*

In thermogravimetric analysis, the loss in mass due to volatilization of the degradation products is monitored as a function of temperature. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for different TPRS samples are shown in Table 1 and Fig. 9. The weight loss of the samples in the first step was mainly referred to water loss.

It can be also seen in Table 1 and Fig. 9 that the TPRS shows the onset decomposition temperatures (T_d) at 178° and 301 °C due to the decomposition temperatures of glycerol and rice starch, respectively. The modification of the TPRS with the cotton fiber causes the improvement of T_d of the TPRS (Table 1). T_d values of the TPRS were 305 °C and 303 °C by the use of 5% and 10%

Table 1
Onset degradation temperatures and percentage weight losses of different TPRS samples obtained from TG and DTG thermograms.

Samples	Onset degradation temperatures (°C)				Weight loss (%)
	Zone 1	Zone 2	Zone 3	Zone 4	
TPRS	178.2	300.9	–	–	52.2
TPRS/5% cotton	190.3	304.6	397.6	–	31.7
TPRS/10% cotton	184.9	303.2	407.8	–	28.0
TPRS/10% LDPE	162.9	293.1	–	448.4	50.6
TPRS/20% LDPE	156.8	294.7	–	429.4	45.5
TPRS/30% LDPE	154.9	300.6	–	447.3	39.9
TPRS/30% LDPE/5% MAPE	155.9	301.0	–	448.3	38.2
TPRS/30% LDPE/5% VTMS	167.5	306.1	–	440.6	29.8

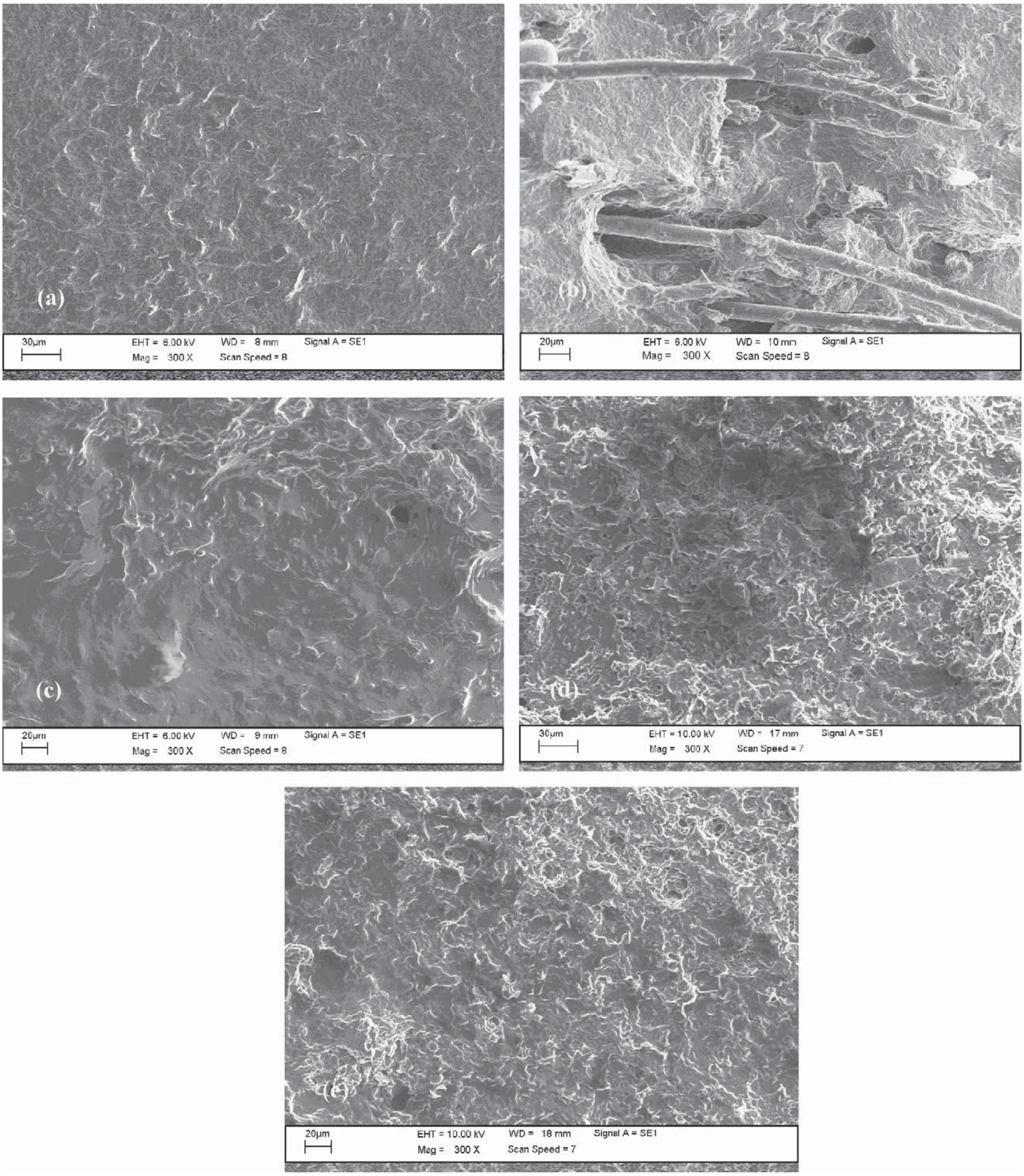

Fig. 7. SEM micrographs of (a) TPRS (b) TPRS/cotton fiber (c) TPRS/LDPE (d) TPRS/LDPE/MAPE and (e) TPRS/LDPE/VTMS.

cotton fiber, respectively. This could be because the TPRS is phase compatible with cotton fiber by the hydrogen bond linkages. In addition, T_d of cotton fiber appeared approximately in the range of 398–408 °C as the third step in the thermograms. However, the weight loss at onset T_d was found to be 52.2%, 31.7% and 28.0% for the TPRS, TPRS/5% cotton and TPRS/10% cotton, respectively. The decrease in percentage weight loss implies that thermal stability of the TPRS/cotton samples tend to increase, due to good adhesion between the TPRS and cotton fiber. Similar decrease in weight loss at onset temperature by the incorporation of fibers into TPS was also reported (Curvelo et al., 2001; Ma et al., 2005).

Nevertheless, the incorporation of LDPE into the TPRS tended to decrease T_d of the rice starch. T_d values of the TPRS/LDPE were found to be slightly lower than T_d of the pure TPRS. This could be possibly because of the different phase incompatibility between TPRS and LDPE. Besides, the T_d of LDPE component was obtained in the range of 429–448 °C. It was also found in Table 1 that percentage weight losses were 52.2%, 50.6%, 45.5% and 39.9% for the TPRS, TPRS/10% LDPE, TPRS/20% LDPE and TPRS/30% LDPE, respectively. The results clearly indicate that the thermal stability of the TPRS is improved by the addition of LDPE. Nevertheless, the incline in percentage weight loss or the enhancement in thermal stability

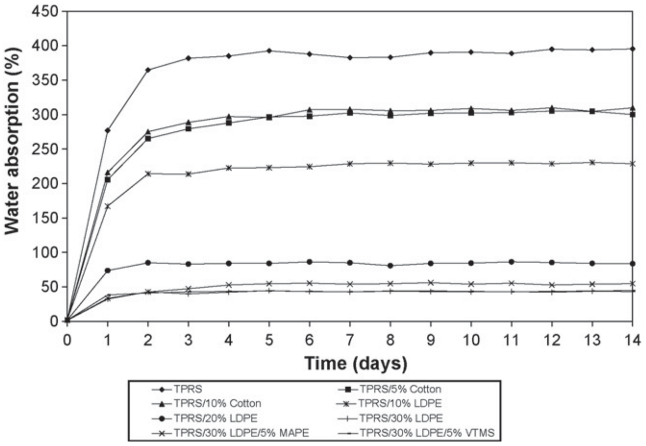

Fig. 8. The relationship between water absorption and time in different TPRS samples at 50% RH.

in TPRS is dominated by the addition of cotton fiber than those of LDPE.

By the use of MAPE and VTMS compatibilizers, it can be seen in Table 1 and Fig. 9 that T_d of the TPRS/LDPE samples slightly is increased. It can be due to the improved phase compatibility between the TPRS and LDPE as previously shown in Fig. 7. Similar to the TPRS/cotton fiber samples, the slightly increase in T_d shows the increase in thermal stability with the presence of MAPE or VTMS compatibilizers in the TPRS/LDPE samples. Percentage weight loss was found to be 39.9%, 38.2% and 29.8% for the TPRS/LDPE, TPRS/LDPE/MAPE and TPRS/LDPE/VTMS, respectively. The decrease in percentage weight losses shows the slight improvement in thermal stability with the addition of MAPE or VTMS compatibilizers.

3.6. Soil burial test

Biodegradable properties of different TPRS specimens can be determined by the soil burial test. It can be seen in Fig. 10 that all of the TPRS samples, especially the TPRS and TPRS/cotton fiber specimens, show the increment in weight after a few days of soil immersion due to the water uptake from the soil; after that, the samples weights tend to decrease and then the samples start to degrade. The pure TPRS sample degraded within 6 days of soil burial test. It should be noted that the TPRS/cotton fiber samples can rapidly absorb water because of the hydrophilic nature of not only the TPRS but also cotton fiber. Percentage weight change in the

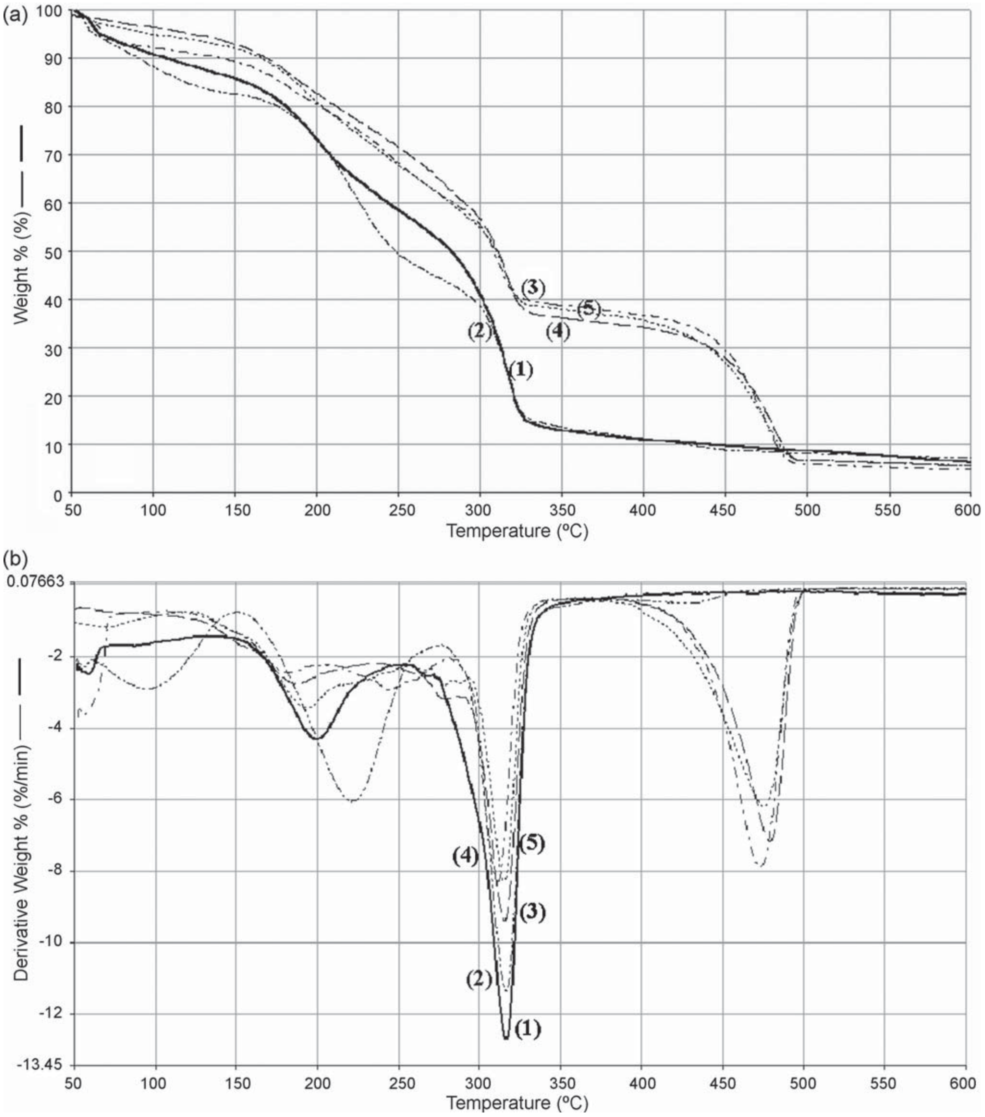

Fig. 9. (a) TG and (b) DTG thermograms of (1) TPRS (2) TPRS/cotton fiber (3) TPRS/LDPE (4) TPRS/LDPE/MAPE and (5) TPRS/LDPE/VTMS.

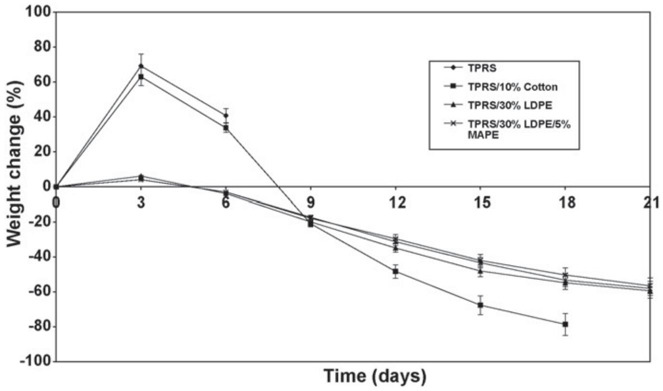

Fig. 10. Percentage weight changes of TPRS samples under soil burial test

TPRS/cotton fiber sample seems to lower than that of the pure TPRS. However, the maximum decrease in weight change was found in the TPRS/cotton fiber sample, presenting the ease of degradability, i.e. the sample can degrade within 18 days of testing. On the contrary, more difficult degradable samples can be clearly obtained in the TPRS/LDPE specimens due to the hydrophobic characteristic of LDPE part. However, the TPRS/LDPE samples with the addition of the MAPE or VTMS compatibilizers caused less percentage weight change than that of the TPRS/LDPE sample without the compatibilizer due to the improved phase compatibility between the TPRS and LDPE.

4. Conclusions

Due to the poor tensile properties and high water absorption of the TPRS, the modification of the TPRS was carried out using cotton fiber or LDPE. It was found that the TPRS/cotton fiber and the TPRS/LDPE presented greater mechanical properties and lower water uptake. By the use of MAPE and VTMS compatibilizers in the TPRS/LDPE, the TPRS/LDPE/MAPE and TPRS/LDPE/VTMS specimens also illustrated the improved tensile properties but slight increase in water absorption, as compared to the TPRS/LDPE. From SEM micrographs, cotton fibers were embedded and wetted by the TPRS matrix; however, the TPRS with LDPE showed the considerable phase separation. However, the phase separation could be reduced by the addition of the MAPE or VTMS compatibilizers. Besides, thermal stability of the TPRS increased significantly with the application cotton fiber. As expected, the faster biodegradability was found in the TPRS/cotton fiber than in the TPRS/LDPE. From this study, the optimum mechanical, thermal, water absorption and biodegradable properties were obtained from the TPRS with the addition of 10% cotton fiber.

Acknowledgements

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Research Article

Property improvement of thermoplastic mung bean starch using cotton fiber and low-density polyethylene

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Due to high water uptake and low mechanical properties of biodegradable thermoplastic starch, thermoplastic starch prepared from mung bean starch (TPMBS) was modified by the incorporation of cotton fiber and low-density polyethylene (LDPE). The effect of different ratios of cotton fiber/LDPE, *i.e.*, 10:0, 7:3, 5:5, 3:7, and 0:10, on water uptake, mechanical, thermal, and biodegradable properties of TPMBS was examined. Different TPMBS samples were prepared using internal mixer for compounding and compression molding machine for shaping samples. It was found that the TPMBS incorporated with 10:0, 7:3, and 3:7 cotton fiber/LDPE showed an increase in the stress at maximum load and Young's modulus. Moreover, the water absorption of all of the modified TPMBS samples tended to decrease as compared to the pure TPMBS. Morphological, thermal, and biodegradable properties of different TPMBS samples were also investigated.

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1 Introduction

Mung bean (*Vigna radiata*) is one of the important legumes in Southeast Asia and in other tropical countries. Mung bean is consumed mainly for its rich protein content (24%) but carbohydrate (62–63%) is its major component. Carbohydrate in mung bean starch consists of approximately 30% amylose [1–3]. Traditionally, mung bean has been used as raw material for producing starch noodle [1]. Mung bean starch noodle is regarded as the best of starch noodles due to its high amylose content, leading to strong gel strength [2].

Starch from various sources has been used as thermoplastic starch (TPS) for production of biodegradable polymers. Starch is not a true thermoplastic but in the presence of plasticizers at high temperature and under shear, it can readily melt and flow, allowing for its use as extruded or injected material, similar to most conventionally synthetic thermoplastic polymers [4]. The major sources of starches that can be used for production of biodegradable polymers include corn [5–10], potato [11], cassava [12, 13], and wheat [14]. However, research study on mung bean starch has been limited only casted films as hard capsules for pharmaceutical applications [3].

