



Morphological characteristics of stearic acid-grafted starch-compatible linear low density polyethylene/thermoplastic starch blown film

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ABSTRACT

The objective of the present work is to verify the possibility of using stearic acid-grafted starch (ST-SA) as a novel compatibilizer for a blend system consisting of linear low density polyethylene (LLDPE) and thermoplastic starch (TPS). ST-SA was successfully synthesized, as confirmed by FTIR and ¹H NMR techniques. The obtained ST-SA was compounded with LLDPE and TPS in a twin-screw extruder. A weight ratio of LLDPE:TPS was fixed at 60:40, while ST-SA concentrations were varied from 1% to 5%. The blends were further converted into films by blown film extrusion. Incorporation of ST-SA improved the extrusion processability and melt flowability of the LLDPE/TPS blends. In addition, the blends became compatible and homogeneous when ST-SA was loaded due to the increased interfacial adhesion between LLDPE and TPS phases. The results suggest that ST-SA, particularly at a content of 1%, could serve as an effective compatibilizer for the immiscible LLDPE/TPS blend system.

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1. Introduction

Polyethylene (PE) is one of the most important thermoplastics used nowadays due to its low price, light weight, durability, chemical inertness, and ease of converting into plastic products of various shapes and sizes. PE films have been utilized in various areas including packaging (e.g. plastic bags, wrap films, labels) and agricultural applications (e.g. mulch film). However, PE is a petroleum-based plastic that is non-biodegradable under normal composting conditions [1], which contributes to the adverse impact of plastic waste on the environment.

Recently, biodegradable plastics have gained considerable interest because they can be degraded by the action of microorganisms found in nature. Thermoplastic starch, or TPS, which is derived from cheap, renewable, biodegradable [2], compostable [3] and non-toxic raw materials, is considered to be one of the cheapest biodegradable plastics with short composting time [3]. TPS has been used as a replacement or substitute for non-biodegradable petroleum-based plastics, including PE, in order to reduce the use of PE and to lower the cost of the final products. However, the hydrophilicity of TPS restricts its compatibility with hydrophobic PE [4,5].

Several studies have reported that incorporation of compatibilizers – e.g. maleic anhydride-grafted polyethylene [6–10], polyethylene-co-vinyl alcohol [11], polyethylene-maleic anhydride terpolymers containing elastomeric segments [8] and

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stearic acid-grafted starch [12] – could improve the compatibility between PE and TPS phases and enhance the properties of the blends. To our knowledge, a starch-based compatibilizer for a PE/TPS blend system has rarely been utilized [12], although it is of interest because it is produced mainly from environmentally friendly and renewable materials, which could result in reduced use of PE in the future, and it is applicable for either bio-based or biodegradable polymeric blend systems. A series of modified granular starch, such as octanoated starch [13], epichlorohydrin cross-linked starch [14], adipate starch [15] and acetylated starch [15], has been blended with PE to overcome the restricted interfacial adhesion between PE and starch granules [15] and to improve the blend properties. However, the amount of the modified starch loaded was rather high, depending on the required weight fraction of starch, resulting in increased cost. Rivero et al. found that octenyl succinylated starch with a content of 10 wt% of starch could act as a compatibilizing agent for the blends of PE and native cassava starch granules; the interfacial adhesion with PE occurred only at the surface of starch granules [16]. Blending PE with TPS was thus expected to offer the interfacial attraction force between PE and starch at the molecular level, as the starch granules are destroyed during the plasticization, resulting in much improved compatibility. Recently, we reported that stearic acid-grafted starch (ST-SA) could improve the tensile strength, secant modulus, extensibility, and UV absorption of the LLDPE/TPS blend, as well as promote diminished water vapor and oxygen permeabilities [12]; however its morphological characteristics and microstructures have not yet been revealed.

Therefore, the present article focuses on the role of stearic acid-grafted starch (ST-SA) as a compatibilizer for a PE/TPS blend system. ST-SA was synthesized and characterized using FTIR and ^1H NMR techniques. The effects of ST-SA on extrusion processability, melt flowability, morphological properties, chemical interaction, and crystallinity of the PE/TPS blend resins and films were also investigated.

