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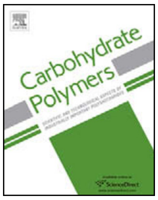

Flexible starch-polyurethane films: Physiochemical characteristics and hydrophobicity

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ABSTRACT

Starch-polyurethane (PU) composite films with improved mechanical and hydrophobic properties were developed in this work. A simple and effective microwave-aided starch gelatinisation instrument was used to prepare glycerol plasticized high amylose starch (HAGS) material. Polyethylene glycol-isocyanate (PEG-iso) linker was prepared by reacting PEG 1000 with hexamethylene diisocyanate (HMDI). PEG-iso linker was then grafted into HAGS forming three dimensional urethane networks (PEG-PU). HAGS-PEG-PU composite blends were prepared and dried at ambient temperature to obtain HAGS-PEG-PU films. The mechanical properties and hydrophobicity (as contact angle, CA) of the HAGS-PEG-PU films were measured and analysed. Fourier transform infrared spectroscopy showed good grafting of PEG-iso into starch structure. Increase of PEG-iso concentration up to 20% (w/w) improved the molecular mixing and interpenetration between the starch and PEG-PU. The HAGS-PEG-PU films had improved hydrophobicity as indicated by CA values ranging from 51 to 110° and very high flexibility as evidenced from elongation at break (ε_B) values from 17 to 1000%. The HAGS-PEG-PU film formulation containing 20% (w/w) PEG-iso provided the best flexibility ($\varepsilon_B > 1000\%$) and hydrophobicity ($CA > 110°$).

1. Introduction

Starch is one of the most promising materials for developing biodegradable packaging due to its abundance in nature, high tensile strength and strong oxygen barrier properties (Liu, Xie, Yu, Chen, & Li, 2009; Menzel et al., 2015; Muscat, Adhikari, Adhikari, & Chaudhary, 2012). However, the properties of currently available thermoplastic starch films are far from meeting the target, especially in terms of surface hydrophobicity, water vapour barrier and mechanical properties (Niazi, Zijlstra, & Broekhuis, 2015; Santayanon & Wootthikanokkhan, 2003). Therefore, modification is necessary to improve the surface hydrophobicity of the starch films.

By mimicking the hydrophobic characteristics of external surface of lotus and other aquatic leaves, popularly known as "lotus effect"(Yan, Gao, & Barthlott, 2011), a water resistant biodegradable material can be engineered which can find greater application in food, pharmaceutical and packaging industry (Cunha & Gandini, 2010a, 2010b). Such hydrophobic properties in food packaging can help minimize effect of variation of relative humidity towards the content, repel water upon contact, and help extend the shelf-life. However, the surface is only considered as hydrophobic when its contact angle measured using pure water is higher than 90° (ASTM, 2013).

In order to introduce hydrophobicity to starch-based packaging, functionalized amphiphilic macromolecules (FAMs) are introduced within the matrix. FAMs covalently bind with hydroxyl terminal on starch backbone, anchor the hydrophobic moieties to the hydrophilic surface of starch film, and improve the film's hydrophobicity. Muscat, Adhikari et al. (2014) covalently anchored the hydrophobic moieties (natural waxes) onto the surface of starch, using Polyethylene glycol (PEG) as FAM, to improve the film's hydrophobicity and water barrier properties. Although desired coverage of film surface by the tested wax samples was not achieved in Muscat et al.' work, nevertheless, they reported achieving a contact angle value of 90° (Muscat, Adhikari et al., 2014).

PEG is neutral, water soluble, non-toxic polyether and possesses minimal reactivity until it is modified with functional groups such as hydroxyl, carboxyl, and amides (Mu et al., 2016). PEG is an amphilipic molecule (i.e. containing hydrophilic and hydrophobic moieties), either linear or branched polyether terminated with hydroxyl groups and a general structure of [HO-$(CH_2CH_2O)_n$ CH_2CH_2-OH]. PEG can be activated by modifying the –OH terminal

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to either carry same or different functional group via the formation of covalent bond (Alkan, Günther, Hiebler, & Himpel, 2012; Movagharnezhad & Najafi Moghadam, 2016). Therefore, PEG is structurally suitable to be attached to the starch matrix. The creation of covalent bond between PEG and starch is a logical approach for modifying the surface properties of starch that provides the desired functionality on the modified surface without altering the bulk composition (Muscat, Adhikari et al., 2014; Rhodes, Sandhu, & Onis, 2011). PEG is introduced into starch as FAM or spacer. The attachment of FAM alters the fundamental properties and the structural conformation of starch by linking macromolecules to surface (Harris, 1992), whereas the spacer helps to reduce steric hindrance between starch and the attached compound (Banerjee, Aher, Patil, & Khandare, 2012; Kawano & Maitani, 2011). The terminal hydroxyl groups of starch enable PEG to be employed as spacer moiety or linker where they are converted to reactive functional groups.

This study employed “graft-to” approach, to graft PEG and starch using isocyanate as coupling agent. The OH group of PEG can be end-capped with isocyanate (-NCO) group to form PEG-isocyanate (PEG-iso) linker. The PEG-iso can interact with hydroxyl group containing matrices (Rhodes et al., 2011; Veronese, 2001) such as starch to form a stable urethane linkage (Prajapati, Patel, & Patel, 2011). Starch chain contains many hydroxyl groups all of which can be modified by introducing PEG-iso. PEG-iso can be attached to the starch molecules to alter is properties and conformation.