Generally, TPS has two main disadvantages compared to most plastics currently in use, *i.e.*, poor mechanical properties and high water uptake. One interesting approach to improve the mechanical properties and reduce the water absorption of TPS is the use of natural fibers to reinforce TPS [7, 8, 13, 15]. For example, it was reported that mechanical strength and modulus of glycerol plasticized corn starch increased *via* Eucalyptus pulp reinforcement [8]. Winceyette fibers were also used successfully to reinforce corn starch plasticized by urea and formamide [7]. Cassava starch films reinforced by cellulose fibers were also prepared and it was found that the mechanical strength and rigidity of the films increased;

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Abbreviations: DTG, thermogravimetric; **LDPE,** low-density polyethylene; **TG,** thermogravimetric; **TPMBS,** thermoplastic mung bean starch; **TPS,** thermoplastic starch.

however, the water vapor permeability of the films decreased [13]. The effect of wheat bran addition on selected properties of cassava starch film was also investigated. It was found that an increase in the fiber (bran) content caused an increase in the storage modulus but a decrease in the loss tangent, moisture content, and water vapor permeability of the film [15].

On another point of view, many studies have focused their attention on blending TPS with synthetic thermoplastic polymers, mainly LDPE or LLDPE [16–19]. Generally, addition of TPS as a minor phase into synthetic thermoplastic matrix as a major phase causes a reduction of the mechanical properties [16–18]. It was reported, for example, that a blend of TPS from wheat starch (0–22% w/w) with LDPE exhibited a decrease in the Young's modulus [16]. Gas permeability and water vapor transmission rate also significantly reduced with the incorporation of potato starch in potato starch/LDPE blend film [19].

In this present study, TPMBS plasticized by glycerol was prepared and modified by reinforcing the mung bean starch with natural cellulosic fibers, *i.e.*, cotton fiber. LDPE was also incorporated into TPMBS due to the hydrophobic characteristics of LDPE, inclusion of an LDPE minor phase into TPMBS matrix was expected to reduce the water uptake of the TPMBS. The effects of cotton fiber and LDPE contents including different ratios of cotton fiber/LDPE on the mechanical properties of the TPMBS were then investigated. The morphology, water absorption, thermal stability, and biodegradability of different TPMBS samples were also examined.

2 Materials and methods

2.1 Materials

Mung bean starch (11.5–13.0% moisture) was obtained from Sittihinan Co., Ltd. (Bangkok, Thailand). The starch contained approximately 30 wt% amylose and 62 wt% amylopectin. The other minor components in the starch were protein, lipid, fiber, and ash. Glycerol (plasticizer) was purchased from Lab System Co., Ltd. (Bangkok, Thailand). Cotton fiber with the aspect ratio of 500:1 were obtained locally and used as received. Low-density polyethylene (LDPE, LD1905F) with melt flow index, MFI of 5.2 g/10 min (tested at 21.6 N and 190°C) was obtained from Thai Polyethylene Co., Ltd. (Bangkok, Thailand).

2.2 Sample preparation

Mung bean starch and glycerol were pre-mixed in polyethylene bag overnight. The weight ratio of mung bean starch and glycerol was maintained at 1:1. Compounding was carried out using an internal mixer (Lab-Tech Engineering, Bangkok, Thailand) at the temperature of 140°C at the speed of 50 rpm for 5 min in order to obtain a homogeneous sample. The processed sample was then compressed at a temperature of 140°C into a 2 mm thick plate. Based on our preliminary study, the ratio and the processing conditions were selected because of the processability. The property modification of the TPMBS was carried out by incorporation of both cotton fiber and LDPE. Cotton fiber and LDPE were added during compounding with the internal mixer. Different ratios of cotton fiber/LDPE, *i.e.*, 10:0, 7:3, 5:5, 3:7, and 0:10 were used; the total content of both cotton fiber and LDPE was maintained at 10% by weight of the starch and glycerol blend.

2.3 Morphology evaluation

A LEO 1455 VP scanning electron microscope (Oberkochen, Germany) was employed to study the morphology of the TPMBS with and without the incorporated cotton fiber and LDPE. Each tested samples was sputter-coated with a thin layer of gold to prevent electrical charge during observation. For fracture view, a sample was immersed into liquid nitrogen before being fractured.

2.4 Mechanical properties evaluation

Mechanical tests were conducted according to ASTM D-638 at the temperature of 23 ± 1°C and relative humidity of 60 ± 5%. A mechanical measurement of each dumbbell-shaped specimen was carried out using a Universal Testing Machine (Lloyd Instrument, LR 5K, West Sussex, UK) with a 100 N load; the crosshead speed was maintained at 40 mm/min. The TPMBS sample was conditioned at the temperature of 23 ± 1°C and relative humidity of 60 ± 5% for 24 h before testing. It should be noted that the mechanical property results of the TPMBS samples were obtained by averaging the measurement results of ten independent specimens.

2.5 Water absorption evaluation

Each newly prepared sample was dried at 105°C for 12 h and then stored at 50% relative humidity at a temperature of 30 ± 2°C prior to water absorption evaluation. 50% relative humidity was obtained using a saturated solution of $CaCl_2$ in a closed vessel. The amount of water absorbed by the sample was determined as the percentage of water absorption as follows (Eq. 1):

$$\text{Water absorption} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

where W_2 and W_1 are the wet weight and the dried weight of the sample, respectively.

2.6 Thermal properties evaluation

Thermogravimetric (TG) and derivative thermogravimetric (DTG) thermograms of a sample were recorded by a TG analyzer (Perkin Elmer, Pyris 1, Massachusetts, USA). A TPMBS sample was tested under nitrogen atmosphere within a temperature range of 50–600°C at a heating rate of 10°C/min. Thermal degradation temperature (T_d) was reported by the onset degradation temperature where the weight loss started to occur. Percentage weight loss was obtained from the onset decomposition temperature determined only for the starch decomposition.

2.7 Biodegradation test

A TPMBS sample with the dimensions of 20×50 mm^2 was buried at approximately 10 cm under the soil surface. The pH and temperature of the soil were maintained at 7 and 32 ± 2°C, respectively. The water content of the soil was in the range of 10–20% and the weight change was recorded daily for 28 days. Average percentage weight change was recorded from three independently tested samples.

3 Results and discussion

3.1 Morphology

Morphology of surface and fracture views of different TPMBS samples were obtained via scanning electron microscopy. For the surface and fracture views of the TPMBS with the addition of 10% cotton fiber (Fig. 1), the fibers were randomly distributed and embedded into the TPMBS matrix, showing strong adhesion between the two different phases. Similar morphology was reported for the cassava starch with incorporation of cellulose fibers [13]. When 15% cotton fiber was added into the TPMBS matrix (Fig. 1c), the surface view micrograph showed similar surface morphology to the TPMBS with the addition of 10% cotton fiber, but more cracks and voids were noticed. For the fracture view micrograph, the TPMBS matrix with addition of 15% cotton fiber, as presented in Fig. 1d, clearly showed cotton fibers floated over the discontinuous TPMBS matrix.

In addition, incompatible phases between TPMBS and LDPE caused clear phase separation as well as long cracks at the interfacial boundary as observed in Fig. 1e. The micrograph also presented both smooth (LDPE) and rough (TPMBS) boundaries. Correspondingly, the fracture view of the TPMBS/LDPE sample showed the evident phase separation between TPMBS and LDPE phases (Fig. 1f). Many long cracks and voids were obviously noticed in the TPMBS/LDPE sample due to the incompatibility between the hydrophilic TPMBS and hydrophobic LDPE. Similar surface morphology was also found in tapioca starch/LDPE blend [20].

When both cotton fiber and LDPE (7:3) were incorporated into the TPMBS matrix, the surface view micrograph showed that the cotton fibers were embedded in the TPMBS matrix as shown in Fig. 1g. Figure 1h represents fracture view of TPMBS with the 7:3 cotton fiber/LDPE. It was found that cotton fibers were wetted by the TPMBS and were floated on the TPMBS matrix. Similar to the surface view in Fig. 1g, no distinct phase separation boundary between the TPMBS and LDPE could be observed. Again, cracks were clearly observed.

3.2 Mechanical properties

Figure 2 shows the mechanical properties of the TPMBS with the incorporation of different contents of cotton fiber and LDPE. Due to the chemical similarity of both mung bean starch and cotton fiber, improvement of the mechanical properties was assumed when both components were mixed. It was found that the addition of 5 and 10% cotton fiber into the TPMBS matrix caused an increase in the stress at maximum load and Young's modulus because of the reinforcement of the high aspect ratio cotton fiber. However, at 15% cotton fiber, stress at maximum load and Young's modulus tended to decrease due to the excessive content of cotton fiber that caused the discontinuity of the TPMBS matrix as previously shown in Fig. 1c and d. Strain at maximum load also continued to decrease with an increase in the cotton fiber contents. Similar trends have been reported for corn starch or cassava starch/cellulose fibers [7, 8, 13, 15].

Addition of 10% LDPE into the TPMBS matrix caused a reduction of the stress at maximum load as shown in Fig. 2 due to the phase incompatibility between the TPMBS and LDPE (Fig. 1e and f). Likewise, it was reported [19, 21–23] that 100% LDPE showed higher stress and elongation than those of LDPE filled with minor contents of TPS. This was explained by the phase incompatibility between hydrophilic TPS and hydrophobic LDPE. By increasing of LDPE content, on the other hand, stress at maximum load and Young's modulus of the TPMBS/LDPE tended to increase (Fig. 2). This behavior is probably caused by the easier flow ability and higher mechanical properties of LDPE. In this study, the maximum mechanical properties could be obtained by adding either 10% cotton fiber or 30% LDPE. It should be noted that the stress at maximum load and Young's modulus of the TPMBS were apparently higher with the application of 10% cotton fiber than those observed when 10% LDPE was added. Because the maximum mechanical properties could obtain in the TPMBS

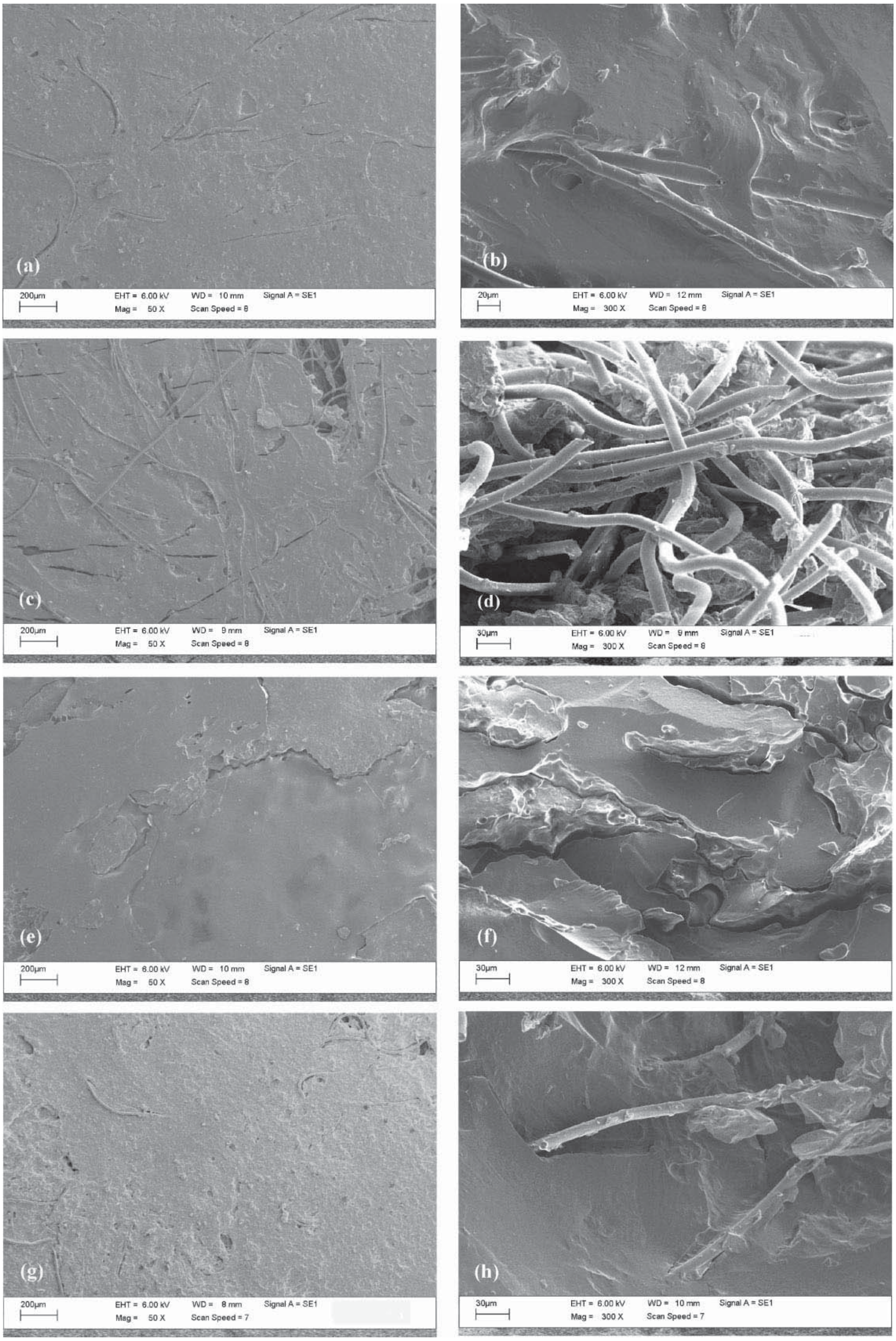

Figure 1. SEM micrographs of surface and fracture views of (a) and (b) TPMBS with 10% cotton fiber (c) and (d) TPMBS with 15% cotton fiber (e) and (f) TPMBS with 10% LDPE, and (g) and (h) TPMBS with both cotton fiber and LDPE ((a), (c), (e), and (g)-surface views and (b), (d), (f), and (h)-fracture views).

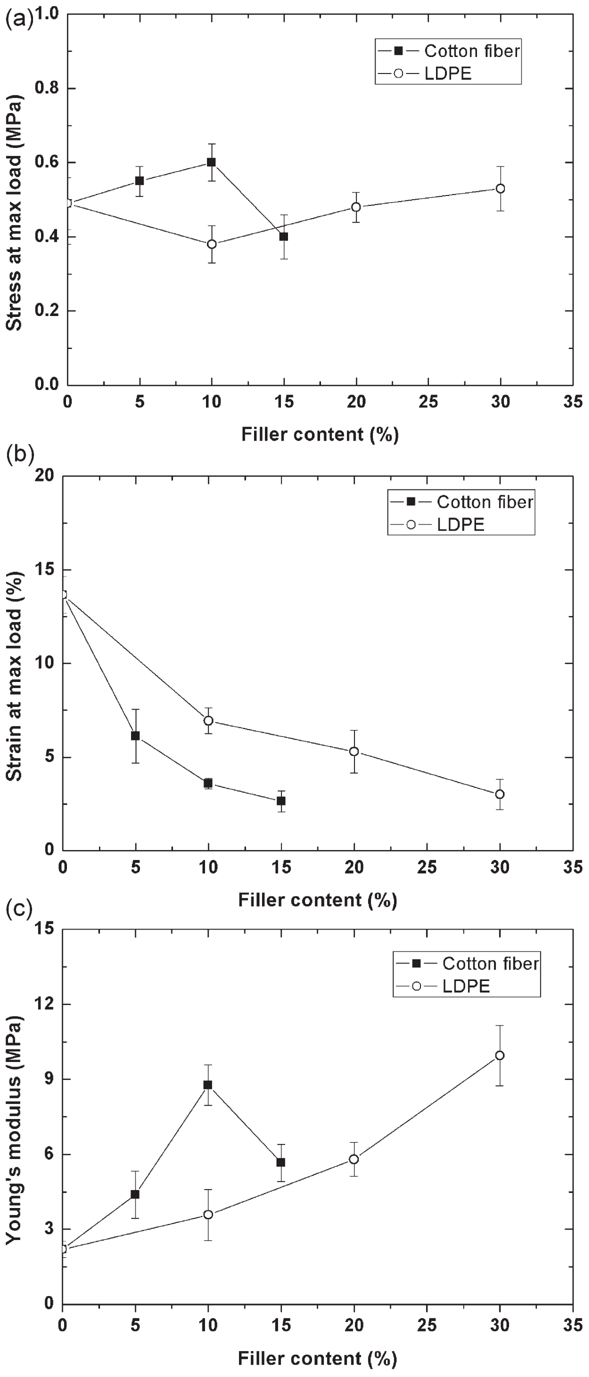

Figure 2. Mechanical properties of different TPMBS samples modified by cotton fiber or LDPE. (a) Stress at maximum load, (b) strain at maximum load, and (c) Young's modulus.

with the addition of 10% cotton fiber; therefore, the use of different ratios of cotton fiber/LDPE were selected and maintained at 10%.

When the TPMBS samples with different ratios of cotton fiber/LDPE, *i.e.*, 10:0, 7:3, 5:5, 3:7, and 0:10 were compared with the pure TPMBS (0:0) (Fig. 3), it was found that the stress at maximum load for the 10:0, 7:3, and 3:7 samples was higher than that of the 0:0 sample and the maximum value of stress at maximum load was found in the 7:3 sample. For strain at maximum load, it tended to decrease for the different ratio samples except for the 7:3 sample. In addition, Young's modulus increased for the different ratio samples with the maximum value for the 7:3 sample. The results indicate that the overall mechanical property of the TPMBS sample can be improved by the addition of either only cotton fiber or by the combination of both cotton fiber and LDPE. The lowest overall mechanical property was found in the 5:5 sample, probably because both modifying agents show the difference in polarity and hydrophilicity. Therefore, no significant reinforcement can be observed. The highest overall mechanical property was found in the 7:3 sample, indicating better reinforcing characteristics of cotton fiber than those of LDPE.