2. Materials and methods

2.1. Materials

Linear low density polyethylene (LL 1001KW), with a density of 0.918 g/cm^3 and a melt flow index (MFI) of 1.0 g/10 min ($190\text{ }^\circ\text{C}/2.16\text{ kg}$; ASTM D1238), was purchased from ExxonMobil (Irving, TX, USA). Cassava starch (99% purity and 11.6% of moisture content) was supplied by Tong Chan Registered Ordinary Partnership (Bangkok, Thailand). Stearic acid and potassium persulfate were products of Ajax Finechem (New South Wales, Australia). Dimethyl sulfoxide (DMSO) was obtained from RCI Labscan (Bangkok, Thailand). Ethanol was purchased from Merck (Darmstadt, Germany). Lugol's solution (1.8% of I_2) was a product of Fisher Science Education (Hanover Park, IL, USA). Glycerol used was a commercial-grade product.

2.2. Synthesis and characterization of stearic acid-grafted starch

Stearic acid-grafted starch (ST-SA) was synthesized according to a method modified from the one reported by Simi and Emilia Abraham [17]. Briefly, cassava starch was dissolved in DMSO (10% w/v) at $100\text{ }^\circ\text{C}$ under reduced pressure for 24 h. Stearic acid (3 mol equivalent to the pyranose ring) and potassium persulfate (1.0% w/w of starch) were subsequently added to the starch solution. The reaction was performed with agitation under reduced pressure at $100\text{ }^\circ\text{C}$ for 6 h. The obtained homogeneous mixture was precipitated in ethanol. The precipitate was then collected by centrifugation at 8000 rpm for 10 min at $25\text{ }^\circ\text{C}$; afterward it was washed several times with ethanol and dried at $45\text{ }^\circ\text{C}$ in a vacuum oven (model VD53; Binder, Tuttlingen, Germany) to provide ST-SA in the form of a yellowish powder.

Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^1H NMR) techniques were applied to characterize the chemical structure of the obtained ST-SA. For FTIR characterization, a sample was ground with potassium bromide (KBr) into a homogeneous fine powder and then hydraulically pressed to form a pellet. The FTIR measurement was performed in a transmission mode by a Bruker Tensor 27 FTIR spectrometer (Bruker, Billerica, MA, USA) over a wavenumber range of $400\text{--}4000\text{ cm}^{-1}$ with 16 scans at a resolution of 4 cm^{-1} . For ^1H NMR analysis, a sample was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6). The measurement was carried out at $80\text{ }^\circ\text{C}$ by a 400 MHz spectrometer (JNM-ECS series; JEOL, Tokyo, Japan).

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

Cassava starch was premixed with glycerol and ST-SA in a kitchen mixer (model HW-3083S; House Worth, Thailand). The weight ratio of starch to glycerol was fixed at 100:40.5, while the contents of ST-SA were varied as 0, 2.5, 7.2 and 11.6 wt%. The mixture was fed into an LTE 20-40 twin-screw extruder with an L/D ratio of 40 (Labtech Engineering, Samut Prakan, Thailand) through an LSF 20-10 twin-screw side feeder (Labtech Engineering). The extrusion was carried out using a barrel temperature profile in a range of $80\text{--}150\text{ }^\circ\text{C}$, a screw speed of 180 rpm and a material feed rate of 18 rpm. The extrudate of thermoplastic starch (TPS) was cut into 2.5-mm-long plastic resins using an LZ 120 pelletizer (Labtech Engineering). Four types of TPS resins, containing ST-SA with different contents of 0, 2.5, 7.2 and 11.6 wt%, were produced.

The as-prepared TPS resins were subsequently compounded with LLDPE in a twin-screw extruder using a barrel temperature profile ranging from $80\text{ }^\circ\text{C}$ to $155\text{ }^\circ\text{C}$, a screw speed of 180 rpm and a material feed rate of 18 rpm. The weight ratio of LLDPE to TPS was fixed at 60:40. TPS resins containing ST-SA with contents of 0, 2.5, 7.2 and 11.6 wt% were used to prepare

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