



## Research article

# Physicochemical evolutions of starch/poly (lactic acid) composite biodegraded in real soil



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## ABSTRACT

Plastic pollution is a major environmental problem and the waste disposal is a challenge in this case. Poly (lactic acid) (PLA) based biodegradable materials is one of the most attractive polymers which can fulfill the current demand. In this work, the degradation of starch/PLA composite was investigated in real soil environment. The weight loss results demonstrated that the degradation rate of PLA could be accelerated by starch. Scanning electrical microscopy (SEM) and Fourier transform infrared (FTIR) results showed that the samples degraded faster with the presence of starch. The mechanical strengths had an abrupt decrease for the starch/PLA composite while that of PLA only decreased in a low degree. The distribution of carboxyl group intensity and carbon atomic percent reflected the heterogeneity of biodegradation for starch/PLA composite in soil. Moreover, the variation of internal carbon atomic percent was higher than that on the surface, demonstrating that the degradation of starch/PLA composite was bulk degradation. Based on the role of starch played in starch/PLA composite and the physicochemical performance evolutions during biodegradation, it should create a scientific basis for people interested in studying the biodegradation of PLA, and provide some knowledge about controlling the biodegradation rate of PLA through adjusting the content of starch in the composite.

## 1. Introduction

In recent years, the world consumption of polymer plastics has increased exponentially (Deroiné et al., 2014). Consequently, plenty of plastic waste are produced and efficient disposal methods are therefore urgently needed. In this case, waste disposal has become a critical issue for building an environmental civilized society. Considering the growing pressure came from limited resources and environmental safety, biodegradable polymers may be a promising way to ease the pressure of plastic waste disposal. Generally, biodegradable polymers are biopolymers that derived from renewable resources such as polysaccharides, glycolipids, lipopolysaccharides, proteins, and polyhydroxyalkanoates (plant/microbial polyesters) (Fliieger et al., 2003; Kalia and Avérous, 2011), or synthesized from renewable resources such as polyesters produced from bio-derived resources (Nampoothiri et al., 2010). The degradation of these biopolymers is considered to take place throughout three stages: biodeterioration, biofragmentation, and assimilation (Lucas et al., 2008). During the degradation process, biopolymers are broken down to short chains and/or oligomers, followed by microbial assimilation and mineralization, forming carbon dioxide, water, methane, biomass and mineral salts (Lv et al., 2017; Lucas et al.,

2008). Among these biopolymers, poly (lactic acid) (PLA) or starch have appeared as the promising biodegradable materials that attract considerable interest in the research community (Deroiné et al., 2014; Pantani and Sorrentino, 2013).

One of the most attractive characteristics of PLA is its potential degradability in soil (Pantani and Sorrentino, 2013), and thus the degradation products (CO<sub>2</sub>, H<sub>2</sub>O etc) can be diverted from landfill to photosynthesis. However, PLA is more expensive and its degradation rate is slow for the short-term applications (Wu and Hakkarainen, 2015; Yang et al., 2015). Starch, an inexpensive and renewable natural polysaccharide, is a potential candidate for preparing PLA-based degradable composite, which can reduce the production costs and accelerate the biodegradation rate (Zhang and Sun, 2004). So far, starch/PLA products have been successfully used in various fields such as packing, fast-food boxes, and plant pots. Such products are used as short-term applications, which should be disposed by an economic and convenient approach. Soil burial or composting is one of the effective and suitable disposed methods to satisfy the economic and convenient demand. Studies on PLA based biodegradable materials with respect to their biodegradation behavior and mechanism are important for their application and development.

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Many studies have been performed on the biodegradation of PLA or starch materials in different environments such as soil and compost (Shogren et al., 2003; Karamanlioglu and Robson, 2013; Kucharczyk et al., 2016; Maran et al., 2014; Rodrigues et al., 2015; Santonja-Blasco et al., 2010; Wang et al., 2015). A study on the biodegradation of poly (3-hydroxybutyrate-co-4-hydroxybutyrate) (P (3HB, 4HB))/PLA blends in natural soil environment showed that the blends exhibited different degradation rates and mechanisms in different soil burial depths (Weng et al., 2013b). Degradation of cassava starch in the indoor soil indicated that starch acted as an energy source for microorganism growth, and its higher water sorption could promote the entry of the soil microorganism (Maran et al., 2014). Biological oxidative degradation mechanisms (oxidative degradation reaction catalyzed by heme proteins and peroxide-activated myoglobin in a mimetic pro-oxidant biological systems) of PLA/thermoplastic starch (TPS) blends in simulated soil suggested that oxidative reactions and the peroxides in the materials had an enhanced effect on the degradation ability of PLA and PLA/TPS blends (Rodrigues et al., 2015).

The degradation behavior and mechanism in soil are complex and unclear due to the complicated environmental conditions (Karamanlioglu and Robson, 2013; Rudnik and Briassoulis, 2011; Lv et al., 2017). As earlier reported, the mechanism of PLA degradation usually started with hydrolysis induced by the diffusion of water into materials, followed by the microorganisms attack and assimilation on the break-down polymer chains produced by hydrolysis (Karamanlioglu and Robson, 2013; Kolstad et al., 2012; Rudnik and Briassoulis, 2011). The degradation rate of PLA was determined by the chemical degradation of hydrolysis, which can be increased by the water content and temperature. Moreover, it can be catalyzed by free carboxyl groups which produced during the hydrolysis process (Deroiné et al., 2014; Martucci and Ruseckaite, 2015).