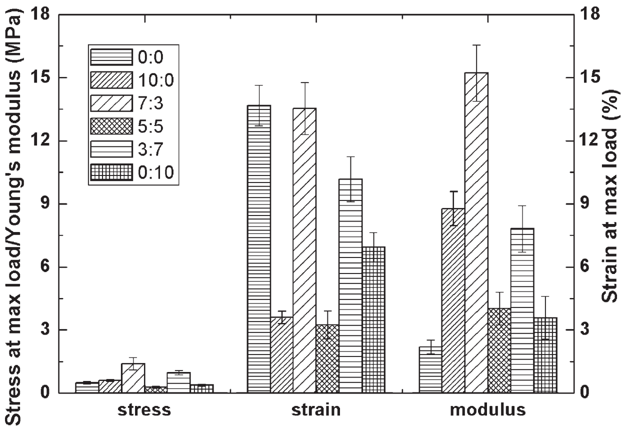

Figure 3. Mechanical properties of TPMBS samples with different ratios of cotton fiber/LDPE.

3.3 Water absorption

As one of the major drawbacks of a starch system is its tendency to absorb water, any improvement in water resistance of the system is very important. The water absorption behavior of different TPMBS specimens conditioned at 30 ± 2°C and 50% RH is illustrated in Fig. 4. Different TPMBS samples, with or without modification, showed water absorption equilibrium within approximately 7 days. The equilibrium water contents for the samples with 0:0, 10:0, and 0:10 cotton fiber/LDPE were roughly 169, 164, and 128%, respectively. It is clear that water absorption of TPMBS with cotton fiber (10:0) was slightly lower that of the pure TPMBS (0:0) due to the less hydrophilic properties of cotton fiber [24]. A slight decrease in the water uptake was also reported for different natural-fiber reinforced TPS [7, 8, 13, 15]. However, addition of LDPE into the TPMBS matrix (0:10) could dramatically

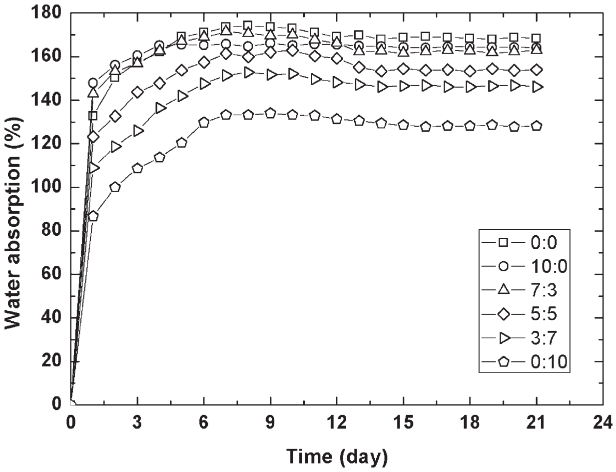

Figure 4. Relationship between water absorption and time of TPMBS samples with different ratios of cotton fiber/LDPE at 30°C and 50% RH.

limit water absorption and reduce the water sensitivity of the TPMBS due to the hydrophobic characteristics of LDPE (Fig. 4).

When different ratios of cotton fiber/LDPE were considered, it was found that the equilibrium water contents were approximately 162, 153, and 146% for the 7:3, 5:5, and 3:7 samples, respectively. As expected, higher contents of LDPE caused larger decline of water absorption of due to the hydrophobicity of non-polar LDPE.

The lowest and highest water uptake was found in the TPMBS with the addition of 0:10 and 10:0 cotton fiber/LDPE, respectively. It should be noted that; although, cotton fiber shows more hydrophilic nature than LDPE, water absorption of the TPMBS can be reduced by the addition of cotton fiber.

3.4 Thermal properties

The TG and DTG thermograms for different TPMBS samples are shown in Table 1 and Fig. 5. The weight loss of different samples in the first step mainly referred to water loss. The onset decomposition temperatures (T_d) found at 176.2° and 295.8°C were due to the decomposition temperatures of glycerol and mung bean starch, respectively (Table 1 and Fig. 5) [7]. Modification of TPMBS with cotton fiber (10:0) caused an improvement of T_d of the TPMBS (Table 1); T_d value of the TPMBS was 303.4°C when 10% cotton fiber was incorporated. This is because of higher thermal stability of cotton fiber and because of phase compatibility between the TPMBS and cotton fiber due to their similar chemical structures; the two structures were linked through hydrogen bonds [7, 8]. In addition, T_d of the cotton fiber appeared at approximately 425.4°C as the third step in the thermograms. Moreover, the weight losses at onset T_d were found to be 56.2 and 36.2% for TPMBS (0:0) and TPMBS/10% cotton (10:0), respectively. A significant decrease in the percentage weight loss indicated that the thermal stability of the TPMBS/cotton fiber samples improved, due to good adhesion between the TPMBS matrix and cotton fiber.

However, addition of LDPE into TPMBS (0:10) tended to maintain T_d of the mung bean starch. It is noted that the T_d of LDPE component was obtained at the temperature of 457.8°C. It was also found that the percentage weight loss was 56.2 and 39.5% for the TPMBS and TPMBS/10% LDPE, respectively. The results clearly indicated that the thermal stability of TPMBS could be improved by the addition of LDPE. Nevertheless, the enhancement in thermal stability of TPMBS was dominated by the addition of cotton fiber rather than LDPE.

When different ratios of cotton fiber/LDPE were examined, it was found that T_d and percentage weight loss values for then 7:3, 5:5, and 3:7 samples were comparable as shown in Table 1. Furthermore, TPMBS with only cotton fiber (10:0) exhibited similar T_d and percentage weight loss values to those of TPMBS with both cotton fiber and LDPE. The results suggested that the thermal stability of TPMBS could be improved by the use of either cotton fiber alone or of the combination of both cotton fiber and LDPE.

Table 1. Onset degradation temperatures and percentage weight losses of different TPMBS samples obtained from TG and DTG thermograms

Sample	Onset degradation temperature (°C)				Weight loss %
	Zone 1	Zone 2	Zone 3	Zone 4	
TPMBS	176.2	295.8	–	–	56.2
TPMBS + 10:0 cotton/LDPE	183.6	303.4	425.4	–	36.2
TPMBS + 7:3 cotton/LDPE	188.3	303.3	400.5	542.7	38.1
TPMBS + 5:5 cotton/LDPE	185.2	305.2	408.6	551.4	37.2
TPMBS + 3:7 cotton/LDPE	185.3	304.8	403.2	547.1	39.5
TPMBS + 0:10 cotton/LDPE	176.4	296.2	457.8	–	39.5

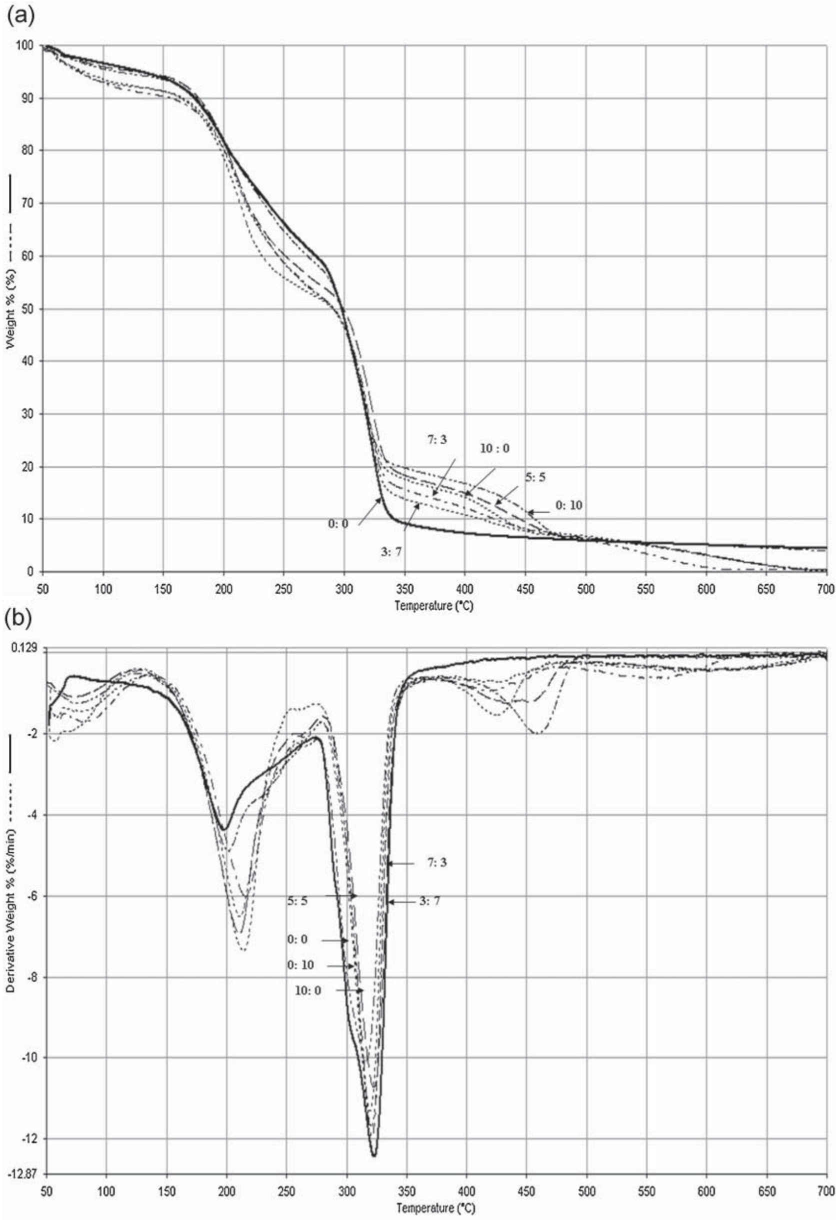

Figure 5. (a) TG and (b) DTG thermograms of different TPMBS samples.

3.5 Biodegradability

Biodegradability of TPMBS samples was examined using the soil burial test. The relationship between the weight change and soil burial time of different TPMBS samples is represented in Fig. 6. All of the TPMBS samples showed an increase in the percentage weight change due to the absorption of water during the first 3–4 days of the test. Then, weight change tended to decrease since the samples start to degrade. Pure TPMBS could degrade more rapidly, within about 8 days of testing. On the other hand, when the TPMBS samples with incorporated cotton fiber or LDPE were examined, the results showed that the highest decrease of weight change was observed in the case of TPMBS reinforced by cotton fiber (10:0). This is because both components could environmentally degrade. As expected, the lowest decrease of weight change was noted in the case of TPMBS/LDPE sample (0:10) due to the non-degradable nature of LDPE. When different ratios of cotton fiber/LDPE in the TPMBS matrix were compared, it can be seen in Fig. 6 that higher ratios of cotton fiber led to higher degradability; higher ratios of LDPE led expectedly to lower degradability. The degradability of different TPMBS samples can be ranked in the following order: 0:0>10:0>7:3>5:5>3:7>0:10.

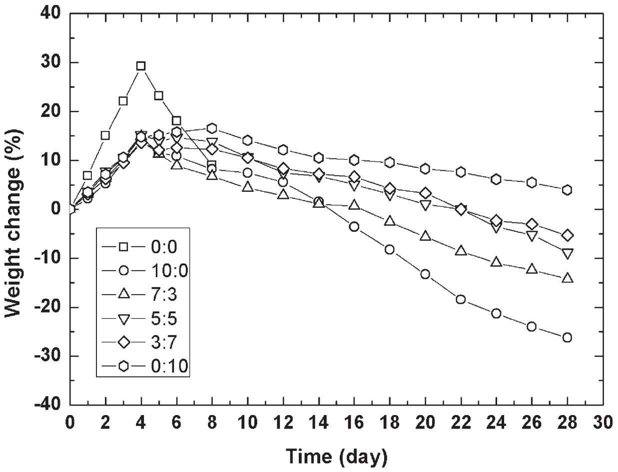

Figure 6. Relationship between percentage weight change and soil burial time of TPMBS samples with in different ratios of cotton fiber/LDPE.

4 Conclusions

TPMBS was prepared using internal mixing and compression molding techniques. Since the TPMBS showed poor mechanical properties and high water absorption, cotton fiber, and LDPE at different ratios were then incorporated into the TPMBS matrix. It was found that the incorporation of cotton fiber into the TPMBS matrix (10:0) caused better improvement of mechanical, thermal, and biodegradable properties than those of LDPE (0:10). The highest mechanical properties was found in the TPMBS with the incorporation of 7:3 cotton fiber/LDPE. As compared to the pure TPMBS, the water uptake of all of the modified TPMBS samples tended to decrease. From TG thermograms, thermal stability of the TPBMS was clearly improved by the inclusion of cotton fiber or LDPE or a combination of cotton fiber and LDPE into the TPMBS. Biodegradability, from soil burial test, showed the decreasing trend when cotton fiber and LDPE were incorporated into the TPMBS, but the TPMBS with the addition of cotton fiber presented more rapid degradability. From this study, the optimum mechanical, thermal, water absorption, and biodegradability were obtained from the TPMBS with 7:3 cotton fiber/LDPE.

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The authors have declared no conflict of interest.

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ORIGINAL PAPER

Effect of Cotton Fiber Contents and Lengths on Properties of Thermoplastic Starch Composites Prepared from Rice and Waxy Rice Starches

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Abstract Biodegradable polymer was prepared as thermoplastic starch (TPS) using rice and waxy rice starches. In order to increase mechanical properties and reduce water absorption of the TPS, cotton fiber was incorporated as the fiber reinforcement into the TPS matrix. The effect of cotton fiber contents and lengths on properties of the TPS was examined. Internal mixer and compression molding machine were used to mix and shape the samples. It was found that the thermoplastic rice starch (TPRS) showed higher stress at maximum load and Young's modulus but lower strain at maximum load than the thermoplastic waxy rice starch (TPWRS). In addition, stress at maximum load and Young's modulus of both TPRS and TPWRS increased significantly with the addition of the cotton fiber. Cotton fiber contents and lengths also affected mechanical properties of the TPRS and TPWRS composites. Moreover, water absorption of the TPRS and TPWRS composites decreased by the use of the cotton fibers. FT-IR and XRD techniques were used to study a change in functional group and crystallinity of the thermoplastic starch composites. Morphological, thermal and biodegradable properties of different thermoplastic starch composites were also investigated.

Keywords Biodegradable polymer · Cellulose fiber · Composite · Thermoplastic starch

Introduction

Starch can be extracted from many botanical sources including rice, corn, cassava, potato and wheat. Starch commonly exists in a granular structure and the granules are mainly composed of two different glucose polymers; amylose and amylopectin molecules [1, 2]. Amylose is a linear polymer of anhydroglucose units linked through α-1-4 glucosidic bonds. Amylopectin is a branched polymer constituted by a backbone structure link amylose with 4–5% of its units bearing β-1-6 glucosidic linkages generating amylose-like branches [1, 2].

Generally, starch contains approximately 25% amylose and 75% amylopectin but waxy genotypes contain considerably higher amounts of amylopectin [1, 2]. However, the proportions of amylose and amylopectin polymers in native starches vary appreciably in starch from different species and even within a given vegetable [2]. As for rice starch (*Oryza sativa*), the non-waxy indica rice starch contains about 17–22% amylose, the non-waxy japonica rice starch contains about 14–18% amylose, but the waxy rice starch contains only small content of amylose (5–7% amylose) [3].

The development of new starch-based materials has gained much interest in recent years due to their biodegradability, low cost and wide availability. Thermoplastic starch (TPS) is one of the starch-based polymers that have been widely investigated [4–14]. Starch can be transformed into TPS through disruption of its granular structure and plasticization in the presence of plasticizer. Under the action of high temperature and shear, the plasticized starch can be turned into TPS and processed using conventionally thermoplastic processing machines used for most synthetic polymers such as extrusion, compression or injection moldings [4–14].

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Nevertheless, TPS has two main limitations, i.e. poor mechanical properties and high water absorption [4, 5, 8, 11–14]. One interesting method to overcome these drawbacks is the use of natural fibers as reinforcement for TPS [4, 5, 11–14]. When natural fibers are mixed with TPS, their mechanical properties are obviously improved due to the chemical similarity of starch and plant fibers [4, 5, 11–14]. It was found that the blending of distinct natural fibers such as eucalyptus, wood pulp, flax, jute and others in starch/cellulose derivatives blends yielded the increase of tensile strength and Young's modulus as well as the decrease in elongation when the fiber content increased [4, 5, 11–14]. A significant improvement in water resistance was also obtained by the addition of cellulose fibers [4, 11–14]. This behavior is related to more hydrophobic characteristic of natural fibers in comparison to starch hydrophilic property. Moreover, thermal stability of TPS was reported to improve by higher hermal resistance of cellulose fibers [4, 5, 13, 14].

There was a report on properties of TPS prepared from rice starch (*Oryza sativa indica*) (TPRS) [14], however, TPS prepared from waxy rice starch (TPWRS), containing lower amylose and higher amylopectin contents, has never been reported. In general, rice starch is friable and brittle; whereas, waxy rice is sticky and elongated. It was expected that different characteristics and contents of amylose and amylopectin in rice and waxy rice starches would lead to various properties of the TPS. In this research, the TPRS and TPWRS sample without cotton fiber reinforcement were prepared using internal mixer and compression molding. As mentioned that properties of TPS could be improved by reinforcing with cellulose fibers; therefore, different TPRS and TPWRS composites were reinforced by cotton fibers in order to improve properties. The effect of cotton fiber contents and lengths on properties of different TPRS and TPWRS composites was also investigated.

Materials and Methods

Materials

Rice starch (11.5–13.0% moisture) was obtained from Bangkok Interfood (Bangkok, Thailand), containing 20 ± 1%wt amylose and 75 ± 2%wt amylopectin. Waxy rice starch (11.0–13.0% moisture) was also obtained from Bangkok Interfood (Bangkok, Thailand), containing 5 ± 1%wt amylose and 95 ± 1%wt amylopectin. Glycerol (plasticizer) was purchased from Lab System Co. Ltd. (Thailand). Cotton fibers were obtained locally and used as-received.

