



Silane modified starch for compatible reactive blend with poly(lactic acid)



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ABSTRACT

A reactive blend of poly(lactic acid) (PLA) and a surface modified starch by silane coupling agent to achieve compatibility is proposed. A detailed structural analysis by using ^1H - ^1H TOCSY NMR spectrum clarifies, for the first time, that chloropropyl trimethoxysilane (CPMS) forms covalent bonds with starch during starch modification and consequently forms covalent bonds with PLA in the step of blending to produce a reactive blend of PLA and CP-starch. The CP-starch covalently bound with PLA provides the compatibility between PLA and starch and also plays the role as nucleating agent as identified from a significant increase of degree of crystallinity (as high as 10–15 times), as well as induces chain mobility, as identified from a slight decrease in glass transition temperature (~ 5 – 10°C). The PLA/CP-starch film performed as well as neat PLA with slight increases in tensile strength and elongation at break, as compared to other PLA/silane modified starch films.

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1. Introduction

PLA is a biodegradable plastic derived from 2-hydroxy propionic acid which is comparable to commodity thermoplastics in terms of high transparency, moderate gas permeability, and high strength. Nevertheless, PLA has limitations regarding price and brittleness. The points to develop PLA, therefore, are mostly related to the cost reduction and the mechanical properties improvement (Garlotta, 2002; Huneault & Li, 2007).

The key to improve the mechanical properties is to initiate a good balance between the crystalline and amorphous phases of PLA. Up to the present, ways to accelerate crystallization, especially the addition of nucleating agent, have been proposed. The nucleating agent plays an important role in reducing the surface free energy barrier toward nucleation resulting in crystallization at a faster rate than the normal crystallization rate (Li & Huneault, 2007). Several nucleating agents such as starch (Cai et al., 2011; Kang, Lee, Lee, Narayan, & Shin, 2008; Ke & Sun, 2003), talc (Haubruge, Daussin, Jonas, & Legras, 2003; Shakoore & Thomas, 2013; Yu et al., 2012), montmorillonite (Chu & Wu, 2007; Nam, Ray, & Okamoto,

2003), hydrazide compounds (Fan et al., 2013; Kawamoto, Sakai, Horikoshi, Urushihara, & Tobita, 2007), etc., have been reported.

Starch is a potential material for blending with PLA not only because it is completely biodegradability but there is also a natural abundance at a low cost. Starch is under strong inter- and intramolecular hydrogen bond networks; therefore, it is insoluble in most solvents and high hydrophilic. The processing of starch to be a plastic material is quite difficult due to degradation without melting at high temperature and the blending of starch with other polymers always faces the problem of phase separation. It is known that the modification of the hydroxyl groups on the anhydroglucose units (AGUs) with the hydrophobic group is a way to obtain compatibility with other polymers (Biswas, Shogren, Kim, & Willett, 2006; Kaur, Ariffin, Bhat, & Karim, 2012; Shogren, 2003; Zhou, Ren, Tong, Xie, & Liu, 2009). For PLA and starch blend in the past, the coupling agents to modify starch in order to form the covalent bonds with PLA such as methylenediphenyl diisocyanate (MDI) (Wang, Sun, & Seib, 2001, 2002a, 2002b), maleic anhydride (MA) (Xiong et al., 2013; Zhang & Sun, 2004b), dioctyl maleate (DOM) (Zhang & Sun, 2004a), etc., were also reported.

On this viewpoint, it comes to our idea that the blend of starch could be practical for the industries if we can modify starch to be reactive enough not only for coupling with the polymer but also for a one-pot reactive blend in processing machine.

