



Effect of stearic acid-grafted starch compatibilizer on properties of linear low density polyethylene/thermoplastic starch blown film



Nattaporn Khanookon^a, Rangrong Yoksan^{a,b,*}, Amod A. Ogale^c

^a Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

^b Center for Advanced Studies for Agriculture and Food, Kasetsart University, Bangkok 10900, Thailand

^c Chemical and Biomolecular Engineering, Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634-0909, USA

ARTICLE INFO

Article history:

Received 22 May 2015

Received in revised form 9 October 2015

Accepted 10 October 2015

Available online 22 October 2015

Keywords:

Polyethylene

Thermoplastic starch

Stearic acid-grafted starch

Blend

Compatibilizer

Properties

ABSTRACT

The present work aims to investigate the effect of stearic acid-grafted starch (ST-SA) on the rheological, thermal, optical, dynamic mechanical thermal, and tensile properties of linear low density polyethylene/thermoplastic starch (LLDPE/TPS) blends, as well as on their water vapor and oxygen barrier properties. Blends consisting of LLDPE and TPS in a weight ratio of 60:40 and ST-SA at different concentrations, i.e. 1, 3 and 5%, were prepared using a twin-screw extruder. The obtained resins were subsequently converted into films via blown film extrusion. Incorporation of ST-SA resulted in a decreased degree of shear thinning, reduced ambient temperature elasticity, and improved tensile strength, secant modulus, extensibility, and UV absorption, as well as diminished water vapor and oxygen permeabilities of the LLDPE/TPS blend. These effects are attributed to the enhanced interfacial adhesion between LLDPE and TPS phases through the compatibilizing effect induced by ST-SA, and the good dispersion of the TPS phase in the LLDPE matrix. The results confirmed that ST-SA could potentially be used as a compatibilizer for the LLDPE/TPS blend system.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

In the last two decades, polyethylene (PE), which is one of the most commonly used thermoplastics in our daily lives, has been blended with thermoplastic starch (TPS) to reduce the cost (Rodríguez-González, Ramsay, & Favis, 2003). PE/TPS blends can be transformed into various kinds of products using different conventional converting processes such as injection molding (Beg, Kormin, Bijarimi, & Zaman, 2015), hot/hydraulic press (Bikiaris & Panayiotou, 1998; Wang, Yu, & Yu, 2005), compression molding (Mortazavi, Ghasemi, & Oromiehie, 2013; Sabetzadeh, Bagheri, & Masoomi, 2012), blown film extrusion (Euaphantasate, Prachayawasin, Uasopon, & Methacanon, 2008; Sabetzadeh, Bagheri, & Masoomi, 2015; Thipmanee & Sane, 2012), etc. Although blown film extrusion is a major converting process for manufacturing flexible films and bags from PE, there are few articles in the literature relevant to the blown film extrusion of PE/TPS blend. The main reason for this is postulated to be the immiscibility

and incompatibility between PE and TPS phases due to the polarity difference (Rodríguez-González et al., 2003; St-Pierre, Favis, Ramsay, Ramsay, & Verhoogt, 1997), resulting in poor mechanical properties. A series of compatibilizers, including maleic anhydride-grafted polyethylene (Bikiaris & Panayiotou, 1998; Cerclé, Sarazin, & Favis, 2013; Mortazavi et al., 2013; Sabetzadeh et al., 2012, 2015; Wang et al., 2005), polyethylene-co-vinyl alcohol (Sailaja & Chanda, 2002) and polyethylene-maleic anhydride terpolymers containing elastomeric segments (Cerclé et al., 2013) have been utilized to provide compatibility between the two polymers and consequently improve the blend properties. Recently, bio-PE has been produced on a large scale and used in place of petroleum-based PE due to its renewability and environmentally friendly aspect. The development of a bio-based compatibilizer is thus important, particularly when fully bio-based plastic products are required.

