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Biodegradation of thermoplastic starch/eggshell powder composites

Munlika Bootklad, Kaewta Kaewtatip*

Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

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ABSTRACT

Thermoplastic starch (TPS) was prepared using compression molding and chicken eggshell was used as a filler. The effect of the eggshell powder (EP) on the properties of TPS was compared with the effect of commercial calcium carbonate (CC). The organic compound on the surface of the eggshell powder acted as a coupling agent that resulted in a strong adhesion between the eggshell powder and the TPS matrix, as confirmed by SEM micrographs. The biodegradation was determined by the soil burial test. The TPS/EP composites were more rapidly degraded than the TPS/CC composites. In addition, the eggshell powder improved the water resistance and thermal stability of the TPS.

1. Introduction

In the last decade, thermoplastic starch (TPS) has been of interest as a polymer that could replace petroleum-derived plastics because it has a low production cost, is readily available, is fully biodegradable and is a renewable agricultural resource (Roz, Carvalho, Gandini, & Curvelo, 2006; Teixeira et al., 2009). Cassava roots have become economically important products of Thailand. Generally, cassava roots are processed as animal feed or are fermented for producing alcoholic beverages. Therefore, the preparation of TPS by using cassava starch not only increases the market value of cassava roots but also helps to solve the accumulation of petroleum-derived plastics in nature that have become a worldwide environmental problem. However, TPS has limitations including its poor long-term stability, poor mechanical properties and poor water resistance (Lopez, Mutje, Carvalho, Curvelo, & Girones, 2013; Roz, Zambon, Curvelo, & Carvalho, 2011). Several research groups have attempted to improve the properties of TPS. Many fillers have been used and some have been effective for improving some of the properties of TPS such as fiber (Gilfillan, Nguyen, Sopade, & Doherty, 2012; Kaewtatip & Thongmee, 2012), clay (Kaewtatip & Tanrattanakul, 2012; Wang, Zhang, Liu, & Wang, 2009), protein (Corradini, Marconcini, Agnelli, & Mattoso, 2011; Kaewtatip, Tanrattanakul, & Kaewtathip, 2013), brucite (Moreira, Pedro, Glenn, Marconcini, & Mattoso, 2013), fly ash (Ma, Yu, & Wang, 2007) and carbon nanotubes (Fama, Pettarin, Goyanes, & Bernal, 2011). However, the hydrophilic characteristics of TPS can cause incompatibility with fillers and some of the fillers are non-biodegradable materials. Currently, most research has been focused on the development of a bio-filler for TPS that will not only improve the compatibility between the TPS and the filler but also can facilitate biodegradation by microorganisms.

Eggshell has been considered to be a good candidate for use as a bio-filler for preparing polymer composites because it is inexpensive, abundant, has low density, is environmentally friendly and is a renewable resource (Kang, Pal, Park, Bang, & Kim, 2010; Toro, Quijada, Arias, & Yazdani-Pedram, 2007). Eggshell is a major waste product of the food industry and is produced in large quantities. Eggshell contains about 95% of calcium carbonate and 5% of organic materials (Ji, Zhu, Qi, & Zeng, 2009; Kang et al., 2010). Eggshell has potential uses for many applications such as a fertilizer, animal feed, for coating pigments, as a catalyst and adsorbent (Cho & Seo, 2010; Tsai et al., 2006; Yoo, Hsieh, Zou, & Kokoszka, 2009). One of its most useful applications is as a filler for synthetic plastics e.g. poly(styrene-b-ethylene/butylene-b-styrene) (Kang et al., 2010), polypropylene (PP) (Toro, Quijada, Arias, et al., 2007; Toro, Quijada, Yazdani-Pedram, & Arias, 2007), epoxy resins (Ji et al., 2009) and low density polyethylene (LDPE) (Shuhadah & Supri, 2009). Toro, Quijada, Arias, et al. (2007) compared the effect of commercial calcium carbonate and eggshell on the properties of a PP composite. They found that eggshell disperses well in the PP matrix due to the higher surface/volume ratio for eggshell than that of commercial calcium carbonate. The toughness of the epoxy resin was improved by using eggshell (Ji et al., 2009). However, there have been few reports on the use of eggshell with starch-based materials. Takamine, Bhatnagar, and Hanna (1995) studied the effect of eggshell on the properties of corn starch extrudates. They suggested

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* Corresponding author. Tel.: +66 74288365; fax: +66 74446925.
E-mail addresses: kaewta.k@psu.ac.th, jumpolymer@hotmail.com (K. Kaewtatip).

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that eggshell brought about nucleation sites for water vaporization as the material exited the die of the extruder. Moreover, eggshell was used as a nucleating agent for preparing starch foam (Xu & Hanna, 2007). It was found that eggshells decreased the cell size and increased the cell population.

The aim of this work was to study the effect of eggshell on the properties of TPS and compare it with the use of commercial calcium carbonate. The morphology of their fractured surfaces, the thermal properties and water absorption of the composites was studied. The surface morphology and weight loss after burial in soil was also investigated.

