

Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites

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Abstract

Glycerol-plasticized thermoplastic pea starch (TPS)/carboxymethyl cellulose (CMC) and TPS/microcrystalline cellulose (MC) composites were respectively prepared by a screw extruder. As the reinforcement filler, the effects of CMC and MC contents on the morphology, thermal stability, dynamic mechanical thermal analysis (DMTA), mechanical properties, as well as water vapor permeability (WVP) were investigated. Scanning electron microscope (SEM) showed that there was good adhesion between starch and CMC or MC, but these superfluous cellulose derivatives resulted in the conglomeration in TPS matrix. MC increased the thermal stability, while CMC impaired it. DMTA revealed that the addition of CMC or MC enhanced the storage modulus and the glass transition temperature of the composites. At the low contents of cellulose derivatives (<9 wt%), the greater CMC or MC content were, the more the tensile strength of the composite. The values of WVP decreased with the increasing of cellulose derivatives. TPS/MC composites had better water vapor barrier than TPS/CMC composites.

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1. Introduction

The improper disposition of the enormous volume of petroleum-derived plastics in the environment has led to environment pollution and raised much interest in edible and biodegradable films from nature polymers, the biodegradable and renewable resources. Starch is one of the most studied and promising raw materials for the production of biodegradable plastics, which is a natural renewable carbohydrate polymer obtained from a great variety of crops. Starch is a low cost material in comparison to most synthetic plastics and is readily available. 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 action of high temperature and shear by melt extrusion (Forssell, Mikkilä, & Moates, 1997; Ma & Yu, 2004).

Unfortunately, the properties of TPS are not satisfactory for some applications such as packaging materials. One approach is the use of fibers as reinforcement for TPS. The fibers described in the literature for this intention are cellulose nanocrystalites (Lu, Weng, & Cao, 2006), natural fibers (Alvarez, Vázquez, & Bernal, 2005; Soykeabkaew, Supaphol, & Rujiravanit 2004) and commercial regenerated cellulose fibers (Funke, Bergthaller, & Lindhauer, 1998). When natural fibers are mixed TPS, their mechanical properties are obviously improved, because the chemical similarities of starch and plant fibers provide a good interaction (Avérous, Fringant, & Moro, 2001; Lu et al., 2006). A significant improvement in water resistance is obtained by adding cellulose crystallites (Lu,

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Weng, & Cao, 2005) or micro-fiber (Dufresne, Dupeyre, & Vignon, 2000; Ma, Yu, & Kennedy, 2005). This behavior is related to the highly crystalline ‘hydrophobic’ character of the cellulose fibers in comparison to starch hydrophilic property. In addition, these authors (Curvelo, de Carvalho, & Agnelli, 2001) demonstrated an improved thermal stability due to a higher and longer thermal resistance of cellulose fibers.

Pea starch is mainly available as a by-product of protein extraction. Therefore, it is considered to be a relatively cheap source of starch compared to corn, wheat and potato starches (Ratnayake, Hoover, & Warkentin, 2002). Carboxymethyl cellulose sodium (CMC) and microcrystalline cellulose (MC) have no harmful effects on human health, and are used as highly effective additive to improve the product and processing properties in various fields of application, from foodstuffs, cosmetics and pharmaceuticals to products for the paper and textile industries. In this paper, CMC and MC were used as the reinforcement filler of glycerol-plasticized thermoplastic pea starch (TPS) matrix. This work focused on processing and characterization of TPS/CMC and TPS/MC composites in terms of the morphology, thermal stability, dynamic mechanical thermal analysis, and water vapor permeability as well as the effect of water contents on mechanical properties. These polysaccharide (thermoplastic starch/cellulose derivatives) composites have the potential to replace conventional packaging such as edible films, food packaging and biodegradable packaging.

2. Experimental

2.1. Materials

Pea starch composed of 35% amylose and 65% amylopectin, and with average particle size of about 30 μm , was supplied by Nutri-Pea Limited Canada (Portage la Prairie, Canada). Granular powders of carboxymethyl cellulose sodium (CMC) and microcrystalline cellulose (MC) with the particle size of 10–50 μm were obtained from Tianjin Fine Chemical Institute. Glycerol, the plasticizer was purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. The preparation of TPS/CMC and TPS/MC composites

Glycerol was blended (3000 rpm, 2 min) with pea starch and CMC (or MC) by use of a High Speed Mixer GH-100Y (made in China), and then stored overnight. The ratio of glycerol and pea starch (wt/wt) was 30:100. The mixtures were manually fed into a single screw Plastic Extruder SJ-25(s) (Screw Ratio $L/D = 25:1$, made in China) operating at 20 rpm. The temperature profile along the extruder barrel was based on four heating zones, which are 130, 140, 140 and 120 $^{\circ}\text{C}$ from feed zone to die. The die has a hole of 3 mm in diameter. Samples were pressed with the flat sulfuration machine into the sheet for testing.

2.3. Scanning electron microscope (SEM)

The fracture surfaces of extruded composite strips were examined using Scanning Electron Microscope Philips XL-3, operating at an acceleration voltage of 20 kV. Composite strips were cooled in liquid nitrogen, and then broken. The fracture faces were vacuum coated with gold for SEM.

2.4. Thermogravimetric analysis (TGA)

The composites for TGA were stored in tightly sealed plastic bags for one week. The thermal properties of the composites were measured with a ZTY-ZP type thermal analyzer. The sample weight varied from 10 to 15 mg. Samples were heated from room temperature to 500 $^{\circ}\text{C}$ at a heating rate of 15 $^{\circ}\text{C}/\text{min}$.

2.5. 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 the 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 2N, corresponding to the maximum displacement amplitude of 30 μm . The range of temperature was from –100 to 100 $^{\circ}\text{C}$. The standard heating rate used was 3.0 $^{\circ}\text{C}/\text{min}$.

2.6. Mechanical testing

Composites were pressed with the flat sulfuration machine into the sheet. The Testometric AX M350-10KN Materials Testing Machine was operated at a crosshead speed of 50 mm/min for tensile testing (ISO 1184–1983 standard). The data was averaged over 5–8 specimens.

In order to analyze the effect of environmental humidity on mechanical properties of the composites, the composites were stored in closed chambers over several aqueous mixtures at 25 $^{\circ}\text{C}$ for a period of time. The materials used were dried silica gel, MgCl_2 saturated solution and NaCl saturated solution, providing RH of 0%, 33% and 75%, respectively.

The original water content (dry basis) of composites was determined gravimetrically by drying small pieces of TPS at 105 $^{\circ}\text{C}$ overnight, and the evaporation of glycerol was negligible (Curvelo et al., 2001). When composites were stored for a period of time at RH of 0% or 75%, water content (C) was calculated on the base of the original weight (W_0), the current weight (W) and the original water content (C_0).

$$C = \frac{W - W_0(1 - C_0)}{W(1 - C_0)} \times 100\% \quad (1)$$

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