Silane coupling agent is known for the function of combining two materials via the hydrolyzable and organofunctional reactive sides (Plueddemann, 1982). In the past, the uses of silane coupling

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agent for the reactive blend between starch and polymers were reported. For example, the compatibility between polyethylene and starch (10 wt%) was successful when the starch was pre-treated with sodium alkyl silicate (Griffin, 1994; Wu, Qi, Liang, & Zhang, 2006) demonstrated the improvement of interfacial adhesion between starch and rubber by using resorcinol-formaldehyde and *N*-β(aminoethyl)-aminopropyl trimethoxy silane.

In the case of PLA and silane treated starch blends, they were widely reported but mainly focused on the changes in mechanical and thermal properties (Liu, Cao, & Ou-Yang, 2013; Pilla, Gong, O'Neill, Rowell, & Krzysik, 2008). Although the use of silane coupling agent for starch and polymer was proven to be practical, the detailed structural analyses have not been completed.

Based on the above mentioned viewpoint, the present work pays an attention on the starch coupling with PLA via silane coupling agent in the reactive blend system. In the first step, a systematic study of coupling reaction between organofunctional silane coupling agents and starch to clarify the optimal type of silane was carried out. A detailed study on chemical structure by NMR technique led us to the qualitative and quantitative analyses for information of the bond formation as well as the degree of substitution of silane. In the second step, the use of the obtained starch coupling with silane for the reactive blend with PLA was focused. In this step, the studies related to (i) the detailed structural analysis to declare the coupling between silane modified starch (silane-starch) and PLA, (ii) the morphological studies to observe compatibility between starch and PLA, (iii) the thermal analysis to evaluate the effect of starch in the blend on the nucleation and the plasticity, and (iv) the tensile test to clarify the mechanical properties of the PLA blended with silane-starch were carried out.

2. Materials and experimental

2.1. Materials

PLA 2002D was purchased from NatureWorks LLC, USA. Casava starch was obtained from ETC International Trading Co., Ltd., Thailand. A series of trimethoxy silane coupling agents – 3-glycidoxypropyl trimethoxysilane (GPMS), 3-aminopropyl trimethoxy silane (APMS), and 3-chloropropyl trimethoxysilane (CPMS) – were bought from Sigma-Aldrich, Germany, with 97–98% purity. All reagents were used without further purification.

2.2. Sample preparations (Scheme 1)

2.2.1. Modification of starch with GPMS, APMS, and CPMS

A trimethoxy silane coupling agent, GPMS (0.1 mol, 22.5 mL), was stirred vigorously with an excess amount of deionized water at 50 °C until the turbidity vanished before mixing with dry starch (1 mol, 162.0 g). The mixture was stirred thoroughly at 50 °C under vacuum for 2 h before filtrating and drying at 70 °C in a hot air oven for a day. The crude product was purified by washing twice with tetrahydrofuran (THF) before drying at 60 °C in a vacuum oven for 6 h to obtain GP-starch, **1**.

FTIR (KBr; ν , cm^{-1}) for GP-starch: 1210 (s, C–O stretching in epoxides), 1100–1000 (s, Si–O–CH₂ stretching), 1100–1000 (s, C–O–C stretching), and 850 (vs, Si–C stretching).

¹H-NMR (δ , ppm, 500 MHz, DMSO-*d*₆, 60 °C) for GP-starch: 1.20 (m, CH₂), 2.08 (s, CH₂), and 3.35 (br, CH) assigned to GPMS, and 3.35–3.85 (br, CH) and 4.73–5.15 (s, CH) assigned to AGUs.

The molar feed ratios between silanol and starch were varied from 0.01:1 to 1:1 to determine the optimal condition. Similarly, other silane coupling agents, APMS (0.1 mol, 17.9 mL) and CPMS (0.1 mol, 19.8 mL), were used to obtain AP-starch (the possible

structures: **2** and/or **3**), and CP-starch (the possible structures: **4** and/or **5**), respectively.

FTIR (KBr; ν , cm^{-1}) for AP-starch: 1575 (br, NH bending), 1150 (s, Si–O–Si stretching), 1100–1000 (s, C–O–C stretching), and 850 (vs, Si–C stretching).