In this study, we report, for the first time, a facile method for preparing HAGS–PEG-PU films via chemisorption of hydroxyl groups of starch with NCOs group of PEG-iso linker without any additive (such as lipids). Adequate dispersion and strong interfacial adhesion between the starch and PEG-PU was achieved by this method and yielded HAGS–PEG-PU film with improved mechanical properties and hydrophobicity. The hydrophobicity, physiochemical characteristics, mechanical properties of synthesised starch-PU films showed that a certain PEG-iso linker to starch ratio achieved very high compatibility between starch and PU and resulted into significantly improved hydrophobicity and flexibility in HAGS-PEG-PU films.

2. Experimental section

2.1. Materials

High amylose (HA) corn starch (Gelose 80) with amylose:amylopectin ratio of (80:20) and moisture content of 14.16% (w/w) was obtained from Ingredion ANZ Pty Ltd. Glycerol (99.5% purity, G), hexamethylene diisocyanate (98% purity, HDI) were purchased from Sigma Aldrich, New South Wales (Australia). Poly (ethylene glycol), (M_W = 1000 g/mol) (PEG 1000) was purchased from Thermo Fisher Scientific and was dried under vacuum at 100 °C for at least 12 h prior use. Starch sample was used as received and the moisture content of the raw materials was measured by gravimetric method and was compensated for while preparing the starch-water slurry before gelatinization.

2.2. Methods

2.2.1. Synthesis of PEG-isocyanate

PEG-isocyanate was prepared by bulk polymerization reaction (Muscat, Adhikari et al., 2014; Yang, Li, & Wen, 1997) where PEG 1000 was reacted with hexamethylene diisocyanate (HDI) at NCO to OH ratio (NCO/OH) of 2.0. HDI was placed in a two-necked round bottom glass reactor under constant nitrogen purge. PEG was added dropwise to isocyanate under constant stirring and heated on an oil bath at 70 °C for 10 min. The completion of the reaction was monitored by the disappearance of OH peak of PEG on Fourier transform infrared (FTIR) spectra at 3384 cm^{-1}. The PEG-iso linker obtained in this way was stored in an air tight container at −5 °C under nitrogen atmosphere before use.

2.2.2. Gelatinisation of starch

Gelatinized starch was prepared by following Muscat et al. (2012) method with slight modification. HA corn starch and glycerol were added into distilled water maintaining a total solid concentration of 5% (w/w). The HA starch: glycerol dry solid ratio was maintained at 80:20. Gelatinisation was carried out using a pressurized Biotage^{TM} microwave reactor (Initiator robot sixty, Biotage AB, Sweden) at 140 °C under constant stirring, with a pressure of 7–8 bar. The suspension was held at 140 °C for 15 min before cooling down. The progress and the completion of starch gelatinization were monitored using a polarized light microscope (Olympus IX70, Japan) fitted with digital camera. This approach was found to be more reliable and effective compared to Parr reactor due to more effective volumetric heating. Mechanical stirrer was used to minimize localized overheating. This reactor was also equipped with a cooling unit to cool down the gelatinized mass or reaction products immediately to 40 °C.

2.2.3. Preparation of HAGS-PEG-PU films

Melted PEG-iso at different concentrations of 2, 5, 10, 15 and 20% (w/w) was added to HAGS suspension at room temperature and thoroughly mixed for 15 min. No catalyst was used in this reaction to get a material that suitable for food contact. The solution was then cast onto a Teflon mould, and was dried at room temperature for 48 h followed by drying in oven at 40 °C for 24 h. Films produced in this way were conditioned in a desiccator containing magnesium nitrate (52.9% RH) for at least 48 h prior to analysis.

2.3. Characterization of HAGS-PEG-PU films

2.3.1. Determination of interaction between HAG and PEG-iso

Specific spectral “signatures” of the HAGS and PEG iso were acquired using an attenuated total reflectance (ATR) FTIR spectroscope (Nicolet 6700, Thermo Scientific, USA) with a diamond coated zinc selenide crystal plate (reflection plate with pressure arm). The spectra in the range of 650 and 4000 cm^{-1} with automatic signal gain were collected in 16 scans at a resolution of 4 cm^{-1} and were averaged.

2.3.2. Acquiring microstructure images

Images of the microstructure of film samples were observed and acquired using a field emission scanning electron microscope (FESEM) (Philip XL-30). To investigate the cross section, samples were immersed in liquid nitrogen for 5 min and fractured. Prior to observation, the samples were mounted on the specimen stub and sputtered with a thin layer of Iridium in order to make the sample more conductive. Finally, the images were taken at an accelerating voltage of 5 kV, spot size 2.0, with 5000× magnification.

2.3.3. Measurement of thermal properties and crystallinity

The thermal properties of HAGS-PEG-PU films (melting and crystallization peaks) were determined by a differential scanning calorimeter (DSC) (DSC 3, Metler Toledo, New Castle, USA), equipped with a quench cooling accessory. The system was calibrated for temperature (T_m) and heat of fusion (ΔH_m) with indium (T_m = 156.6 °C, ΔH_m = 28.51 Jg^{-1}) and zinc (T_m = 419.5 °C, ΔH_m = 107.03 Jg^{-1}). The samples (about 5 mg) were hermetically sealed in aluminium pans and an empty pan was used as reference. The specimens were scanned at 10 K min^{-1} over a temperature range of −50–90 °C to remove the thermal history. The specimens were heated for two consecutive runs at the above specified temperature range.