Sample Preparation

Either rice or waxy rice starch was pre-mixed with glycerol in polyethylene bags. The weight ratio of rice starch and glycerol was maintained at 2:1. Blending was carried out using a high-speed mixer (Lab-Tech Engineering, Thailand) at the temperature of 160 °C at the rotor speed of 40 rpm for 5 min in order to obtain a homogeneous material. The processed samples were then compressed at the temperature of 160 °C into 2 mm thick plates. The property modification of the TPRS and TPWRS composites was carried out using cotton fibers. Different contents of cotton fiber, i.e. 5, 10 and 15% were added into the TPRS and TPWRS matrix and two averaged different lengths of cotton fibers were used, i.e. 2.11 and 5.27 mm, corresponding to the aspect ratios of 167:1 and 417:1, respectively.

IR Spectroscopic Study

FTIR spectra of different TPRS and TPWRS composites were recorded on a Spectrum 2000 GX spectrometer (Perkin Elmer, USA) using KBr disk technique with a resolution of 4 cm^{-1} in a spectral range of 4,000–600 cm^{-1} using 16 scans per sample.

X-Ray Diffraction

Wide angle X-ray diffraction measurements were carried out using a D8 Advance X-ray diffractor (Bruker, Madison, USA), CuK_{α} radiation (wavelength 0.1542 nm) operating at 40 kV and 35 mA. The scattering angle (2θ) covered the range from 3° to 60° (θ is the Bragg angle) with a step size of 0.02° and a sampling interval of 10 s.

Morphology

A LEO 1455 VP scanning electron microscope (Oberkochen, Germany) was employed to study the morphology of the TPRS and TPWRS composites with and without the incorporated cotton fiber. Each tested sample was sputter-coated with a thin layer of gold to prevent electrical charge during observation and a sample was immersed into liquid nitrogen before being fractured.

Mechanical Properties

Mechanical tests were conducted according to ASTM D-638 at the temperature of 23 ± 1 °C and relative humidity of 60 ± 5%. A mechanical measurement of each dumbbell-shaped specimen was carried out using a Universal Testing Machine (Lloyd Instrument, LR 5 K, West Sussex, UK) with a 100 N load; the crosshead speed was maintained at 40 mm/min. It should be noted that the mechanical property results of the TPRS and TPWRS composites were obtained by averaging the measurement results of ten independent specimens.

Water Absorption

Newly prepared sample was dried at 105 °C for 3 h and then stored at 50% relative humidity at a temperature of 30 ± 2 °C prior to water absorption evaluation. The 50% relative humidity was obtained using a saturated solution of $CaCl_2$ in a closed vessel. The amount of water absorbed by the sample was determined until the constant weight was obtained. The percentage of water absorption was calculated as follows:

$$\text{Water absorption} = (W_2 - W_1)/W_1 \times 100$$

where W_2 and W_1 are the wet weight and the dried weight of the sample, respectively.

Thermal Properties

TG and DTG thermograms of a sample were recorded by a thermogravimetric analyzer (Perkin Elmer, Pyris 1, Massachusetts, USA). A TPS sample without or with cotton fiber reinforcement was tested under nitrogen atmosphere within a temperature range of 50–600 °C at a heating rate of 10 °C/min. Thermal degradation temperature (T_d) was reported by the onset degradation temperature where the weight loss started to occur. Percentage weight loss was obtained from the onset decomposition temperature determined only for the starch decomposition.

Biodegradation by Soil Burial Test

A composite sample with the dimensions of 20 × 50 mm was buried at approximately 10 cm under the soil surface. The pH and temperature of the soil were maintained at 7 and 32 ± 2 °C, respectively. The water content of the soil was in the range of 30–40% and the weight change was recorded daily for 22 days. Averaged percentage weight change was recorded from three independently tested samples.

Results and Discussion

IR Spectroscopic Study

IR spectra of both TPRS and TPWRS composites without/with cotton fiber reinforcement display the typical profile of polysaccharide and are shown in Fig. 1a and b, respectively. The peak in the range of 1,020–1,030 cm^{-1} and 1,075–1,155 cm^{-1} are attributed to C–O stretching of C–O–C group in the anhydroglucose ring and C–O stretching of C–O–H group, respectively. The wavenumbers in the range of 1,400–1,450 cm^{-1} are assigned for O–H bonding. The peak position approximately at 1,646 cm^{-1} is due to the bound water present in the starch. The band at 2,840–3,000 cm^{-1} is associated with C–H stretching. A broad band due to hydrogen bonded hydroxyl group (O–H) appeared at 3,300–3,500 cm^{-1} and is attributed to the complex vibrational stretching, associated with free, inter and intra molecular bound hydroxyl groups.

For the TPRS and TPWRS composites reinforced with cotton fibers, it can be observed that the broad band at 3,300–3,500 cm^{-1} slightly shifted to lower wavenumber by the addition of cotton fiber. The peak position shift indicates the increasing of intermolecular hydrogen bonding by the addition of cotton fiber. It was known that, if two polymers were compatible, a distinct interaction (hydrogen bonding or dipolar interaction) existed between the chains of one polymer and those of the other, causing the IR spectra of the composites to change (e.g. band shifts, broadening) [15].

X-Ray Diffraction

X-ray diffraction technique is used to identify crystal structure and regular molecular arrangement presented in native and processed starches. The X-ray diffraction patterns of native rice starch, TPRS, cotton fiber and its corresponding composite are shown in Fig. 2. Native rice starch (Fig. 2a) showed a typical A-type X-ray diffraction pattern, typical of cereal crystalline structure, with strong peaks at 2θ of 14.9°, 16.9° and 22.9° [16]. For the TPRS without cotton fiber (Fig. 2b), the majority of starch granules have been gelatinized and hence the glucosidic chains are retrodraded into the V form. The retrograded TPRS sample without cotton fiber reinforcement gives V-type diffraction pattern with the main peaks at 2θ of 13.1° and 20.0° [17]. In cotton fiber (Fig. 2c), the main peaks were observed at 2θ of 18.0°, 22.5° and 25.7°, which are typical of cellulose I structure [18]. Figure 2d shows the diffraction pattern of the TPRS composite and the main peaks are located approximately at 2θ of 13.1°, 18.0°, 20.0°, 22.5° and 25.7°, corresponded to the diffraction patterns from both cotton fiber and TPRS components. Similar result was observed in the thermoplastic corn starch/bacterial cellulose composite [13]. The results indicate that the cotton fiber caused the increase in crystallinity in the TPRS composite.

The X-ray diffraction patterns of native waxy rice starch, TPWRS, cotton fiber and TPWRS composite are shown in Fig. 3. Native waxy rice starch (Fig. 3a) also showed a typical A-type X-ray diffraction pattern with

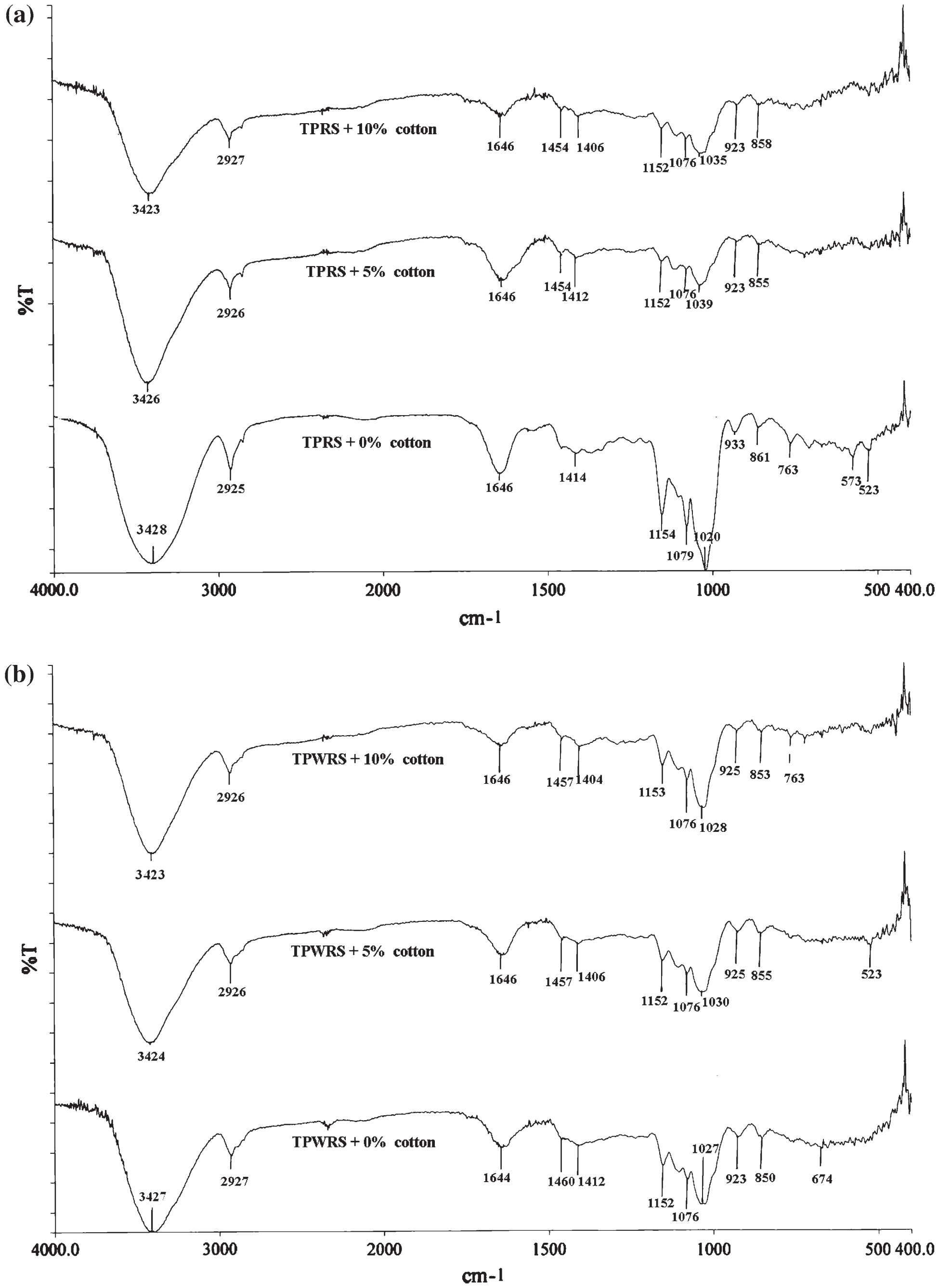

Fig. 1 FT-IR spectra of the **a** TPRS and **b** TPWRS composites with different cotton fiber contents

strong peaks at 2θ of 15.1°, 17.1° and 23.1° [16]. The TPWRS sample without cotton fiber reinforcement (Fig. 3b) showed only main peak at 2θ of 20.2°. Similar to the TPRS composite, the TPWRS composite (Fig. 3d) showed the diffraction peaks from both cotton fiber reinforcement and the TPWRS matrix.

Morphology

Morphological structure of polymer is a very important characteristic because it determines property of polymer. SEM micrographs of the fractured surfaces of the TPRS, TPWRS and their composites are shown in Fig. 4. Rough surfaces of the TPRS and TPWRS sample without cotton fiber reinforcement could be observed as presented in Fig. 4a and d, respectively.

For the TPRS composite reinforced by cotton fiber with 2 mm length, the SEM micrograph in Fig. 4b showed the long cotton fiber embedded into the rice starch matrix and the fiber surface was wetted by rice starch matrix, indicating of the phase compatibility. Similar morphology was found in the TPWRS composite as presented in Fig. 4e. It

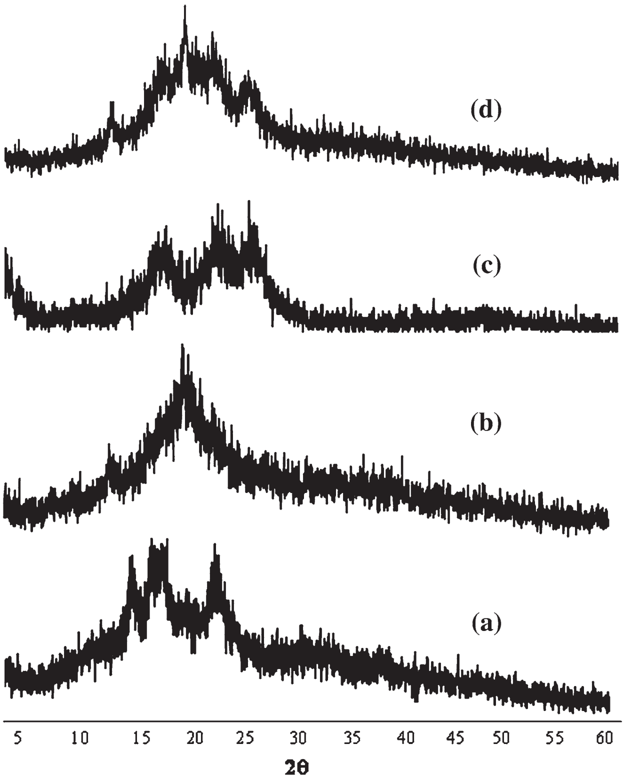

Fig. 2 X-ray diffraction pattern of **a** native rice starch, **b** TPRS, **c** cotton fiber and **d** TPRS reinforced by cotton fiber (10%-2 mm)

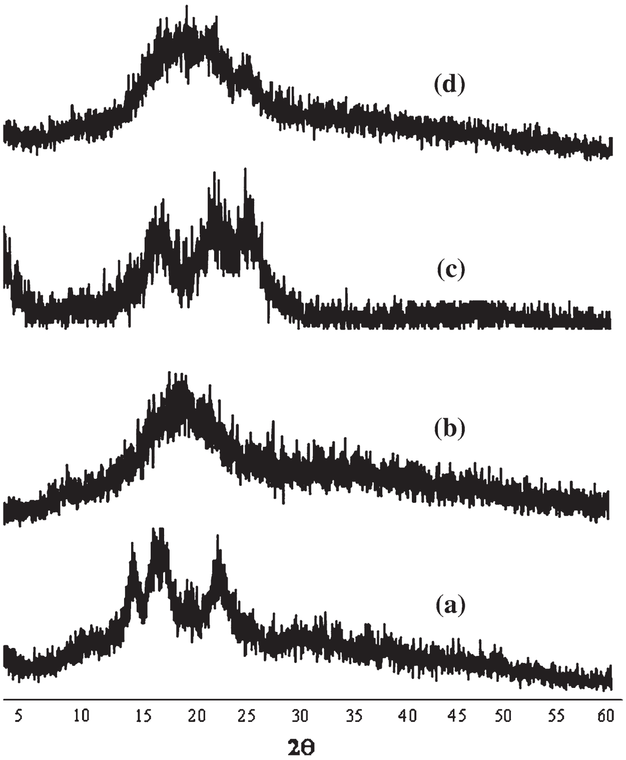

Fig. 3 X-ray diffraction pattern of **a** native waxy rice starch, **b** TPWRS, **c** cotton fiber and **d** TPWRS reinforced by cotton fiber (10%-2 mm)

should be noted that more voids could be observed in the TPWRS composite. The TPRS and TPWRS composites with the addition of 5 mm length cotton fiber (Fig. 4c–f) show the similar morphology as observed in the TPRS and TPWRS composites with the addition of 2 mm cotton fiber (Fig. 4b–e). However, more cracks and voids can be noticed with the use of 5 mm cotton fiber.

Mechanical Properties

Mechanical properties of different TPRS and TPWRS composites are shown in Fig. 5. It can be seen in Fig. 5 that, without cotton fiber reinforcement, the TPRS sample shows higher stress at maximum load and Young's modulus but lower strain at maximum load than those of the TPWRS sample due to the greater amylose content of rice starch causing the stiffness of the starch sample. The results confirmed the earlier report by P. Myllärinen et al. [19] that amylose film showed higher stress but lower strain than amylopectin film. Similarly, the TPRS composite reinforced by cotton fiber also show higher stress at maximum load and Young's modulus but lower strain at maximum load that those of the TPWRS composite.

Figure 5 also shows the relationship between cotton fiber content on the mechanical properties of different TPRS and TPWRS composites. Incorporation of 5% and 10% cotton fiber into either TPRS or TPWRS matrix caused an significant increase in the stress at maximum load (Fig. 5a) and Young' s modulus (Fig. 5b). The results suggest that cotton fiber can reinforce the TPRS and TPWRS matrix due to the similar chemical structure of the fiber and the starch, the increase of hydrogen bond as shown by IR spectra in Fig. 1 and the fiber surface wetting as presented by SEM micrograph in Fig. 4. However, at 15% cotton fiber, stress at maximum load and Young's modulus tended to be maintained. Strain at maximum load also continued to decrease with the increase in the cotton fiber contents. Similar trends have been reported for corn starch or cassava starch/cellulose fibers [7, 8, 13, 14].