¹H NMR (δ , ppm, 500 MHz, D₂O, 60 °C) for AP-starch: 0.58 (s, CH₂), 1.60 (s, CH₂), and 2.82 (s, CH₂) assigned to APMS, and 3.63–3.80 (br, CH), 3.90 (s, CH₂), and 5.15 (s, CH) assigned to AGUs.

FTIR (KBr; ν , cm^{-1}) for CP-starch: 1275 (s, CH₂–Cl wagging), 1100–1000 (s, Si–O–CH₂ stretching), 1100–1000 (s, C–O–C stretching), 890 (s, C–Cl stretching), and 850 (vs, Si–C stretching).

¹H NMR (δ , ppm, 500 MHz, DMSO-*d*₆, 60 °C) for CP-starch: 0.8 (s, CH₂), 1.85 (s, CH₂), and 3.60 (br, CH₂) assigned to CPMS, and 3.40–3.70 (br, CH) and 4.73–5.15 (s, CH) assigned to AGUs.

2.2.2. Blending of PLA with GP-starch, AP-starch, and CP-starch

GP-starch was blended with PLA resin at weight ratios (PLA/GP-starch) of 90/10, 70/30, and 50/50 by using a Labtech Engineering LTE 20–40 counter-rotating twin screw extruder. The temperature and screw speed settings were in the range of 150–165 °C and 25–40 rpm, respectively. The 90/10 blend was blown to obtain a PLA/GP-starch film with ~0.10 mm thickness by using a Labtech Engineering LE 20–30 single-screw extruder equipped with a Labtech Engineering LF-400 blown film unit. Other films, PLA/AP-starch and PLA/CP-starch, were prepared with similar procedures.

2.3. Characterizations

2.3.1. Structural characterization

The detailed structural analyses were completed by using a Bruker Equinox 55/FRA106S Fourier transform infrared (FT-IR) spectrometer (a resolution of 2 cm^{-1} (32 scans), in the range of 4000–400 cm^{-1}), and a Bruker Biospin Avance 500 NMR (nuclear magnetic resonance) spectrometer (based on ¹H–¹H TOCSY (total correlation spectroscopy) NMR spectrum at 60 °C). Deuterated dimethyl sulfoxide (DMSO-*d*₆) was the NMR solvent for GP-starch, CP-starch, and their silanols while deuterium oxide (D₂O) was for AP-starch and APMS silanol. In the cases of PLA/silane-starch blends, the samples of the 50/50 weight ratio were used and dissolved in deuterated chloroform (CDCl₃).

The degree of substitution (DS) of silane on starch was calculated from ¹H NMR spectra using Eq. (1):

$$DS = \frac{\text{integration of } (-\text{CH}_2-) \text{ at } 1.6\text{--}2.0 \text{ ppm}}{2 \times 3 \times \text{integration of } (-\text{CH}-) \text{ at } 5.0\text{--}5.3 \text{ ppm}} \quad (1)$$

where the integrations of (–CH₂–) at 1.6–2.0 ppm and (–CH–) at 5.0–5.3 ppm represent the methylene protons of silane and the methine proton of AGU, respectively.

2.3.2. Contact angle measurement

Starch, GP-starch, AP-starch, and CP-starch were pressed to form pellets before measuring the contact angle with a KRÜSS DSA 10 drop shape analysis system.

2.3.3. Thermal analyses

Thermal analyses were evaluated by using a TA Instruments Q50 thermal gravimetric analyzer (TGA), in the range of 30–700 °C with a heating rate of 5 °C/min under nitrogen flow (10 mL/min), and a Netzsch 200 F3 Maia differential scanning calorimeter (DSC), the sample (10 mg) was sealed in an aluminum pan and heated from –20 °C to 200 °C (heat–cool–heat) with a heating and cooling rate of 5 °C/min under nitrogen flow (50 mL/min). The degree of

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