



Properties of biodegradable citric acid-modified granular starch/thermoplastic pea starch composites

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ABSTRACT

Pea starch-based composites reinforced with citric acid-modified pea starch (CAPS) and citric acid-modified rice starch (CARS), respectively, were prepared by screw extrusion. The effects of granular CAPS and CARS on the morphology, thermal stability, dynamic mechanical thermal analysis, the relationship between the mechanical properties and water content, as well as the water vapor permeability of the composite films were investigated. Scanning electron microscope and X-ray diffraction reveal that the reinforcing agents, the granules of CAPS and CARS, are not disrupted in the thermoplastic process, while the pea starch in the matrix is turned into a continuous TPS phase. Granular CAPS and CARS can improve the storage modulus, the glass transition temperature, the tensile strength and the water vapor barrier, but decrease thermal stability. CARS/TPS composites exhibit a better storage modulus, tensile strength, elongation at break and water vapor barrier than CAPS/TPS composites because of the smaller size of the CARS granules.

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1. Introduction

Mounting environmental and legislative pressure for reducing petroleum-based plastics waste, and rapid increases in the cost of petroleum, have primed the development of bio-based materials from renewable resources. Among the biopolymers, starch is considered to be one of the most promising materials for biodegradable plastics because of its universality, renewability, and low cost. Starch has been investigated widely for the potential manufacture of products such as water-soluble pouches for detergents and insecticides, flushable liners and bags, and medical delivery systems and devices (Fishman, Coffin, & Konstance, 2000). Native starch commonly exists in a granular structure, which can be processed into thermoplastic starch (TPS) under the high temperature and shear of melt extrusion. (Forsell, Mikkilä, & Moates, 1997; Ma, & Yu, 2004a). Unfortunately, TPS exhibits many disadvantages such as a strong hydrophilic character (water sensitivity) and poor mechanical properties compared to conventional polymers (Averous, & Boquillon, 2004), which make it unsatisfactory for applications such as packaging materials. Generally, there are two approaches to mitigate these shortcomings. One approach is to blend starch with biodegradable polymers such as polylactide,

polycaprolactone (Sarazin, Li, & Orts, 2008), and poly(propylene carbonate) (Ma, Yu, & Zhao, 2006). However, these polymers are very expensive, and starch is immiscible with them at the molecular level. The other approach is the reinforcement of TPS with mineral, cellulose or starch nanocrystal fillers. A significant improvement in mechanical properties and water resistance of TPS has been reported by such reinforcement. Mineral fillers such as kaolin (de Carvalho, Curvelo, & Agnelli, 2001) and clay (Park, Li, & Jin, 2002; Wilhelm, Sierakowski, & Souza, 2003) with polar groups were easily associated with TPS. Cellulose fillers used as reinforcing agents in TPS matrices include cellulose nanocrystals (Cao, Chen, Chang, Stumborg, & Huneault, in press; Lu, Weng, & Cao, 2006), natural fibers (Alvarez, Vázquez, & Bernal, 2005; Soykeabkaew, Supaphol, & Rujiravanit, 2004), cellulose derivatives (Ma, Chang, & Yu, 2008) and commercially regenerated cellulose fibers (Funke, Bergthaller, & Lindhauer, 1998). The chemical similarities of starch and plant fibers provide a sound basis for good interaction (Avérous, Fringant, & Moro, 2001; Lu et al., 2006). In addition, waxy maize starch nanocrystals, from the hydrolysis of native granules, have been used as a reinforcing agent in TPS prepared by casting (Angellier, Molina-Boisseau, & Dole, 2006). It is necessary to decrease the temperature of gelatinized starch before adding starch nanocrystals, otherwise the nanocrystals also gelatinize.

Pea starch is mainly available as a by-product of protein extraction. It is therefore considered to be a relatively cheap source of starch as compared to corn, wheat, and potato starches (Ratnayake,

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Hoover, & Warkentin, 2002). Citric acid (CA) is recognized as nutritionally harmless compared to other substances used for starch derivatization. (Xie & Liu, 2004). CA-modified starch is a granular resistant starch, which displays many of the physiological benefits of dietary fiber such as calorie reduction and colonic health benefits. These granules are not gelatinized during the processing of TPS, therefore CA-modified starch can be used as a reinforcing agent in TPS prepared by both melt extrusion and casting methods. In this paper, CA-modified pea starch (CAPS) and CA-modified rice starch (CARS) are used as reinforcing agents in glycerol-plasticized thermoplastic pea starch (TPS) matrices. This work is focused on the preparation and characterization of CAPS/TPS and CARS/TPS composites in terms of morphology, X-ray diffractometry, thermal stability, dynamic mechanical thermal analysis, and water vapor permeability, as well as the effect of water content on mechanical properties. This work also studied the size effect of reinforcing agents on the properties of the resultant composites as granules of rice starch are significantly smaller than those of pea starch. New applications for citric acid-modified granular starch as a reinforcement filler in starch-based biocomposites are explored in this work. These starch derivative/TPS composites may have great potential to replace conventional packaging such as edible films, food packaging, and biodegradable packaging.