When different lengths of cotton fiber is considered, it was found from Fig. 5 that the addition of the 2 mm length cotton fiber into the TPRS and TPWRS composites leaded to greater stress at maximum load and Young's modulus than those of the 5 mm length cotton fiber due to the higher surface area of the low aspect ratio of the cotton fiber. In addition, the use of 10 mm cotton fiber caused more fiber agglomeration as shown in Fig. 4c–f, resulting in the lower stress at maximum load and Young's modulus of the TPRS and TPWRS composites. On the contrary, the addition of the 2 mm length cotton fiber into the TPRS and TPWRS

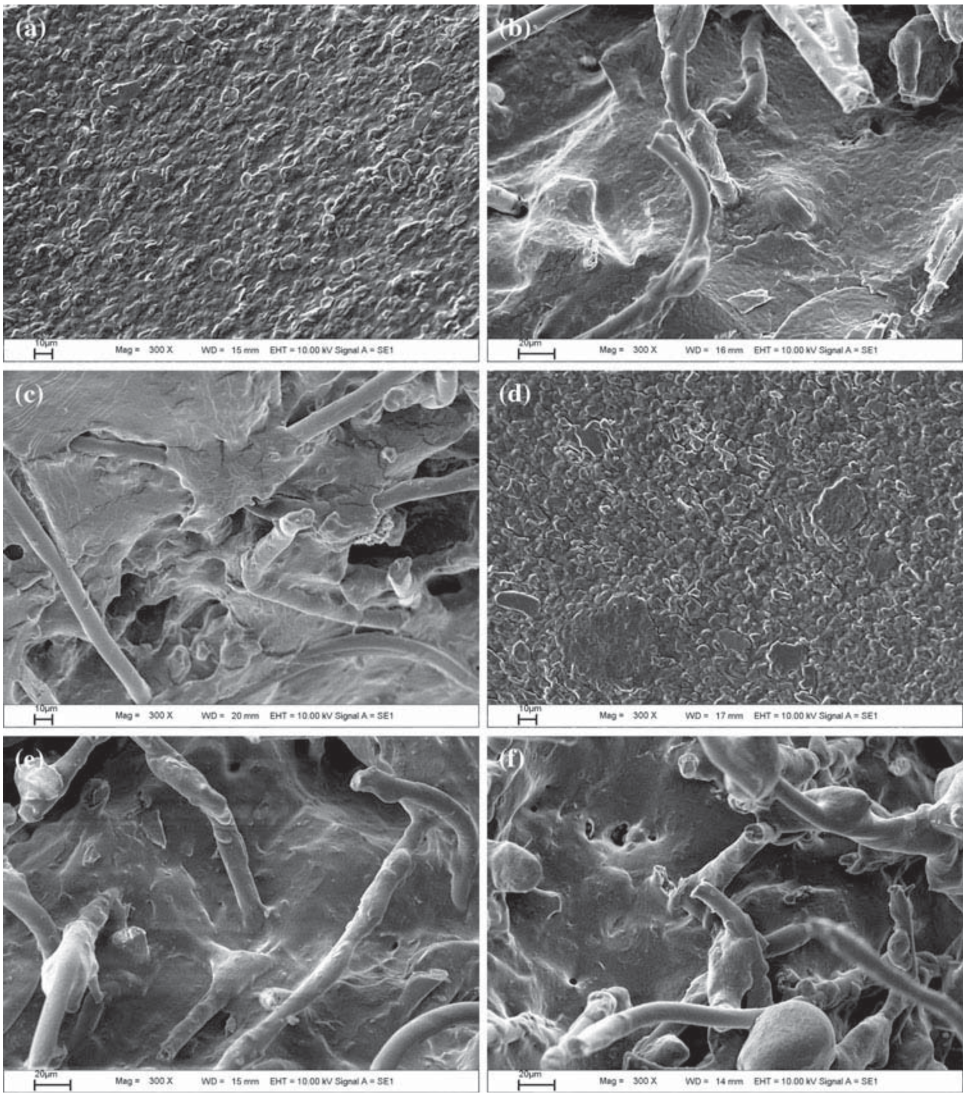

Fig. 4 SEM micrographs of **a** TPRS, **b** TPRS with cotton fibers (10%-2 mm), **c** TPRS with cotton fibers (10%-5 mm), **d** TPWRS, **e** TPWRS with cotton fibers (10%-2 mm), and **f** TPWRS with cotton fibers (10%-5 mm)

matrices leaded to lower strain at maximum load than those of the 5 mm length cotton fiber.

The maximum stress at maximum load and Young's modulus was found for both TPRS and TPWRS with the addition of 10 and 15% cotton fiber; however, strain at maximum load was higher in the TPRS and TPWRS with 10% cotton fiber. In this study, the maximum mechanical properties could be obtained by the use of TPRS and TPWRS matrix reinforced by 10% and 2 mm cotton fiber. The stress at maximum load increased approximately 116 and 82% and the Young's modulus increased approximately 103 and 222% for the TPRS and TPWRS composites reinforced by 10% and 2 mm cotton fibers, respectively. Nevertheless, the strain at maximum load decreased approximately 70.9 and 77.9% for the TPRS and TPWRS composites, respectively.

Water Absorption

Water sensitivity is an important criterion for many applications of TPS materials. The results of water absorption experiments, performed at the temperature of 30 °C and 50% relative humidity, are shown in Fig. 6. It can be seen that the TPRS and TPWRS samples without cotton fiber reinforcement showed the increase of water absorption at the first stage, but the more rapid water absorption was found in the TPWRS sample because of the greater content of the more branched structure of amylopectin molecule. After that, the percentage water absorption tended to increase slowly and reached its maximum within 7 days for the TPRS sample and 4 days for the TPWRS sample.

The addition of cotton fiber into the TPRS and TPWRS matrices clearly caused the decrease of water absorption, as

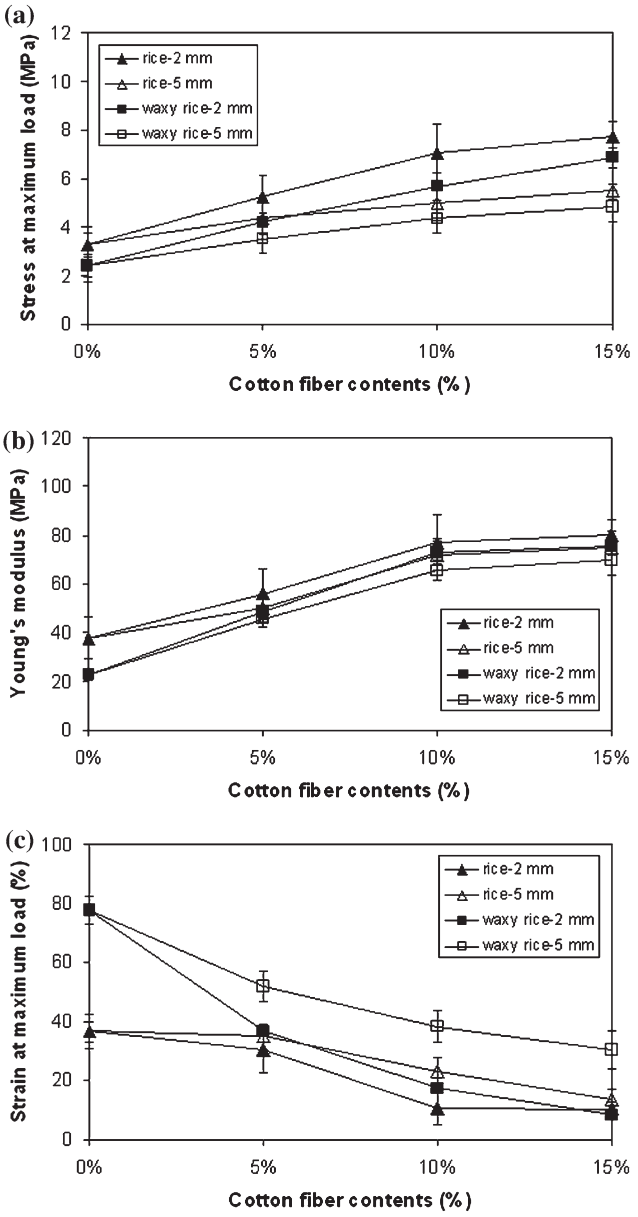

Fig. 5 Mechanical properties of the TPRS and TPWRS composites reinforced by different contents and lengths of cotton fibers **a** stress at maximum load, **b** Young's modulus, and **c** strain at maximum load

presented in Fig. 6. The result is caused by different absorption characteristics between the TPS and cotton fiber. Generally, moisture absorption of cotton fiber is approximately 7.0–8.0%; whereas, it is in the range of 11.5–13.0% for the starch [18]. In addition, the drop of water absorption may also be attributed to the establishment of hydrogen bonding between the fiber and the hydroxyl functional group of TPRS and TPWRS matrix as shown by IR spectra in Fig. 1. It should be mentioned that water absorption of the TPRS and TPWRS composites was relatively high, compared with the water absorption of the native starch and cotton fiber. This could be because starch granules have been gelatinized and retrograded, as shown by XRD patterns in Figs. 2, 3. The lowest water absorption was obtained from the TPRS matrix with the reinforcement of 10%wt cotton fiber. However, cotton fiber length did not show the significant effect on the water absorption of the TPRS and TPWRS composites.

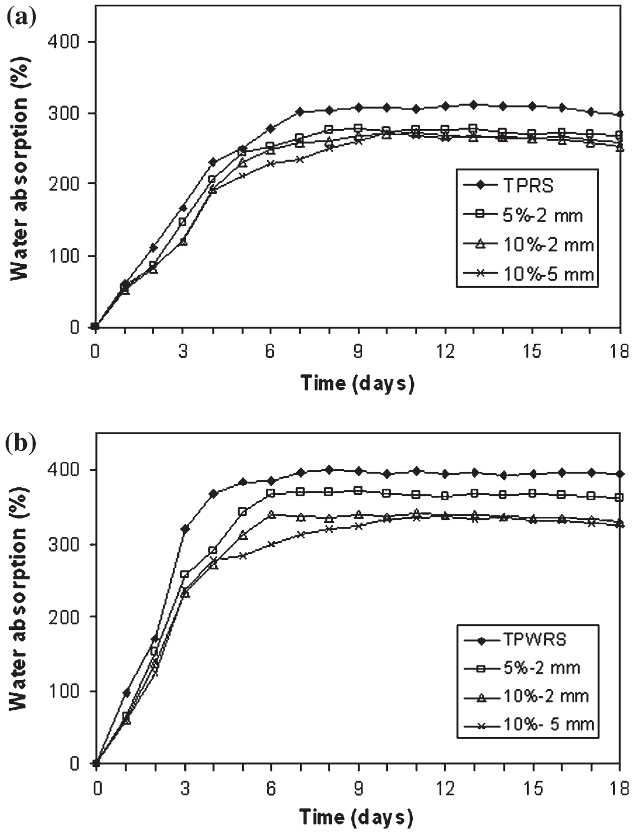

Fig. 6 Water absorption of **a** TPRS and **b** TPWRS composites determined at 30 °C and 50% RH

Thermal Properties

Thermogravimetric analysis of the composite materials was carried out to assess their thermal stability and degradation temperatures. The two weight losses, at around 100 °C and 160 °C were related to the volatilization of water and glycerol, respectively (Fig. 7). The maximum degradation step at 290–310 °C is assigned to the degradation of starch [5]. Cotton fiber also showed the last degradation step at the temperature of approximately 400 °C.

It can be seen in Table 1 that the TPRS and TPWRS composites reinforced by cotton fiber promoted an increase in the onset decomposition temperature of starch. This could be described as the TPRS and TPWRS is phase compatible with cotton fiber by the increase of hydrogen bond linkages as shown in FTIR spectra in Fig. 1. The

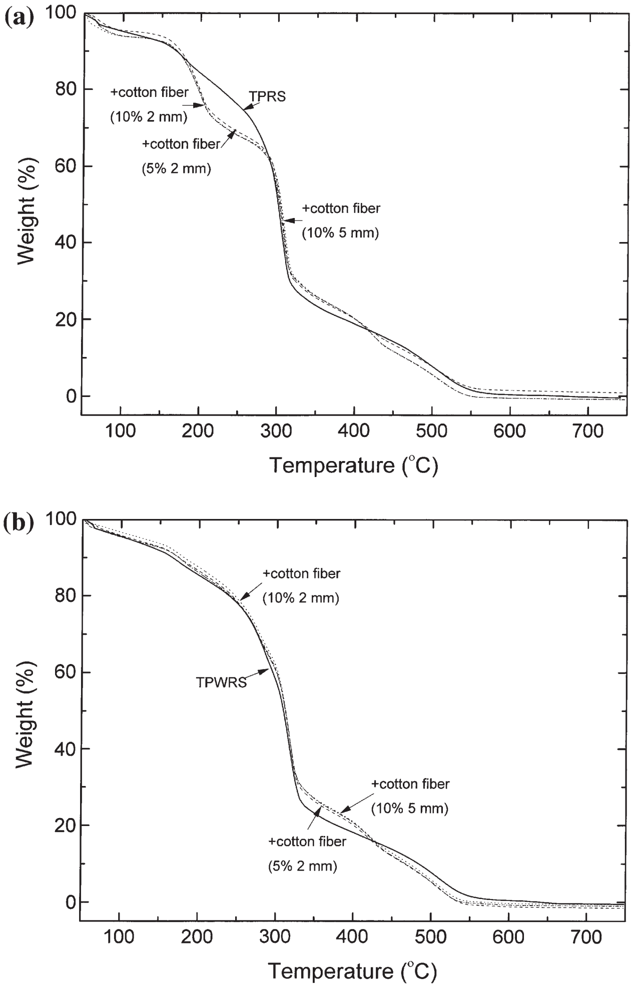

Fig. 7 TGA thermograms of **a** TPRS and **b** TPWRS composites

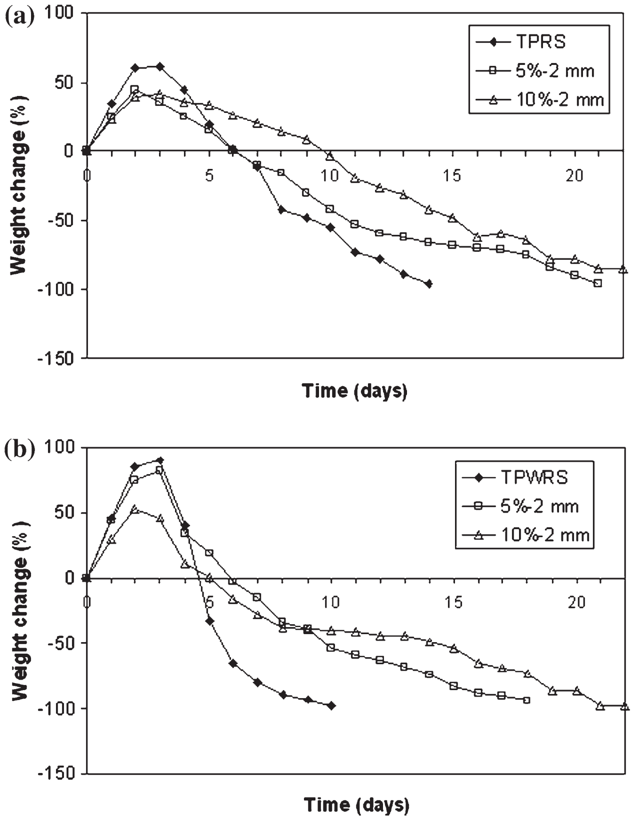

Fig. 8 Weight changes of **a** TPRS and **b** TPWRS composites under soil burial test

addition of low amounts of cotton fibers to the TPRS and TPWRS matrix also resulted in a significant increase in the thermal stability of the composites as indicated by the decrease of percentage weight loss (Table 1), regardless of the cotton fiber contents and lengths. This can be explained by the higher stability of the cotton fibers and particularly by the good compatibility between the two carbohydrate components of the composites [4, 5]. It should be noted that a strong shoulder in the thermogram existed at the temperature range of 150–200 °C was observed only in the TPRS composites. The observed strong shoulder in the thermograms could be probably because of different amounts of non-absorbed glycerol by cotton fiber and starch. This observation was also reported in the TPS/Eucalyptus composite prepared from corn starch [5].

Biodegradation

Biodegradable properties of different TPRS and TPWRS composites can be determined by soil burial test. Figure 8

Table 1 Onset degradation temperatures and percentage weight losses of different TPRS and TPWRS composites

Samples	Onset degradation temperature (°C)			Weight loss (%)
	Step 1 (glycerol)	Step 2 (starch)	Step 3 (fiber)	
TPRS	165.2	294.3	–	59.8
+5%-2 mm	173.5	296.3	400.5	44.9
+10%-2 mm	174.9	297.9	400.7	44.3
+10%-5 mm	170.4	301.0	403.4	48.7
TPWRS	145.5	292.5	–	65.8
+5%-2 mm	150.4	294.9	398.0	63.0
+10%-2 mm	158.7	295.0	407.3	61.7
+10%-5 mm	159.8	295.6	400.2	60.3

showed the percentage weight change of different TPRS and TPWRS composites. All of the composites, showed the increment in weight after a few days of soil immersion due to water absorption from the soil. The result was related to the water uptake as shown in water absorption property in Fig. 6. After that, the sample weight tended to decrease and then the starch sample started to degrade by micro-organisms existed in soil. Especially, the TPWRS sample without cotton fiber reinforcement degraded within 10 days, but the TPRS sample without cotton fiber reinforcement degraded within 14 days. Regardless of starch type, the percentage weight change in the TPRS and TPWRS composites reinforced by cotton fiber was lower than that of the TPRS and TPWRS samples without cotton fiber reinforcement and the TPRS and TPWRS composites degraded within approximately 20 days. This is due to the phase compatibility of the TPRS and TPWRS matrix and cotton fiber reinforcement.

Conclusions

Thermoplastic starch could be prepared from rice and waxy rice starches. It was found that, without cotton fiber reinforcement, the TPRS sample (higher content of amylose) showed higher stress at maximum load, Young's modulus, lower water absorption, higher thermal stability and slower biodegradation in soil than the TPWRS sample (lower content of amylose). For both TPRS and TPWRS composites, mechanical properties increased; however, water absorption decreased by the cotton fiber reinforcement. Thermal degradation temperature and thermal stability of the TPRS and TPWRS composites were also improved by reinforcing with cotton fibers. For biodegradable property, cotton fibers could extend the decay of the TPRS and TPWRS matrices. Cotton fiber contents and lengths greatly affected only the mechanical properties of both TPRS and TPWRS composites. The best optimum properties were obtained from the TPRS with 10% and 2 mm cotton fiber reinforcement.

