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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:

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

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.