2. Materials and methods

2.1. Materials

Pregelatinized cassava starch (PD 10370) was kindly supplied by Siam Modified Starch Co., Ltd. The starch was dried at 105 °C for 48 h in an oven and kept in a desiccator prior to use. The chicken eggshell was obtained from waste at a local market. Eggshells were washed in water to remove any impurities, dried in a hot air oven and ground by a Motar grinder, FRITSTSCH (Germany). After grinding, the eggshell powder was dried in a hot air oven until a constant weight was achieved and kept in a desiccator prior to use. The particle size of the eggshell powder was 26.26 ± 9.48 μm. Typical compositions of the eggshell powder was 95% by weight of calcium carbonate and 5% by weight of organic materials such as collagen, sulfated polysaccharides and other proteins (Kang et al., 2010). Commercial calcium carbonate was purchased from Kitpiboon Co., Ltd. The glycerol was from Ajax Finechem.

2.2. Preparation of the composites

Pregelatinized cassava starch, glycerol (45 parts per hundred of the total weight of the pregelatinized cassava starch) and filler (commercial calcium carbonate or eggshell powder) (0, 10, 20, 30, 40 and 50 wt.%, dry starch basis) were mixed in polyethylene bags until a homogeneous material was obtained. After that, TPS and the composites were prepared by using a compression molding machine at 160 °C for 10 min and a pressure of 200 kg/cm^2 was directly applied to the sample.

2.3. Characterization of the composites

Wide angle X-ray diffraction (XRD) studies were carried out using a Phillips diffractometer (Model PW 1830) with copper as a target material. The scanning regions of the diffraction angle 2θ were 5–90°. The samples were conditioned at 55 ± 2% RH and 25 ± 3 °C.

The morphology of the samples was examined using a scanning electron microscope (SEM) (Quanta 400, FEI). The TPS and composites were immersed in liquid nitrogen before fracturing. All specimens were first coated with a thin layer of gold.

The thermal decomposition temperatures of the TPS and the composites were obtained using a PerkinElmer® TGA 7. The thermogravimetric analyzer (TGA) was operated at a heating rate of 10 °C/min from 50 to 600 °C under a nitrogen atmosphere.

2.4. Soil burial degradation test

Soil burial degradation test was carried out according to Riyajan, Sasithornsonti, and Phinyocheep (2012). Small pieces of samples (dimensions 15 mm × 15 mm × 1 mm) were buried in natural soil at a depth of 7 cm in Hat Yai, Songkhla, Thailand. The average environmental temperature was 30 ± 5 °C and the relative humidity (RH) was 50–60%. After 15 days and 30 days, the samples were collected, washed with distilled water several times and dried in the oven at 105 °C for 24 h.

The weight loss was calculated using Eq. (1) (Franco, Cyras, Busalmen, Ruseckaite, & Vazquez, 2004; Phua, Lau, Sudesh, Chow, & Ishak, 2012):

$$\text{Weight loss} \quad (\%) = \left[\frac{w_{initial} - w_{final}}{w_{initial}}\right] \times 100 \qquad (1)$$

where $w_{initial}$ and w_{final} was the weight of sample before and after soil burial degradation test, respectively.

2.5. Water absorption measurement

The samples were stored at 55%RH for 30 days before testing and were then dried in the oven at 105 °C for 24 h. These samples were weighed immediately after being removed from the oven. The water absorption was calculated as follows Eq. (2) (Huang, Yu, & Ma, 2004; Ma et al., 2007):

$$\text{Water absorption} \quad (\%) = \left[\frac{w_1 - w_2}{w_2}\right] \times 100 \qquad (2)$$

where w_1 was the weight of sample before drying and w_2 was the weight of sample after drying. All measurements were performed in triplicate.

3. Results and discussion

3.1. Characterization of fillers

The physical properties of commercial calcium carbonate and eggshell powder such as density, surface area and oil absorbent value has been reported in many articles (Ji et al., 2009; Toro, Quijada, Arias, et al., 2007; Tsai et al., 2006). Thus, the morphology and XRD patterns of commercial calcium carbonate and eggshell powder were studied. Fig. 1(a) presents the SEM micrograph of the commercial calcium carbonate. The shape of the commercial calcium carbonate was plate-like, whereas the morphology of the eggshell powder was similar to that of commercial calcium carbonate (Fig. 1(b)). A similar morphology of eggshell powders has been detected by other authors (Toro, Quijada, Arias, et al., 2007; Toro, Quijada, Yazdani-Pedram, et al., 2007). In contrast, the XRD diffraction pattern of the commercial calcium carbonate and eggshell powder are shown in Fig. 2(a) and (b), respectively. The XRD diffraction pattern of the eggshell powder was similar to the XRD diffraction pattern of the commercial calcium carbonate. The result was compared with previous reports (Ji et al., 2009; Kang et al., 2010) which showed that the main component of the eggshell powder was 95% calcium carbonate.

3.2. Morphology

SEM micrographs of the fractured surfaces of the TPS, TPS/CC composites and TPS/EP composites are presented in Fig. 3. TPS shows a clear and smooth surface (Fig. 3(a)). For the fractured surfaces of the composites, a coarse surface with cavities was observed (Fig. 3(b)–(e)). Although, TPS/CC composites seem to have similar morphology to that found in the TPS/EP composite there was some agglomerates of commercial calcium carbonate in the matrix. Moreover, large holes were present in the fractured surface of the TPS/CC composites due to the pull-out of the commercial calcium carbonate agglomerates. The TPS/EP composites showed good dispersion and the eggshell powder was embedded in the TPS matrix. The eggshell powder demonstrated a better adhesion to the TPS matrix than the commercial calcium carbonate due to the presence