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Keywords (separated by '-')	Agar - Biodegradable polymer - Fiber - Thermoplastic starch
Footnote Information	

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ORIGINAL PAPER

Effect of Agar and Cotton Fiber on Properties of Thermoplastic Waxy Rice Starch Composites

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R. Kongjindamunee · S. Surakit**

Abstract Biodegradable polymer from thermoplastic waxy rice starch (TPWRS) was prepared by internal mixer and compression molding. Since tensile properties and water uptake of the TPWRS was still the main disadvantages, the TPWRS sample was, therefore, modified by agar and/or cotton fibers. The effect of different ratios of agar:cotton fibers on properties of the TPWRS matrix were also studied. It was found that new hydrogen bonds could be found for the TPWRS matrix with the addition of different ratios of agar: cotton fibers by the detection of IR peak shift. Tensile properties of the TPWRS sample were significantly improved by the addition of agar or cotton fibers and the highest tensile properties were obtained from the TPWRS composite modified with 4:6 agar:cotton fibers. In addition, thermal degradation temperature and thermal stability of the starch were improved by the incorporation of agar and/or cotton fibers. Moreover, color measurement, morphology, water uptake and biodegradability from soil burial test were also examined.

Keywords Agar · Biodegradable polymer · Fiber · Thermoplastic starch

Introduction

Recently, there has been an increasing interest in the development of biodegradable polymers owing to the growing problem of waste disposal of synthetic plastics. Most synthetic plastics cannot decompose naturally, which has caused the serious environmental problem of pollution from the waste polymers. Biodegradable polymers, currently used in packaging, agricultural and medical applications, are polymers such as carbohydrates and proteins which completely degrade by the action of biological organisms.

Starch, one type of carbohydrates, is one of the most studied natural polymers for the production of biodegradable polymers [1]. Starch is totally biodegradable in a wide variety of environmental conditions and that permits the development of totally biodegradable starch products. Starch consists of primarily linear and branched chains of glucose molecules, named as amylose and amylopectin, respectively. Amylose is essentially a crystalline linear molecule with a few branches and is soluble in hot water; whereas, amylopectin is a highly branched molecule and is insoluble in hot water.

Starch exists in a granular form in its natural state, but it can behave like a thermoplastic material in the presence of plasticizers, such as, glycerol, water, sorbitol and others. At high temperature and under shear, it readily melts and flows, allowing it to be processed by injection, extrusion or blow molding, similar to most conventional synthetic thermoplastics. This material is named thermoplastic starch (TPS) [2–9]. Several attempts [2–13] have been made to reduce hydrophilic character and increase tensile properties of TPS, as these limit its use in a wide range of applications.

Blending is a useful method for improving or modifying properties of TPS. TPS has been blended with synthetic polymers such as high-density polyethylene (HDPE) [10], linear low-density polyethylene (LLDPE) [11]; however, the degradation duration is still very high due to the

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non-biodegradable synthetic polymers. In addition, TPS has been reported to be blended with natural polymers such as chitin [12], zein [13], etc. It was found [12] that the incorporation of chitin into thermoplastic corn starch resulted in materials with higher modulus and lower water uptake. Similar results were also reported for thermoplastic corn starch filled with zein protein [13].

Another popular technique for improving properties of TPS is to reinforce TPS with natural fibers. TPS has also been reinforced by natural fibers such as Eucalyptus wood pulp [2], winceyette [3], coconut [6], bacterial cellulose [7], cotton [8, 9], etc. as a suitable reinforcing component for thermoplastic materials. Most of these works focused on tensile properties and have showed that the incorporation of these fibers increases tensile strength and elastic modulus but decreases elongation [2, 3, 6–9]. In addition, a significant improvement in water resistance was also obtained by the addition of cellulose fibers [2, 3, 6–9].

Agar is a cell wall polysaccharide extracted with water from Gelidiaceae and Gracilariaceae families of seaweeds and is a heterogeneous mixture of two polysaccharides: agarose and agaropectin [14–16]. Agarose is a linear polymer based on the—(1,3)-β-D-galactopyranose-(1,4)-3,6-anhydro-α-L-galactopyranose unit. Agaropectin is a heterogeneous mixture of smaller molecules that occur in lesser amounts. Their structures are similar but slightly branched and sulfated and they may have methyl and pyruvic acid ketal substitutes. Because of the ability to form very hard gels at very low concentrations, agar has been used extensively as a gelling agent, thickeners and stabilizers in food industry. Agar has already been made as films and hydrogels [14–16]. It was found that the addition of agar enhanced tensile strength and reduced water vapor permeability of potato starch casted film [14]. Agar was also blend with cassava starch for forming emulsified films using hydrogenated vegetable oil as dispersed phase [15]. It was reported [15] that, with the presence of vegetable oil, tensile strength, elongation and water vapor permeability of the cassava starch casted film were lower than those of agar film. Moreover, improved melting temperature and tensile properties were observed in an agar-poly(vinyl alcohol) blend hydrogel [16]. So far, the effect of agar on the performance of TPS, processed under high temperature and shear force, has not been investigated.

Therefore, both agar and cotton fibers were selected to modify properties the TPS prepared from waxy rice, thermoplastic waxy rice starch (TPWRS). The objective of this work is to study the effect of agar and cotton fibers on properties of TPWRS, with glycerol as plasticizer. Different ratios of agar: cotton fibers were varied to study properties of different TPWRS composites. Various techniques were used to characterize properties of the TPWRS reinforced composites, i.e. FTIR, SEM and TGA. In addition, color measurement, tensile, water uptake and biodegradation properties of different TPWRS composites were also examined.

Materials and Methods

Materials

Waxy rice starch (11.5–13.0% moisture) was obtained from Bangkok Interfood (Bangkok, Thailand), containing 5 ± 1%wt amylose and 95 ± 2%wt amylopectin. Glycerol (plasticizer) was purchased from Lab System Co. Ltd. (Thailand). Agar (*Gelidium amansii*) and cotton fibers (*Gossypium herbaceum*) were obtained locally and used as-received.

Sample Preparation

Waxy rice starch was firstly pre-mixed with glycerol in polyethylene bag and left overnight. The weight ratio of waxy rice starch and glycerol was maintained at 2:1. Blending was carried out using a high-speed mixer (Lab-Tech Engineering, Thailand) at the temperature of 150 °C with the rotor speed of 50 rpm for 5 min. in order to obtain a homogeneous material. The processed sample was then compressed at the temperature of 150 °C into 2 mm thick plates. Under the processing condition, the crystal structure of the native starch was changed into V-type. The same processes were also used for the preparation of different TPWRS composites. The property modification of different TPWRS composites was carried out by using different ratios of agar:cotton fibers, i.e. 0:0, 10:0, 8:2, 6:4, 4:6, 2:8 and 0:10. It should be noted that the content of agar and/or cotton fibers was maintained at 10% by weight of the TPWRS composite. The averaged length of each fiber was roughly 2 mm, giving L/D ratio of approximately 450:1.

IR Spectroscopic Study

FTIR spectra of a composite sample were recorded on a Spectrum 2000 GX spectrometer (Perkin Elmer, USA) using KBr disk technique with a resolution of 4 cm^{-1} in a spectral range of 4,000–600 cm^{-1} using 16 scans per sample.

Color Measurement

Color parameters i.e. L^*, a^*, and b^* were measured with the Miniscan XE plus Spectrophotometer (Hunterlab, USA) using D65/10° illuminant evaluated by CIE $L^* a^* b^*$ system. In this system, L^* represented lightness, a^* redness if positive and greenness if negative and b^* yellowness if positive and blueness if negative. In addition, C^* and H^0 showed chroma and hue angle in color space of a composite, respectively. C^* and H^0 could be calculated from the following equations:

$$C^* = \sqrt{a^{*2} + b^{*2}} \tag{1}$$

$$H^0 = \tan^{-1}\frac{b^*}{a^*} \tag{2}$$

It should be noted that ten measurements were carried out for each composite to obtain averaged color parameters.

Morphology

A LEO 1455 VP scanning electron microscope (Oberkochen, Germany) was employed to study the morphology of a composite sample. Each tested sample was sputter-coated with a thin layer of gold to prevent electrical charge during observation and a composite was immersed into liquid nitrogen before being fractured.

Tensile Properties

Tensile tests were conducted according to ASTM D-638 at the temperature of 23 ± 1 °C and relative humidity of 60 ± 5%. A tensile measurement of each dumbbell-shaped specimen was carried out using a Universal Testing Machine (Lloyd Instrument, LR 5 K, West Sussex, UK) with a 100 N load; the crosshead speed was maintained at 40 mm/min. It should be mentioned that the tensile property results of a composite sample were obtained by averaging the measurement results of ten independent samples.

Water Uptake

Newly prepared sample was dried by a hot-air oven at 105 °C for 3 h and then stored at 50% relative humidity at a temperature of 30 ± 2 °C prior to water uptake evaluation. The 50% relative humidity was obtained using a saturated solution of $CaCl_2$ in a closed vessel. The amount of water absorbed by a composite sample was determined until the constant weight was obtained. The percentage of water uptake was calculated as follows:

$$\text{Water uptake} = (W_2 - W_1)/W_1 \times 100 \tag{3}$$

where W_2 and W_1 were the wet weight and the dried weight of a sample, respectively.

Thermal Properties

TG and DTG thermograms of a composite specimen were recorded by a thermogravimetric analyzer (Perkin Elmer, Pyris 1, Massachusetts, USA). A composite sample was tested under nitrogen atmosphere within a temperature range of 50–600 °C at a heating rate of 10 °C/min. Thermal degradation temperature (T_d) was reported by the onset degradation temperature where the weight loss started to occur. Percentage weight loss was obtained from the onset decomposition temperature determined only for the starch decomposition.

Biodegradation by Soil Burial Test

A rectangular composite sample with the dimensions of $20 \times 50 \times 2\ \text{mm}^3$ was buried in soil, approximately 10 cm under the soil surface. The pH and temperature of the soil were measured daily and were approximately at 7 ± 1 and 32 ± 2 °C, respectively. The water content of the soil was in the range of 10–20% and the weight change was recorded daily for 90 days. Averaged percentage weight change was recorded from three independently tested samples.

Results and Discussion

IR Spectroscopic Study

IR spectrum of the TPWRS sample (0:0) presented in Fig. 1 shows the typical pattern of polysaccharide. The wavenumber in the range of 1,400–1,450 cm^{-1} was assigned for O–H bending. The peak position located approximately at 1,650 cm^{-1} was caused by the bound water present in the starch. The band approximately at 2,900 cm^{-1} was characteristic of C–H stretching from CH_2 and/or CH_3. A broad band appeared at 3,300–3,500 cm^{-1} was attributed to hydrogen bonded hydroxyl group (O–H) from the complex vibrational stretching, associated with free, inter and intra molecular bound hydroxyl groups.

Since agar consists of polysaccharides, i.e. agarose and agaropectin, the chemical structure of starch and agar are quite similar. The main functional group of agarose and agaropectin is also hydroxyl groups. Therefore, the addition of agar into the TPWRS matrix (10:0) showed the similar IR peak positions and no distinct new peak position could be observed (Fig. 1). Nevertheless, the addition of cotton fibers into the TPWRS matrix (4:6 and 0:10) as shown in Fig. 1 caused the new wavenumber at around 720 cm^{-1}, assigned for CH_2 rocking arisen from cotton fibers.

The analysis of FT–IR spectra of polymer blends enabled the hydrogen bond interactions to be identified [17]. It was known that, if two polymers were compatible, a distinct interaction (hydrogen bonding or dipolar interaction) existed between the chains of one polymer and those

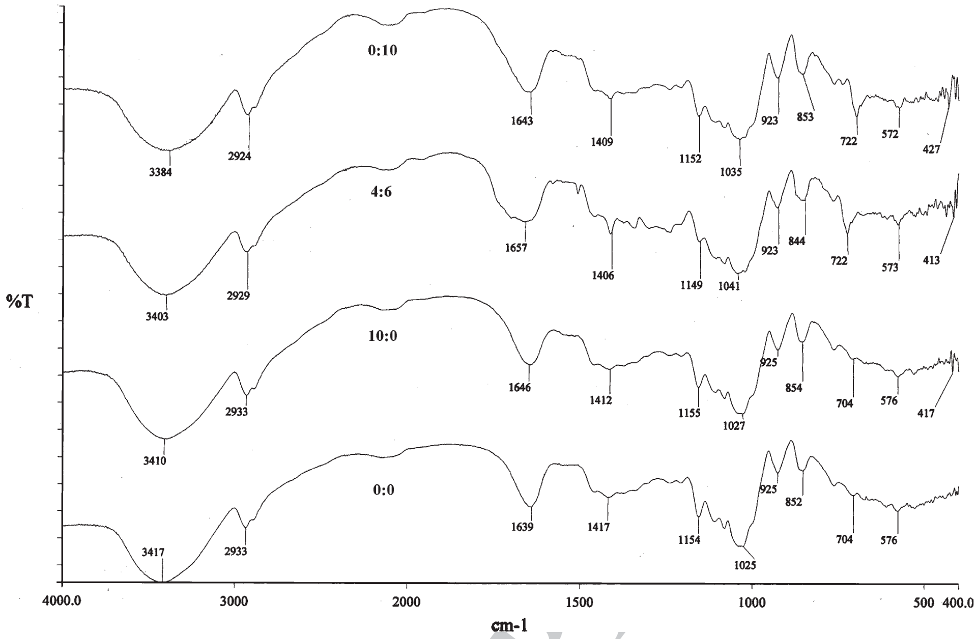

Fig. 1 FT–IR spectra of different TPWRS composites with the addition of different ratios of agar:cotton fibers **a** 0:0 **b** 10:0 **c** 4:6 and **d** 0:10

of the other, causing the IR spectra of the composites to change (e.g. band shifts, broadening) [17, 18]. For different TPWRS composites modified by different ratios of agar:cotton fibers (Fig. 1), it can be observed that the broad band at 3,300–3,500 cm^{-1} (O–H stretching) and also the single band at 1,417 cm^{-1} (O–H bending) slightly shifted to lower wavenumber. The peak position shift indicates the increasing of intermolecular hydrogen bonding in the TPWRS composites by the addition of agar and cotton fibers.

Color Measurement

Color difference between the TPWRS and their composites can be identified using colorimeter. Color parameters of different TPWRS composites with the modification of agar and/or cotton fibers were measured and presented in Table 1. It was found that the addition of agar into the TPWRS matrix (10:0) caused the reduction of the lightness of the TPWRS sample (0:0). On the other hand, the lightness of the sample increased with the inclusion of cotton fibers, especially with the highest content of cotton fibers (0:10).

For a^* (redness–greeness), all composites showed red color in nature but different TPWRS composites with the incorporation of different ratios of agar and cotton fibers caused more redness than that of the TPWRS without any modification. b^* value presents yellowness and blueness and it was observed that all composites represented yellow color without significant difference.

Chroma or C^* was found to increase slightly for the TPWRS matrix with the addition of agar and/or cotton fibers, regardless of different ratios of agar: cotton fibers. Hue angle shown by H^0 value was changed with the use of agar and/or cotton fibers. The TPWRS sample showed hue angle in yellow color; whereas, the TPWRS composites with agar and/or cotton fibers showed hue angle in red–yellow color. The color measurement data indicates that the inclusion of agar and/or cotton fibers into the TPWRS matrix caused a slight change in the overall color.

Table 1 Color parameters of different TPWRS composites

TPWRS (agar:cotton fibers)	L^*	a^*	b^*	C^*	H^0
0:0	40.1	1.1	24.4	24.2	87.6
10:0	29.5	8.3	26.4	27.7	72.5
8:2	39.1	9.2	28.4	29.9	72.1
6:4	36.7	10.1	28.6	30.3	70.6
4:6	45.1	6.7	27.3	28.2	76.1
2:8	48.4	6.6	28.8	29.5	77.1
0:10	52.7	3.8	26.9	27.2	81.9

Morphology

Morphology of different TPWRS composites as presented in Fig. 2 was examined by SEM technique. It was shown by Fig. 2a that the fractured surface of the TPWRS sample (0:0) was homogeneous and smooth but the addition of agar into the TPWRS matrix (10:0) still gave the homogeneous material but with the grooved fracture surface (Fig. 2b), indicating of the phase compatibility between the TPWRS and agar components.