Starch is a polysaccharide of glucose bearing a large number of hydroxyl groups, which impart its hydrophilicity and can be chemically modified. The esterification of starch with long-chain fatty acids such as oleic acid (Simi & Emilia Abraham, 2007), stearic acid (Simi & Emilia Abraham, 2007; Varavinit, Chaokasem, & Shobsngob, 2001) and its derivatives such as fatty acid chlorides, e.g. octanoyl chloride, lauroyl chloride and palmitoyl chloride (Namazi, Fathi, & Dadkhah, 2011), is an approach to produce hydrophobic starch or amphiphilic starch, depending on the substitution degree. The

* Corresponding author at: Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand. Tel.: +66 2 562 5097; fax: +66 2 562 5046.

E-mail address: rangrong.y@ku.ac.th (R. Yoksan).

hydrophobically modified starches are mostly applied as a drug delivery carrier (Namazi et al., 2011; Simi & Emilia Abraham, 2007) or as a flavor encapsulant (Varavinit et al., 2001) and as an emulsifier (Nilsson & Bergenstahl, 2006) in pharmaceutical, biomedical and food applications. To our knowledge, there are no reports in the literature about the utilization of fatty acid-grafted starch as a compatibilizer for the PE/TPS blend system.

Therefore, the present article aims to report the effect of fatty acid-grafted starch, i.e. stearic acid-grafted starch (ST-SA) on the rheological, thermal, optical, dynamic mechanical thermal, and tensile properties of the low-density polyethylene/thermoplastic starch (LLDPE/TPS) blend resins and blown films, as well as on their water vapor and oxygen barrier properties. The obtained LLDPE/TPS blown films could potentially be applied as packaging film for grocery bags, shopping bags, supermarket carrier bags, etc. This system is expected to be used as a model for developing a compatibilized bio-PE/TPS blend in the near future.

2. Materials and methods

2.1. Materials

Linear low density polyethylene (LLDPE, LL 1001KW), with a density of 0.918 g/cm³ was a product of ExxonMobil (Irving, TX, USA). The melt flow index (MFI) of LLDPE, measured according to ASTM D1238-10, procedure A (ASTM, 2010a), using a temperature of 190 °C, a load cell of 2.16 kg and a preheating time of 6 min, was 1.0 g/10 min. Cassava starch (99% purity, 22% amylose content and 11.6% moisture content) with particle sizes in the range of 8–20 μm was purchased from Tong Chan Registered Ordinary Partnership (Bangkok, Thailand). Stearic acid, potassium persulfate, sodium nitrate and calcium chloride were supplied by Ajax Finechem (New South Wales, Australia). Dimethyl sulfoxide (DMSO) was obtained from RCI Labscan (Bangkok, Thailand). Ethanol was purchased from Merck (Darmstadt, Germany). Glycerol used was a commercial grade product.

2.2. Synthesis of ST-SA

ST-SA with a degree of substitution of stearyl chains of 0.01 was synthesized via condensation reaction. Stearic acid (3 mol equivalent to pyranose ring) and potassium persulfate (1.0% w/w of starch) were added to a solution of cassava starch in DMSO (10% w/v). The mixture was mechanically stirred at 100 °C for 6 h under reduced pressure to remove by-product (water) from the condensation reaction. The obtained homogeneous solution was precipitated in ethanol; the precipitate was then collected by centrifugation at 18,800 × g for 10 min at 25 °C, washed several times with ethanol, and dried at 45 °C in a vacuum oven (model VD 53; Binder, Tuttlingen, Germany). The chemical structure of ST-SA was characterized by FT-IR and ¹H NMR techniques. A sample was ground with potassium bromide (KBr) into a homogeneous fine powder and then hydraulically pressed to form a pellet prior to FTIR measurement using a Bruker Tensor 27 FTIR spectrometer (Bruker, Billerica, MA, USA) over a wavenumber range of 400–4000 cm⁻¹ with 16 scans at a resolution of 4 cm⁻¹. ¹H NMR analysis of a sample dissolved in deuterated dimethyl sulfoxide (DMSO-d₆) was performed at 80 °C using a 400 MHz spectrometer (JNM-ECS series; JEOL, Tokyo, Japan). The degree of substitution (DS) of stearyl chains onto starch molecules was calculated from the peak integral ratio of stearic acid protons to starch protons, i.e. DS = (I_{0.8–1.2/31})/(I_{3.3–5.6/7}).