2. Experimental

2.1. Materials

Pea starch (PS) composed of 35% amylose and 65% amylopectin was supplied by Nutri-Pea Limited Canada (Portage la Prairie, Canada). Rice starch (RS) containing 32% amylose and 68% amylopectin was obtained from Shanghai Starch Institute (Shanghai, China). Glycerol, the plasticizer, and citric acid (CA) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Production of CAPS and CARS

CAPS and CARS were produced based on the method of (Xie & Liu, 2004) with some modifications. CA (40 g) was dissolved in 100 mL of water and the pH of the solution was then adjusted to 3.5 with 10 M NaOH. The citric acid solution was mixed with 100 g dried PS or RS in a glass tray and stored for 12 h at room temperature. The tray was then dried at 60 °C for 6 h. The mixture was then ground and dried in a forced air oven for 1.5 h at 130 °C. The dry mixture was washed three times with water to remove unreacted CA. CAPS and CARS were air-dried at room temperature and finally ground.

2.3. The preparation of CAPS/TPS and CARS/TPS composites

Glycerol was blended (3000 rpm, 2 min) with pea starch and CAPS (or CARS) by use of a High Speed Mixer GH-100Y, and stored overnight. The ratio of glycerol to pea starch (wt/wt) was 30:100. The filler loading level (0, 3, 6, 9, or 12 wt%) was based on the pea starch. The mixtures were manually fed into a single screw Plastic Extruder SJ-25(s) (Screw Ratio L/D = 25:1) operating at 25 rpm. The temperature profile along the extruder barrel was based on four heating zones, 130, 140, 150, and 130 °C, from feed zone to die. The die was a round sheet with 3 mm diameter holes. Samples were pressed, using a flat sulfuration machine, into a sheet for testing.

2.4. Determination of the molar degree of substitution by CA

The molar degree of substitution (MS) is the number of CA per anhydroglucose unit (AGU) in starch. MS was determined using the method of Xing et al. (Xing, Zhang, & Ju, 2006) with minor mod-

ification. Approximately 1.0 g of dry CAPS or CARS was accurately weighed and placed into a 250 mL conical flask. Then 50 mL of 75% ethanol solution was added, and the conical flask was agitated and warmed at 50 °C for 30 min and then cooled to room temperature. Standard 0.500 M aqueous sodium hydroxide solution (20 mL) was added; the conical flask was tightly stoppered and agitated with a magnetic stirrer for 24 h. The excess alkali was back-titrated with a standard 0.200 M aqueous hydrochloric acid solution and re-titrated 2 h later to account for any further alkali that may have leached from the starch. Each sample was measured in triplicate. MS of CA substitution was 0.085 for CAPS and 0.089 for CARS.

2.5. Fourier transform infrared (FT-IR) spectroscopy

PS, RS, CAPS, CARS powders were measured with a BIO-RAD FTS3000 IR Spectrum Scanner.

2.6. Scanning electron microscope (SEM)

PS, RS, CAPS, CARS powders and the fracture surfaces of extruded composite strips were examined using a scanning electron microscope Philips XL-3, operating at an acceleration voltage of 20 kV. PS, RS, CAPS, CARS powders were suspended in ethanol. The suspension drops were drawn on a glass flake, dried to remove ethanol, and then vacuum coated with gold for SEM. Composite strips were cooled in liquid nitrogen, and then broken. The fracture faces were vacuum coated with gold for SEM.

2.7. X-ray diffractometry

The extruded composite strips were pressed at 10 MPa using a flat sulfuration machine and the slices were placed in a sample holder for X-ray diffractometry. PS, RS, CAPS, CARS powders were tightly packed into the sample holder. X-ray diffraction patterns were recorded in the reflection mode in angular range 10–30° (2 theta) at ambient temperature by a BDX3300 diffractometer, operated at the CuK α wavelength of 1.542 Å. Radiation from the anode, operated at 36 kV and 20 mA, monochromized with a 15 μ m nickel foil. The diffractometer was equipped with 1° divergence slit, a 16 mm beam bask, a 0.2 mm receiving slit and a 1° scatter slit. Radiation was detected with a proportional detector.

2.8. Thermogravimetric analysis (TGA)

PS, RS, CAPS, CARS powders were dried in the oven at 105 °C for 4 h. The composites for TGA were stored in tightly sealed plastic bags for one week. Thermal properties of the powders and composites were measured with a ZTY-ZP type thermal analyzer. Sample weight varied from 10 to 15 mg. Samples were heated from room temperature to 450 °C at a heating rate of 15 °C/min in a nitrogen atmosphere.

2.9. Dynamic mechanical thermal analysis (DMTA)

The composites for DMTA were stored at 33% relative humidity (RH) for one week. The DMTA, using a Mark Netzsch DMA242 analyzer, was performed on thick specimens (40 \times 7 \times 2 mm) in a single cantilever-bending mode at a frequency of 3.33 Hz and a strain \times 2 N, corresponding to the maximum displacement amplitude of 30 μ m. The temperature range was from –100 to 100 °C. The standard heating rate used was 3.0 °C min⁻¹.

2.10. Mechanical testing

Composites were pressed with a flat sulfuration machine into a sheet. The Testometric AX M350-10KN Materials Testing Machine

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