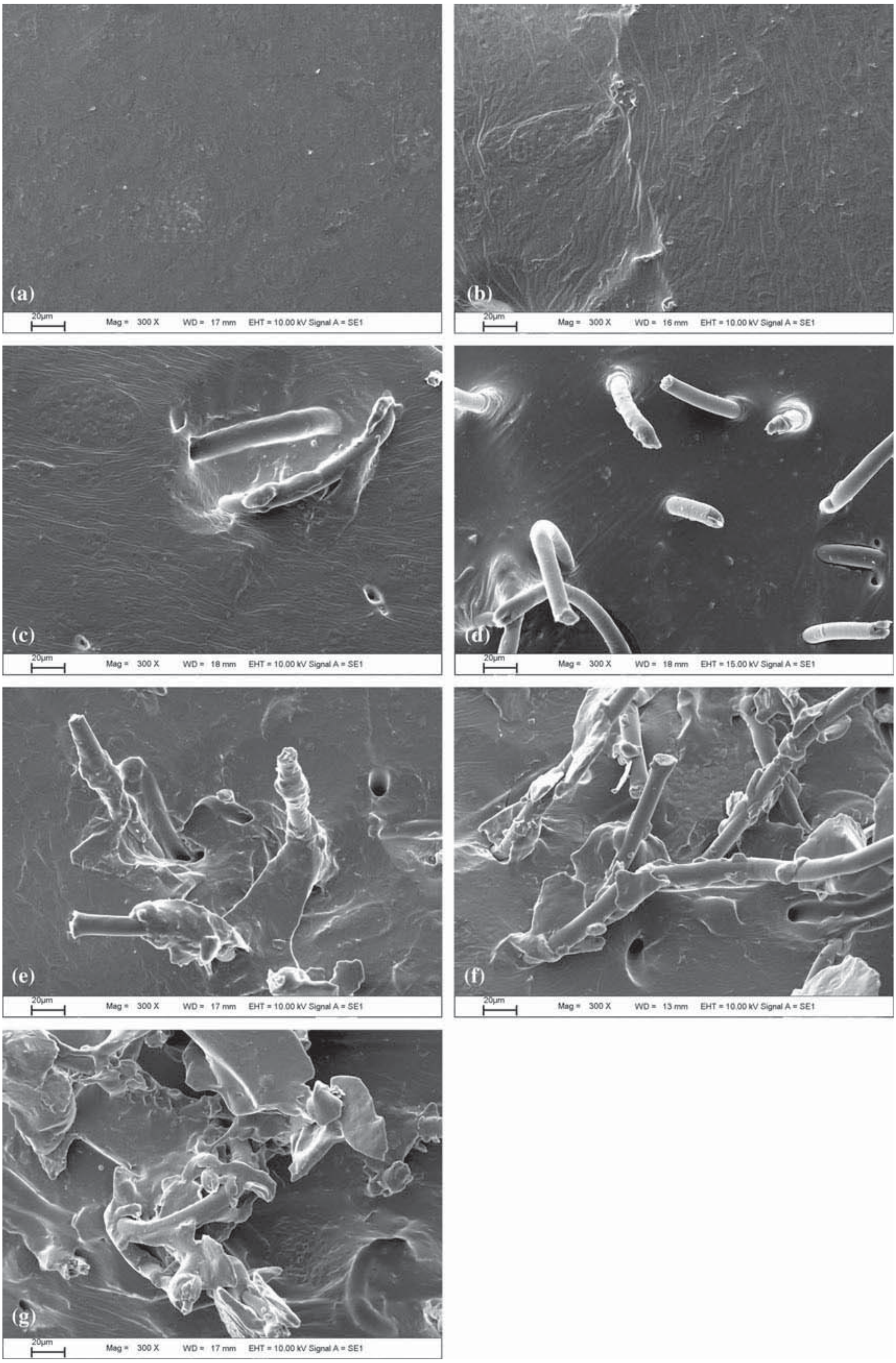

Fig. 2 SEM micrographs of fracture surfaces of different TPWRS composites with the addition of different ratios of agar:cotton fibers **a** 0:0 **b** 10:0 **c** 8:2 **d** 6:4 **e** 4:6 **f** 2:8 and **g** 0:10

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The incorporation of both agar and cotton fibers into the TPWRS matrix (at the ratios of 8:2, 6:4, 4:6 and 2:8) showed that the cotton fiber reinforcements were embedded randomly in the TPWRS matrix (Fig. 2c–f). In addition, the cotton fiber surfaces were wetted by the TPWRS matrix as presented in Fig. 2c–f, indicating of good interfacial adhesion arisen from the structural compatibility between the cotton fiber reinforcement and the TPWRS matrix. Moreover, the inclusion of only cotton fibers into the TPWRS matrix (0:10) also caused the fiber surface wetting as shown in Fig. 2g.

Tensile Properties

Tensile properties of different TPWRS composites are shown in Fig. 3. It was found that the stress at maximum load and Young's modulus of the TPWRS matrix increased by the addition of either agar (10:0) or cotton fibers (0:10). This is due to the similar chemical structures of the starch, agar and cotton fiber, leading to the increase of hydrogen bonds observed by IR peak shifts in (Fig. 1). The increase of the stress at maximum load and Young's modulus was also caused by the good phase compatibility between the starch and agar components (Fig. 2b) or by the cotton fiber surface wetting (Fig. 2g). It should be noted that the stress at maximum load and Young's modulus of the TPWRS matrix added by cotton fibers (0:10) were apparently higher than that of added by agar (10:0), possibly due to the fibrous nature of cotton fibers.

When different ratios of agar:cotton fibers were considered, it was noticed that the increasing content of cotton fibers (at the ratios of 10:0, 8:2 and 6:4) tended to cause higher stress at maximum load and Young's modulus but the highest stress at maximum load and Young's modulus was obtained from the TPWRS composite added by agar and cotton fibers at the ratio of 4:6. After that, at higher content of cotton fiber (at the ratios of 2:8 and 10:0), the stress at maximum load and Young's modulus tended to decrease. Nevertheless, the incorporation of both agar and cotton fibers into the TPWRS matrix at the ratio of 4:6 caused higher stress at maximum load and Young's modulus than that of only cotton fibers at the ratio of 0:10. The results indicates that tensile properties of the TPWRS matrix can be best improved by using 4:6 agar:cotton fibers, causing approximately 120 and 1,100% increase of the stress at maximum load and Young's modulus, respectively.

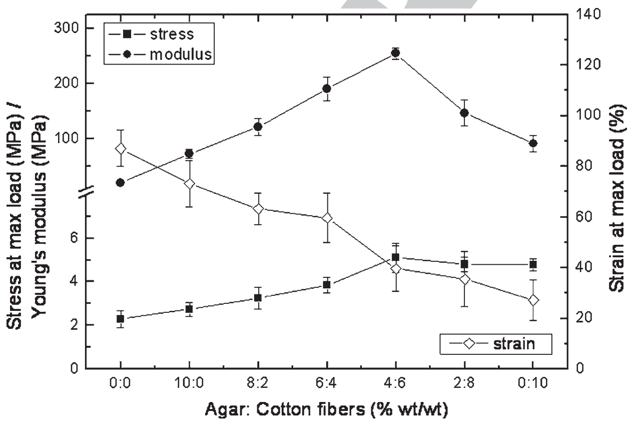

Fig. 3 Tensile properties of different TPWRS composites

For the strain at maximum load (Fig. 3), it was found that the addition of either agar (10:0) or cotton fibers (0:10) clearly caused the reduction of the strain at maximum load, especially for cotton fibers. The increase content of cotton fibers also dropped the strain at maximum load. This is caused by the low extendibility of cotton fibers. Similar increase of stress and decrease of strain for different TPS materials have been reported for corn, cassava, rice or waxy rice starch/cellulose fibers [2, 3, 7–9].

Water Uptake

Water uptake is a significant concern for many applications of TPS materials. The results of water uptake experiments, performed at the temperature of 30 °C and 50% relative humidity, are shown in Fig. 4. It can be seen that the TPWRS sample without modification showed the increase of water uptake during the 7 days of testing. After that, the percentage water uptake tended to increase slowly and reached its maximum within 10 days.

The TPWRS matrix modified by 10:0 and 8:2 agar: cotton fibers caused the similar value of water uptake of the TPWRS composites, as presented in Fig. 4 even though agar can form gel and absorb water into its gel structure [14]. Generally, moisture absorption of cellulose fibers is

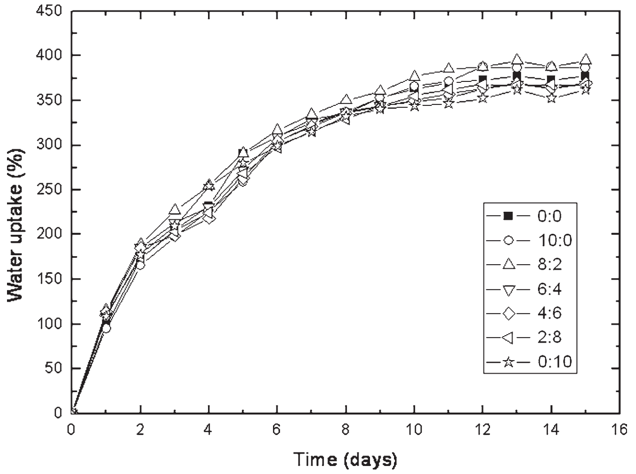

Fig. 4 Water uptake of different TPWRS composites with the addition of different ratios of agar:cotton fibers

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apparently lower than starch [19, 20]. Therefore, the addition of more content of cotton fibers into the TPWRS matrix caused the slightly drop of water uptake of the TPWRS composites. Similar observation was also reported for TPS reinforced by cellulose fibers [6, 7, 10–13].

Thermal Properties

Thermal stability and degradation temperatures of different TPWRS composites were examined using TG technique. The two weight losses, at around 100 and 160 °C were related to the volatilization of water and glycerol, respectively (Fig. 5). The degradation step at about 270 °C was attributed to the degradation of agar [21] and also of the waxy rice starch [9]. The maximum degradation step at approximately 310 °C was assigned to the degradation of starch [2]. Cotton fibers also showed the last onset degradation step at the temperature around of 350 °C.

It can also be seen in Table 2 that the TPWRS composites modified by agar (10:0) caused an increase in the onset decomposition temperature of starch. This could be described as the TPWRS matrix formed new hydrogen bond linkages with agar as shown in FTIR spectra in Fig. 1. The inclusion of cotton fibers into the TPWRS matrix (0:10) also increased the onset degradation temperature of starch. By the use different ratios of both of agar and cotton fibers, the onset degradation temperatures of the TPWRS matrix also increased as shown in Table 2. The results reveal that the onset degradation temperature of the TPWRS matrix can be improved by using agar, cotton fibers or the combination of agar and cotton fibers.

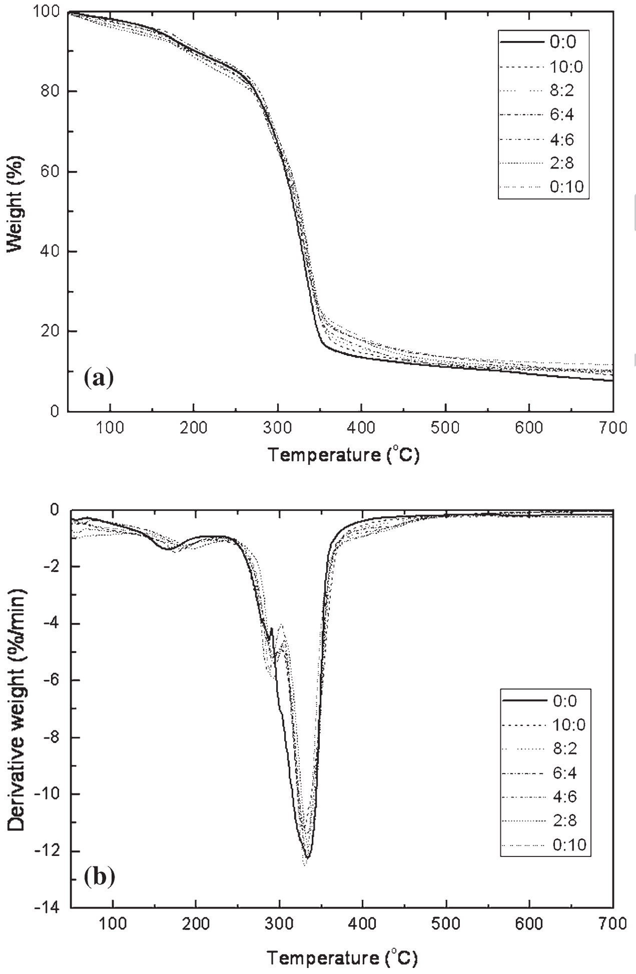

Fig. 5 **a** TG and **b** DTG thermograms of different TPWRS composites with the addition of different ratios of agar:cotton fibers

It was also found that thermal stability of different TPWRS composites were significantly increased, as indicated by the decrease of percentage weight loss (Table 2), by the addition of only low contents of agar and/or cotton fibers into the TPWRS matrix. No significance difference in weight loss was found for different TPWRS composites modified by different ratios of agar:cotton fibers. Similar improved thermal stability of TPS/natural fibers was observed in different TPS from corn starch/Eucalyptus fiber [2], corn starch/winceyette fiber [3], rice starch/cotton fiber [8], waxy rice starch/cotton fiber [9]. This can be explained by the higher thermal stability of the fibers.

Biodegradation

Soil burial test was carried out in order to determine biodegradability of different TPWRS composites. The results in Fig. 6 showed that all of the TPWRS composites presented the increment in weight after a few days of soil immersion due to water uptake from the soil. After that, the composite weight tended to decrease and then the TPWRS composites continued to degrade by micro-organisms existed in soil and also by hydrolysis. After 90 days, the percentage weight change of the TPWRS matrix modified by different ratios of agar:cotton fibers were approximately −8.1, −10.2, 9.7 and −8.6%, for the ratios of 0:0, 10:0, 4:6 and 0:10, respectively. The results suggest that the TPWRS composites with the modification of agar and/or cotton fibers can degrade similar as the TPWRS without the modification.

Conclusions

Properties of the TPWRS sample could be modified by agar and/or cotton fibers. The IR peak shifts were observed when agar and/or cotton fibers were incorporated into the TPWRS matrix. It was also found that the highest lightness, lowest redness and lowest water uptake was found in the TPWRS with the addition of cotton fiber (0:10). Tensile properties of the TPWRS matrix was also higher with the addition of cotton fiber than those of agar; however, the

Table 2 Thermal degradation temperatures and weight losses of different TPWRS composites

Agar:Cotton fibers	Onset degradation temperature (°C)				Weight loss (%)
	Step 1 (glycerol)	Step 2 (agar)	Step 3 (starch)	Step 4 (fiber)	
0:0	162.0	–	309.0	–	63.0
10:0	157.6	270.2	319.9	–	54.2
8:2	164.2	275.3	317.2	356.7	52.9
6:4	158.4	272.6	319.2	354.2	51.9
4:6	153.7	272.9	315.3	355.8	52.2
2:8	168.0	279.7	323.0	357.2	50.8
0:10	164.9	–	320.6	350.5	52.7

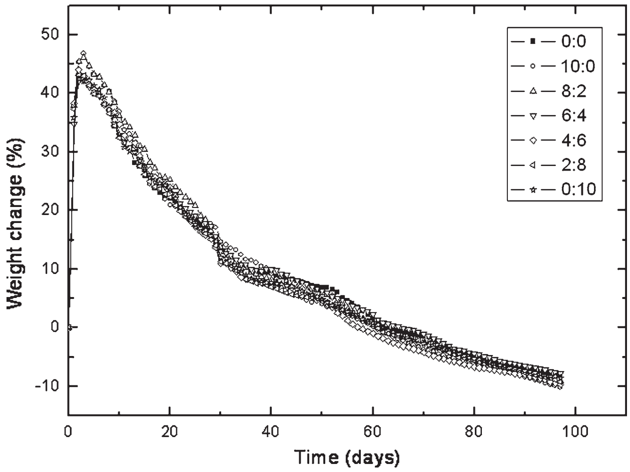

Fig. 6 Weight changes of different TPWRS composites with the addition of different ratios of agar:cotton fibers

highest stress at maximum load and Young's modulus was found in the TPWRS matrix with the inclusion of both agar and cotton fibers at the ratio of 4:6. Onset degradation temperature and thermal stability of the TPWRS matrix were also improved by the use of agar and/or cotton fibers, regardless of different ratios of agar:cotton fibers. In addition, the TPWRS composites with the incorporation of agar and/or cotton fibers could degrade similar as the TPWRS without any modification. The best optimum properties were obtained from the TPWRS composite with the addition of both agar and cotton fibers at the ratio of 4:6.

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Effect of silk protein fibers on properties of thermoplastic rice starch

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Abstract

Biodegradable polymer was prepared as thermoplastic starch (TPS). Due to poor mechanical properties and high water absorption of TPS, thermoplastic rice starch (TPRS) was modified by reinforcing with natural silk protein fibers, as an alternative choice of fiber reinforcement. Different contents and lengths of silk fibers were varied and used as the reinforcement. Internal mixer and compression molding machine were used to mix and shaped the TPRS/silk composites. It was found that stress at maximum load and Young's modulus of the TPRS/silk composites significantly increased with the incorporation of silk fibers. Water absorption of the TPRS/silk composites was also dropped by the addition of silk fibers. Moreover, thermal degradation temperatures of the TPRS/silk composites shifted to higher temperatures by the inclusion of the silk fibers. Functional group analysis and X-ray diffraction patterns were analyzed by FI-IR and XRD techniques, respectively. Furthermore, color measurement, morphology and biodegradation by soil burial test were carried out for different TPRS/silk composites.

Keywords: biodegradable polymer, mechanical properties, polymer composites

Introduction

The growing use of biodegradable polymers leads to an increasing research interest for improving mechanical properties, decreasing cost and lessening environmental problems. Starch is a potentially useful material for biodegradable polymers because of its natural abundance and low cost. Starch is a low cost material in comparison to most synthetic thermoplastics and is readily available. Starch has been investigated widely for the potential manufacture of products such as water soluble pouches for detergents and fertilizers, flushable liners and bags including medical delivery devices [1]. In recent years, thermoplastic starch (TPS)-plasticized starch processed under high temperature and high shear force-has attracted considerable attention and has offered an interested alternative for synthetic polymers where long-termed durability is not needed and rapid degradation is an advantage. However, compared with conventional synthetic thermoplastics, biodegradable products based on TPS, unfortunately, still exhibit many disadvantages, such as water sensitivity, brittleness and poor mechanical properties [2-8].

In order to improve properties of TPS, many researches reported results on the addition of natural cellulose fibers, such as Eucalyptus wood pulp [2], winceyette [3], ramie [5], bacterial cellulose [6], cotton [7], sisal [8], etc. as a suitable reinforcing component for thermoplastic materials. Most of these works focused on mechanical properties and showed that the incorporation of these fibers into TPS caused the increase of tensile strength and elastic modulus but the decrease of elongation [2-8]. In addition, a significant improvement in water resistance was also obtained by the addition of cellulose fibers [2-4, 6-7]. Moreover, thermal stability of TPS was stated to improve by higher thermal resistance of cellulose fibers [2-4, 7]. It can be observed that these fibers are selected because of their composed cellulose structures and of the structural compatibility between starch and cellulose fibers; nevertheless, natural silk protein fibers have not been used as reinforcement in TPS.