ST-SA: FTIR (cm⁻¹): 3294 (–OH stretching), 2916 and 2419 (–CH– stretching), 1701 (C=O stretching), 1643 (–OH bending), and 1016 and 949 (–CO stretching) (Fig. S1). ¹H NMR (DMSO-d₆, 80 °C, ppm): 3.3–5.6 (methine and methylene protons of pyranose

ring) and 0.8–1.2 (methine and methylene protons of stearic acid) (Fig. S2). DS of the synthesized ST-SA was 0.01.

2.3. Preparation of LLDPE/TPS blend resins and films containing ST-SA

TPS was firstly prepared by compounding cassava starch, glycerol (28.8 wt%) and ST-SA in a twin-screw extruder (LTE-20-40; Labtech Engineering, Samut Prakan, Thailand; L/D = 40) using a barrel temperature ranging from 80 to 150 °C, a screw speed of 180 rpm and a material feed rate of 18 rpm. The concentration of ST-SA was varied to obtain the final LLDPE/TPS blends with different ST-SA contents of 0, 1, 3 and 5%.

The as-prepared TPS was then blended with LLDPE in a twin-screw extruder using a barrel temperature profile ranging from 80 to 155 °C, a screw speed of 180 rpm and a material feed rate of 18 rpm to obtain the LLDPE/TPS blend (Fig. S3). The weight ratio of LLDPE:TPS used was 60:40. Four types of LLDPE/TPS blend resins containing different concentrations of ST-SA (0, 1, 3 and 5%) were then converted into films by blown film extrusion using an LE 25-30/C single-screw extruder with an L/D ratio of 30 connected to an LF 400 film-blowing attachment (Labtech Engineering). Blown film extrusion was carried out at a temperature range of 130–150 °C, a screw speed range of 30–50 rpm and a take-off speed of 2.6 m/min. The obtained LLDPE film and LLDPE/TPS blend films were semitransparent; however, LLDPE film surface was glossy, while LLDPE/TPS blends look matt (Fig. S4). The thickness of the obtained LLDPE and LLDPE/TPS blend films was in the range of 30–50 μm.

2.4. Properties testing of LLDPE/TPS blend resins and films containing ST-SA

2.4.1. Determination of rheological properties

Rheological properties of resin samples were investigated using a rotational cone and plate geometry rheometer (ARES advanced rheometric expansion system; TA Instruments, New Castle, DE, USA) with a cone angle of 3° at low shear rate (0.01–5.0 s⁻¹) and an advanced capillary rheometer (RH7; Malvern Instruments, Worcestershire, UK) at high shear rate (10²–10⁴ s⁻¹). The samples were stored in a desiccator containing saturated magnesium nitrate solution at 30 °C (52% relative humidity, RH) for 2 days. After equilibrating the samples at 150 °C for 5 min, the rheological measurement was performed at a constant temperature of 150 °C (Elanmugilan, Sreekumar, Singha, Al-Harhi, & De, 2013; Wang, Yu, Ma, & Wu, 2007), which was the maximum blown film extrusion temperature. At this temperature, all samples were completely melted even under applying low shear force (Fig. S5). For the rheological measurement by a rotational cone and plate geometry rheometer, the weight of sample used was 50 g and an Orchestrator software was applied for the data acquisition. The higher sample weight of 150 g was used for the analysis by a capillary rheometer and the data acquisition was obtained using a Rosand Flowmaster software. Each sample was measured at least in duplicate.

The power-law model frequently used to express the behavior of non-Newtonian fluids is presented as a relationship between shear viscosity and shear rate (Eq. (1)), or shear stress and shear rate (Eq. (2)):

$$\eta = K\dot{\gamma}^{n-1} \quad (1)$$

where η is the dynamic viscosity (Pa s), $\dot{\gamma}$ is the shear rate (s⁻¹), K is the consistency coefficient (Pa s^{*n*}) or consistency index and n is the power-law index. Shear-thinning behavior is described when $n < 1$.

$$\tau = K\dot{\gamma}^n \quad (2)$$

Download English Version:

<https://daneshyari.com/en/article/1383152>

Download Persian Version:

<https://daneshyari.com/article/1383152>

[Daneshyari.com](https://daneshyari.com)