

# Preparation and characterization of acorn starch/poly(lactic acid) composites modified with functionalized vegetable oil derivatives



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## ABSTRACT

Composites of acorn starch (AS) and poly(lactic acid) (PLA) modified with dimer fatty acid (DFA) or dimer fatty acid polyamide (DFAPA) were produced by a hot-melt extrusion method. The effects of DFA and DFAPA contents on the mechanical, hydrophobic, thermal properties and melt fluidity of the composites were studied under an invariable AS-to-PLA mass ratio of 40/60. SEM and DMA research results show that the compatibility of AS/PLA composites are determined by the dosage of DFA or DFAPA. The hydrophobicity and melt fluidity of composites are improved with the addition of DFA and DFAPA. The glass transition temperatures of the composites are all reduced remarkably by additives DFA and DFAPA. However, DFA and DFAPA exert different effects on the mechanical properties of AS/PLA composites. In the DFAPA-modified system, the tensile and flexural strength first increase and then decrease with the increase of DFAPA dosage; the mechanical strength is maximized when the dosage of DFAPA is 2 wt% of total weight. In the DFA-modified system, the tensile and flexural strength decrease with the increase of DFA dosage.

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## 1. Introduction

With the widespread concerns of environmental pollution and the forthcoming depletion of fossil fuels in recent decades, considerable research efforts have been devoted to design and preparation of novel industrial products using cheap natural bio-materials as raw materials, such as starch, cellulose, vegetable oil and chitin (Bendaoud & Chalamet, 2015; Pircher et al., 2014; Sharmin, Zafar, Akram, Alam, & Ahmad, 2015; Široký et al., 2012).

Starch, an abundant, biodegradable, inexpensive and renewable natural polymer, can be blended with many commercially available biodegradable thermoplastic polymers to form various novel biodegradable composites. Currently, there are many biodegradable polymers in the industrial market, such as poly-(lactic

acid) (PLA) (Oksman, Skrifvars, & Selin, 2003), polycaprolactone (PCL) (Newman, Bello, & Laredo, 2015), poly(butylene succinate) (PBS) (Deng & Thomas, 2015), poly(hydroxybutyrate-covalerate) (PHBV) (Jost & Langowski, 2015) and poly(esteramide) (PEA) (Ali Mohamed, Salhi, Abid, El Gharbi, & Fradet, 2014; Zafar, Zafar, Sharmin, & Ahmad, 2010). Among them, PLA has received much attention because of its high rigidity, excellent mechanical performance, biodegradability, compatibility and hydrophobicity (Garlotta, 2001; Hamad, Kaseem, & Deri, 2010). PLA is a favorable matrix material for preparing natural resource-based composites because of its superior biodegradability and biological compatibility (Mohanty, Misra, & Hinrichsen, 2000).

Starch/PLA composites display many advantages, such as biodegradability, low cost, low density, high toughness, high thermal resistance and renewability (Mano, Koniarova, & Reis, 2003; Park, Im, Kim, & Kim, 2000). As reported, PLA can be advantageously mixed with starch granules to form composites with lower production cost and superior mechanical/degradable properties. However, the incompatibility of starch with the PLA matrix leads to poor interfacial adhesion and easy detachment (Liu et al., 2002; Wang, Sun, & Seib, 2002). Rigid starch granules might make the

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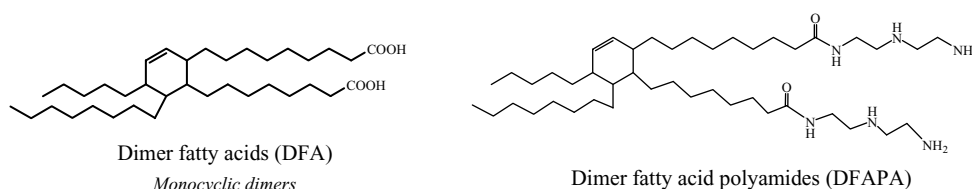


Fig. 1. Commonly typical molecular structure of DFA and DFAPA.

resulting composites even more brittle than PLA. In addition, the water absorption of starch granules decides the poor moisture resistance of the composites (Ke & Sun, 2001; Wang, Yu, Chang, & Ma, 2008). These drawbacks lead to deterioration of mechanical properties and restrict their usability in special circumstances. In order to solve these issues, a general measure is adding some modifying agents (e.g. compatibilizers, plasticizers, flexibilizers, and hydrophobic agent) into the compositing system (Huneault & Li, 2007; Ke & Sun, 2004; Martin & Averous, 2001; Zhang & Sun, 2004). These modifying agents can improve the compatibility between PLA and starch granules, plastify starch granules to enhance their dispersity into PLA matrix, and improve the toughness of PLA matrix or the hydrophobicity of composites.