In natural soil environment, the temperature is usually far below the glass transition temperature of PLA. The chains motion is difficult and the growth of the microorganism is limited, resulting in a low degradation rate of PLA. Reports showed that lactic acid (degradation products) was not detected even after one year for the PLA films degraded in outdoor soil (Gallet et al., 2000), and only small weight changes could be detected for the PLA (Shogren et al., 2003). All of these results demonstrated that the soil burial degradation of PLA was slow. However, the propagation and growth of the microorganism in soil can be stimulated by the starch in PLA based composites, and the degradation of composites can be therefore accelerated. In addition, starch can be biodegraded quickly and completely. Consequently, it will be an efficient method to improve the biodegradability and expand the application of PLA based materials.

Although there has been some literature focusing on the biodegradation of PLA materials, further study on the degradation of starch/PLA composites in soil are still needed. The role that starch play in PLA degradation remains controversial. Whether starch changed the degradation mechanism was not clear. And the literature reported that the addition of starch enhanced the degradation ability of the composite systems, but there was no literature reported the acceleration effect of starch on the PLA matrix exactly. In our study, we analyzed the weight loss of each component in the starch/PLA composites to confirm whether the starch has an acceleration effect on the PLA matrix. The degradation behavior and homogeneity of starch/PLA composite have not been studied comprehensively. Fourier transform infrared (FTIR), Infrared microscopy (IRM) and X-ray Photoelectron Spectroscopy (XPS) were used to investigate the chemical changes and degradation homogeneity of starch/PLA composite during the soil burial process.

## 2. Experimental section

### 2.1. Materials

PLA (306 DX) was supplied by Ningbo Huanqiu Plastic Products Co.,

Ltd. (Ningbo, Zhejiang, China) with a specific gravity of 1.25 g/cm<sup>3</sup> and melt flow index of 12–13 g/10min (190 °C). Corn starch, food grade, was obtained from Changling Jilong corn Development Co., Ltd. (Changling, Jilin, China).

The PLA pellets and corn starch were dried in a vacuum oven for 8 h at 50 °C. The starch/PLA 30/70 (w/w) was first extruded in a twin-screw extruder (L/D ratio of 40, Nanjing Giant SHJ-20). The temperature profile during extrusion was 135-150-170-170-135 °C from the hopper to the die. Afterwards, the standard specimens were processed by means of injection molding (JPH180C, Guangdong ONLY Machinery Co., Ltd.). The temperature profile of injection molding was the following: 180-180-170-170 °C.

### 2.2. Soil burial degradation experiments

Biodegradation experiments were performed in outdoor soil conditions within the campus of the Northeast Forestry University, Harbin, China. PLA and starch/PLA samples were weighed and buried 10–15 cm below the soil surface. Samples were retrieved from the soil at the end of each targeted degradation time interval (10 or 20 days), then washed gently with water to remove soil debris. Subsequently, the samples were dried at 35 °C until their weights stabilized to constant values. After drying, samples were weighed to determine final weight after the degradation period in soil.

The weight loss (WL) of the samples was estimated with equation (1):

$$WL = \frac{W_0 - W_t}{W_0} \times 100\% \quad (1)$$

Where  $W_0$  was the initial dry mass before degradation,  $W_t$  was the residual dry mass after degradation at an exposure time  $t$ . An average of at least five measurements was calculated to obtain the reported results.

### 2.3. Component content analysis

The starch/PLA composite was dissolved in tetrahydrofuran (THF) using a magnetic stirrer. After complete dissolution of the PLA in composite, the solution was filtrated to separate starch and PLA-THF solution. More THF was then added into the filter cake for further stirring and wash the starch component three times to separate the components completely. After the separation, excess and massive methanol was poured into the PLA-THF solution to precipitate out the PLA component. The PLA, THF, and methanol mixture was then centrifuged at 8000 rpm (LG20-W, Jingli centrifuge Co., Ltd.) for 10 min, the precipitate product was washed with methanol three times, then the precipitate of PLA component was obtained. Finally, both the starch and PLA components were vacuum dried at 40 °C for 48 h, and weighed them respectively. The procedure is illustrated in Scheme 1.

The component content in the starch/PLA composite could then be calculated using equation (2).

$$C_S = \frac{m_s}{m_s + m_p} \times 100\% \\ C_P = \frac{m_p}{m_s + m_p} \times 100\% \quad (2)$$

Where  $C_S$  is the content of starch in the corresponding starch/PLA sample;  $C_P$  is the PLA content in the corresponding composite;  $m_s$  is the weight of the separated starch; and  $m_p$  is the PLA weight of the dry PLA precipitation.

### 2.4. Scanning electron microscopy (SEM)

The evolution with the degradation time of the surfaces morphology and fractured surfaces morphology were monitored with a scanning electron microscopy (SEM, JSM-7500F, JEOL) using 5 kV as operating voltage. The exposed surfaces of the samples were previously sputter-

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