Silk fibers are fine, strong, continuous filaments produced by the larva of certain insects, especially the silkworm, when constructing their cocoons. The best-known type of silk is obtained from the cocoons of the larvae of the mulberry silkworm *Bombyx mori* reared in captivity (sericulture). They are often used for clothing, furnishing and upholstery applications [9-10].

The silk polymer is a chain of amino acids forming a protein (polypeptide) called fibroin. The fibroin in silk is composed of 15-18 amino acids, depending on the type of silk fiber. Three amino acids- glycine, alanine and serine- make up approximately 86% of the fibroin polymer [9]. These are not bulky amino acids because their substitution groups are small. Silk is estimated to be 70-75% crystalline and correspondingly 25-30% amorphous. The main chains lie close enough together that numerous hydrogen bonds are formed. Ionic bonds are formed also but are not the major force of attraction between the fibroin chains [9]. Silk is one of the strongest natural fibers and shows high strength, elongation and also toughness. Moreover, silk shows high softening temperature and it decomposes at high temperature [9]. As the main chain of the silk fibroin is polypeptide, silk fibers are expected to form hydrogen bonds with the cellulose chain of the TPRS matrix; therefore, properties of TPS could be modified using silk fibers as reinforcement and as an alternative fiber other than cellulose fibers.

In this present work, thermoplastic rice starch (TPRS) was prepared and reinforced by silk fibers. The effect of silk contents and lengths on properties of the TPRS/silk composites was examined. Various techniques were used to characterize properties of the TPRS/silk composites, i.e. FTIR, SEM and TGA. In addition, color measurement, mechanical, water absorption and biodegradation properties of different TPRS/silk composites were also examined. Properties of the TPRS/silk composite were also compared with TPRS/cotton composite.

Materials and Method

Materials

Rice starch (11.5%-13.0% moisture) was obtained from Bangkok Interfood (Bangkok, Thailand), containing 20 ± 1 %wt amylose and 75 ± 2 %wt amylopectin. Glycerol (plasticizer) and stearic acid (processing aid) were purchased from Lab System Co. Ltd. (Thailand). Degummed silk fibers (*Bombyx mori*) were obtained from Jul Thai Silk, Co. Ltd. (Petchaboon, Thailand). The averaged diameter of the silk fiber was 9.6 ±1.5 μm. Cotton fibers (*Gossypium herbaceum*) with the averaged diameter of 10.3 ±1.2 μm were obtained locally and used as received.

Sample preparation

Rice starch was firstly pre-mixed with glycerol in polyethylene bag and left overnight. The weight ratio of rice starch and glycerol was maintained at 2:1. The TPRS/silk composite was contained 2 wt% of stearic acid by weight of starch. Blending of the TPRS matrix and the silk fiber reinforcement was carried out using a high-speed mixer (Lab-Tech Engineering, Thailand) at the temperature of 160°C at the rotor speed of 40 rpm for 5 min. in order to obtain a homogeneous material. The processed composite was then compressed at the temperature of 170°C into 2 mm thick plates. Different contents of silk fiber, i.e. 0%, 5%, 10% and 15% were added into the TPRS matrix and the different lengths of silk fiber was roughly 2 mm, 5 mm and 10 mm, corresponding to the L/D ratios of approximately 205/1, 520/1 and 1040/1, respectively. For comparison, cotton fibers were manually cut into 2 mm length, corresponded to the L/D ratio of approximately 195/1. The TPRS/cotton fiber composite was then prepared at the same processing conditions as that of the TPRS/silk composites.

IR spectroscopic study

FTIR spectra of a composite specimen were recorded on a Spectrum 2000 GX spectrometer (Perkin Elmer, USA) using KBr disk technique with a resolution of 4 cm^{-1} in a spectral range of 4000-600 cm^{-1} using 16 scans per sample.

X-ray diffraction

Wide angle X-ray diffraction measurements were carried out using a D8 Advance X-ray diffractometer (Bruker, Madison, USA), with CuK_α radiation (wavelength 0.1542 nm) operating at 40 kV and 35 mA. The scattering angle (2θ) covered the range from 3° to 60° (θ is the Bragg angle) with a step size of 0.02° and a sampling interval of 10s.

Water absorption

A newly prepared composite was dried at 105°C for 3 h and then stored at 50% relative humidity at a temperature of 30±2 °C prior to water absorption evaluation. The 50% relative humidity was obtained using a saturated solution of $CaCl_2$ in a closed vessel. The percentage of water absorption was calculated as follows:

$$\text{Water absorption} = (W_2 - W_1)/W_1 \times 100$$

where W_2 and W_1 are the wet weight and the dried weight of a composite sample, respectively.

Morphology

A JEOL-6400 scanning electron microscope (Tokyo, Japan) was employed to study the morphology of a composite sample. Each tested sample was sputter-coated with a thin layer of gold to prevent electrical charge during observation and a composite was immersed into liquid nitrogen before being fractured.

Mechanical properties

Mechanical tests were conducted according to ASTM D-638 at the temperature of 23±1°C and relative humidity of 60±5%. A mechanical measurement of each dumbbell-shaped specimen was carried out using a Universal Testing Machine (Lloyd Instrument, LR 5K, West Sussex, UK) with a 100 N load; the crosshead speed was maintained at 40 mm/min. It should be noted that the mechanical property results of a composite were obtained by averaging the measurement results of ten independent specimens.

Thermal properties

TG and DTG thermograms of a composite specimen were recorded by a thermogravimetric analyzer (Perkin Elmer, Pyris 1, Massachusetts, USA). A composite sample was tested under nitrogen atmosphere within a temperature range of 50-700°C at a heating rate of 10°C/min. Thermal degradation temperature (T_d) was reported by the onset degradation temperature where the weight loss started to occur. Percentage weight loss was obtained from the onset decomposition temperature determined only for the starch decomposition.

Biodegradation by soil burial test

A rectangle composite sample with the dimensions of 20×50 mm was buried at approximately 10 cm under the soil surface. The pH and temperature of the soil were maintained at 7 and 32 ± 2°C, respectively. The water content of the soil was in the range of 30-40% and the weight change was recorded daily for 30 days. Averaged percentage weight change was recorded from three independently tested samples.

Results and Discussion

IR spectroscopic study

IR spectrum of the TPRS sample without silk fiber reinforcement displays the typical profile of polysaccharide and is shown in Figure 1. A broad band appeared at 3300-3500 cm^{-1} was attributed to hydrogen bonded hydroxyl group (O-H) from the complex vibrational stretching, associated with free, inter and intra molecular bound hydroxyl groups. The band at 2840-3000 cm^{-1} was characteristic of C-H stretching. The peak position approximately at 1650 cm^{-1} was due to the bound water present in the starch. The wavenumber in the range of 1400-1450 cm^{-1} were assigned for O-H bending. The peak in the range of 1075-1155 cm^{-1} and 1030-1040 cm^{-1} were caused by C-O stretching of C-O-H group and by C-O stretching of C-O-C group in the anhydroglucose ring, respectively.

The analysis of FT-IR spectra of polymer blends enabled the hydrogen bond interactions to be identified [11]. It was known that, if two polymers were compatible, a distinct interaction (hydrogen bonding or dipolar interaction) existed between the chains of one polymer and those of the other, causing the IR spectra of the composites to change (e.g. band shifts, broadening) [11-12]. For the TPRS composites reinforced with silk fibers (Figure 1), it can be observed that the broad band at 3300-3500 cm^{-1} (O-H stretching) and also the single band at 1414 cm^{-1} (O-H bending) slightly shifted to lower wavenumber by the addition of different contents and lengths silk fibers. The peak position shift indicates the increasing of intermolecular hydrogen bonding by the addition of silk fibers. Additionally, the extra wavenumber appeared at 800 cm^{-1} was due to tyrosine residue in silk fibroin. The peak position at 1261 cm^{-1} was arisen from amide III silk conformation of random coil and α-helix [13-14]. The possible interaction between the TPRS matrix and silk fiber reinforcement was represented in Figure 2. The main interaction appeared to be hydrogen bonds between the two different components.

X-ray diffraction

X-ray diffraction technique can be used to identify crystal structure and regular molecular arrangement of starch. The X-ray diffraction patterns of different TPRS/silk composites are shown in Figure 3. Generally, native rice starch showed a typical A-type X-ray diffraction pattern, typical of cereal crystalline structure, with strong peaks at 2θ of 14.9°, 16.9° and 22.9° [15]. For the TPRS without fiber reinforcement, the starch granules were gelatinized and hence the glucosidic chains were retrograded into the V form. The retrograded TPRS sample without fiber reinforcement (Figure 2) showed V-type diffraction pattern with the main peaks at 2θ of 13.1° and 20.0° [15].

Different TPRS/silk fiber composites represented the diffraction patterns at 2θ of 13.1° and 20.0° as shown in Figure 2. Silk fibers also showed the diffraction peaks at 2θ of 20.0°, related to fibroin β–sheet [10]. The peak at 2θ of 20.0° was, therefore, overlapped by both silk fiber reinforcement and TPRS matrix. It should be noted that the intensity of the peaks at 2θ of 20.0° of different TPRS/silk composites clearly increased by the silk reinforcement. No significant difference in XRD patterns could be observed for different TPRS/silk composites reinforced by different contents and lengths of the silk fibers.

Water absorption

Water absorption is a significant consideration for many applications of TPS materials. The results of water absorption experiments, performed at the temperature of 30°C and 50% relative humidity, are shown in Figure 4. It can be seen that different TPRS/silk composites showed the increase of water absorption at the first stage. After that, the percentage water absorption tended to increase slowly and reached its maximum within 7 days. The addition of silk fibers into the TPRS matrix clearly caused the decrease of water absorption of the TPRS/silk composites, as presented in Figure 4. The drop of water absorption may also be attributed to different water absorption characteristics of the silk and starch. Generally, moisture absorption of silk is lower than that of starch [9-10]. Moreover, it may be due to the establishment of hydrogen bonding between the silk fiber and the hydroxyl functional group of TPRS matrix as shown by IR spectra in Figure 1. It was also found that different contents and lengths of the silk fibers caused the similar water absorption behavior in different TPRS/silk composites.

Morphology

Morphological structure of the TPRS/silk composites is a very significant characteristic since it determines TPRS property. Morphology of different TPRS/silk composites as presented in Figure 5 was examined by SEM technique. It was shown that, in all TPRS/silk composites with different silk contents and lengths, the silk fibers were also randomly distributed and embedded into the TPRS matrix. The elongated fracture surface of the silk fibers was also observed. Furthermore, the surface of the silk fibers was also wetted by the TPRS matrix, indicating of the good adhesion between the silk reinforcement and the TPRS matrix.

Mechanical properties

Mechanical properties of different TPRS/silk composites are shown in Figure 6. It can be seen in Figures 6(a)-6(b) that stress at maximum load and Young’s modulus of the TPRS sample significantly increased with the incorporation of silk reinforcement. The addition of 5% and 10% silk fiber into the TPRS matrix caused an increase in the stress at maximum load and Young’s modulus. This could be due to the reinforcing effect of the silk fibers caused by the interactions between the TPRS matrix and the silk reinforcement (Figure 1) and by the surface wetting morphology as observed from SEM micrographs in Figure 5. However, at 15% silk fiber, the stress at maximum load and Young's modulus tended to decrease. This could be due to too excessive content of light weight silk fibers loaded into the TPRS matrix. As expected, strain at maximum load of all TPRS/silk composites continued to decrease with increase contents of the silk fibers as shown in Figure 6(c). Similar trends of mechanical properties have been reported for corn starch or cassava starch/cellulose fibers [2-4, 6-7].

When different silk fiber lengths, i.e. 2 mm, 5 mm and 10 mm, was considered, it was found from Figure 6 that the shorter the silk fiber length, the higher the stress at maximum load of the TPRS/silk composites. Similarly, Young's modulus of the TPRS/silk composites increased with the shorter lengths of the silk fibers. This is because of more surface area of the lower aspect ratio of the silk fibers. As expected, the use of 2 mm length of silk fibers caused the lowest the strain at maximum load of the TPRS/silk composites. It should be noted that the use of 5 mm silk fibers resulted in the similar mechanical properties as those of 10 mm silk fibers. From this study, the highest stress at maximum load and Young's modulus was obtained from the TPRS/silk composite with the addition of 10% and 2 mm silk reinforcement.

Thermal Properties

Thermogravimetric analysis of different TPRS/silk composites was carried out to assess their thermal stability and degradation temperatures. The two weight losses, at around 100°C and 190°C were related to the volatilization of water and glycerol, respectively (Figure 7 and Table 1). The maximum degradation step at 290-310°C was assigned to the degradation of starch [2]. Silk fibers also showed the last degradation step at the temperature range of 420-440°C.

It can also be seen in Table 1 that the TPRS composites reinforced by silk fibers caused an increase in the onset decomposition temperature of starch. This could be described as the TPRS matrix formed hydrogen bond linkages as shown in FTIR spectra in Figure 1. The addition of low amounts of silk fibers to the TPRS matrix also resulted in a significant increase in the thermal stability of the composites as indicated by the decrease of percentage weight loss (Table 1). This can be explained by the higher thermal stability of the silk fibers. Similar improved thermal stability and degradation temperature of TPS/cellulose fibers was observed in different TPS from corn starch/Eucalyptus fiber [2], corn starch/winceyette fiber [3], rice starch/cotton fiber [7]. The difference of silk fiber contents and lengths on thermal properties of different TPRS/silk composites could not be observed.

Biodegradation

Biodegradable property of different TPRS/silk composites was determined by soil burial test. Generally, both starch and silk fibroin can be classified as enzymatically biodegradable materials [15-16]. Figure 8 shows the percentage weight change of different TPRS/silk composites. All of the composites, showed the increment in weight after a few days of soil immersion due to water absorption from soil. It should be mentioned that at the first few days of testing, different TPRS/silk composites showed lower percentage weight change than that of the TPRS sample without silk fiber reinforcement. This behavior could be related to lower water absorption characteristics of the TPRS/silk composites.

After that, the weight of all of the TPRS/silk composites tended to decrease and then started to degrade by micro-organisms existed in soil. The TPRS sample without silk fiber reinforcement degraded completely within 25 days. The percentage weight change in the TPRS/silk composites was higher than that of the TPRS sample without silk fiber reinforcement. After 30 days, the percentage weight change of the TPRS/silk composites was approximately -70%. No significant difference in weight change could be observed from different contents and lengths of the silk fiber reinforcement in the TPRS/silk composites.

Comparison of properties for TPRS/silk and TPRS/cotton composites

Table 2 shows properties of the TPRS/silk composite compared with the TPRS/cotton composite. Both silk and cotton fibers were fixed at 10% wt and 2 mm length. Generally, elongation and elastic recovery of silk fibers is higher than those of cotton fibers but stress or tenacity of silk fiber is apparently lower than that of cotton fibers [9-10]. Nevertheless, it can be observed from Table 2 that the stress and strain at maximum load as well as Young's modulus of the TPRS/silk and TPRS/cotton composites were comparable, indicating that mechanical properties of both composites were comparable. Since water absorption of silk fibers is higher than that of cotton fibers [9-10], water absorption values at 50%RH at day 20 were about 315% and 310% for the TPRS/silk and TPRS/cotton composites, respectively.

For thermal property, both silk and cotton fibers caused the increase of the onset thermal degradation temperatures of the starch matrix similarly, even though thermal degradation temperature of silk fibers is generally higher than cotton fibers [9-10]. The only significant difference that can be observed is that the TPRS/silk composite can decomposed in soil more rapid than the TPRS/cotton composite. At day 25, percentage weight changes for the TPRS/silk and TPRS/cotton composites were approximately -67% and -59%, respectively. This is because the protein structure in silk fibers can easily decompose, compared with the cellulose structure in cotton fibers [17]. The comparable properties suggest that silk fibers can be used as the reinforcement in the TPRS matrix similar as cotton fibers.

Conclusion

Properties of the TPRS sample could be modified by reinforcing with natural silk protein fibers. New hydrogen bonds could form between the TPRS matrix and the silk fiber reinforcement by the detection of IR peak shifts. Mechanical properties of the TPRS matrix could be improved by the incorporation of silk fibers. Silk contents and lengths were found to affect only mechanical properties of the TPRS/silk composites. The highest stress at maximum load and Young's modulus of the TPRS/silk composites was obtained from the addition of 10% and 2 mm silk reinforcement. Water absorption of the TPRS matrix decreased with the inclusion of the silk fibers. Thermal degradation temperatures and thermal stability of the TPRS matrix were also improved by the addition of the silk fiber reinforcement. Moreover, mechanical and thermal properties including water absorption of the TPRS/silk and TPRS/cotton composites were comparable.

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Figure Captions

Figure 1	FT-IR spectra of different TPRS/silk composites
Figure 2	Possible interactions between the TPRS matrix and silk fiber reinforcement
Figure 3	X-ray diffraction patterns of different TPRS/silk composites
Figure 4	SEM micrographs of fractured surfaces of different TPRS/silk composites (a) 5% 2 mm (b) 10% 2 mm and (c) 10% 10 mm
Figure 5	Mechanical properties of different TPRS/silk composites (a) stress at maximum load (b) Young’s modulus and (c) strain at maximum load
Figure 6	Water absorptions of different TPRS/silk composites, determined at 30°C and 50% RH
Figure 7	(a) TG and (b) DTG thermograms of different TPRS/silk composites
Figure 8	Weight changes of different TPRS/silk composites under soil burial test

Table Captions

Table 1 Thermal degradation temperatures and weight losses of different TPRS/silk composites

Table 2 Property comparison of TPRS/silk and TPRS/cotton composites