Compatibilizers suitable for starch/PLA composites generally contain some reactive functional groups such as anhydride, carboxylic acid and isocyanate groups (Ohkita & Lee, 2004; Wang et al., 2002a,b; Wu, 2005). These groups could form a crosslinking structure at the interface between the molecular chains of PLA matrix and the hydroxyl groups on the surface of starch granules during hot-melting blending. However, the addition of compatibilizers could further reduce the toughness of composites. Another method to improve the compatibility of PLA/starch composites is to plastify starch granules. Through high-temperature and high-shear melt extrusion with plasticizers, native starch granules can be processed into thermoplastic starch (TPS) by destroying the strong intermolecular hydrogen of starch. The commonly-used plasticizers are water, polyhydric alcohols, polyamine, glycerol, citrate, polyethylene glycol (PEG) and urea. However, plasticizers may cause degradation of PLA during hot-melting blending. Also the migration, and water/moisture absorption of plasticizers could reduce the overall properties of composites, which limits their wide application (Yew, Mohd, & Mohd Ishak, 2005). Thus, the ability of universal plasticizers is very limited in improving the compatibility and mechanical properties of modified composites.

Recently, bio-based plasticizers have attracted great attention due to their renewability and the occurrence of energy crisis. The use of vegetable oils in preparation PLA/Starch composites has been studied extensively. When pure triglyceride oils were added as toughening agents to prepare PLA/Starch composites, the PLA and oil formed a phase separated mixture. Meanwhile, the hydrophobic oil also could cause weak interaction between starch and vegetable oil. Thus, the addition of pure vegetable oils cannot toughen the PLA matrix of composites. However, many derivatives of triglyceride oils (e.g. ESO and TMA) have functional groups that can improve the compatibility and toughness of composites (Xiong et al., 2013; Zhu et al., 2013). Our motivation is to create a series of high-performance modified PLA/starch composites using two novel plant-oil derivatives containing amido or carboxyl groups.

Starch is a major carbohydrate in corn, wheat, potato and rice seed endosperms. Exploring starch-based plastic products is considered as an effective way to solve the increasingly serious problem of plastic waste. However, food security and hunger are still severe, many countries have legislated against the use of grain resources as industrial feedstock. Therefore, it is urgent to develop materials based on non-food starch resource. Acorn starch (AS), a natural forestry starch resource extracted from acorn kernels, is rich

in amylopectin which complicates its digestion, and in low toxic tannin acid which is difficult to remove (Lee, Kim, & Katsuyoshi, 1998). Thus, abundant corn starch resource is abandoned. The utilization of non-food AS resource in material field is an advisable way to replace traditional food starch resource. Dimer fatty acids (DFA) and dimer fatty acid polyamides (DFAPA), derived from unsaturated fatty acids of vegetable oils, are eco-friendly and commercially available chemical feedstock (Hablot, Tisserand, Bouquey, & Avérous, 2011; Heidarian, Ghasem, & Daud, 2005; Liu, Jiang, & Chen, 2012). With reactive functional carboxyl and amide groups, DFA and DFAPA (typical molecular structures shown in Fig. 1) are good candidates for preparation of oil-modified Starch/PLA composites. Herein, we report a “One-step extrusion” strategy to prepare two series of modified AS/PLA composites using DFA or DFAPA as a modifier, respectively. The mechanical, thermal, and microstructural properties of the composites, as well as the effects of functional amido or carboxyl on their overall properties were investigated.

## 2. Experimental

### 2.1. Materials

Acorn starch (AS) was purchased from Dragon Flying Acorn Development Co., Ltd, Huadian, China. The amylose, amylopectin, water, carbohydrates, protein, ash, crude fat and tannins content of acorn starch were 16.52, 61.10, 10.98, 2.92, 3.42, 2.68, 1.09 and 5.04 wt%, respectively. Dimer fatty acid (DFA) and dimer fatty acid polyamide (DFAPA) were purchased from Nature Fine Chemicals Co., Ltd., Nanjing, China and used as received. PLA, extrusion grade, was purchased from Nature Works Co., Ltd. (America),  $[M_n] = 87,500$ ,  $[M_w] = 169,000$ .

### 2.2. Preparation of composites

AS/PLA composites and their modified composites were prepared according to the following procedure. AS, PLA and DFA (or DFAPA) were weighed, respectively. AS and PLA were in an invariable AS-to-PLA mass ratio of 40/60, and the addition of DFA (or DFAPA) is 1–8 wt% of AS/PLA total weight. First, they were mixed proportionally. Second, the blends were placed into a high speed mixer to obtain homogeneous mixtures. The composites were thereafter extruded on a CTE20 (China) twin-screw extruder. The extruded material was granulated into pellets having lengths of about 1.0–2.0 mm after aircooling. The optimized preparation conditions were as follows: the temperatures of the five heating zones were 155, 165, 175, 168, 165 °C, respectively, the shearing speed was 400 rpm, the adding rate of raw materials was 15 g/min, and the vacuum degree in the 4th heating zone was  $-0.04$  MPa for the extraction of water vapor. The processing pictorial diagram is displayed in Fig. 2. The composites are denoted as follows: DFA2/AS40/PLA60 means that the composite has a DFA-to-AS-to-PLA mass ratio of 2/40/60.

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