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Preparation and characterization of dry method esterified starch/polylactic acid composite materials

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ABSTRACT

Corn starch and maleic anhydride were synthesized from a maleic anhydride esterified starch by dry method. Fourier transform infrared spectroscopy (FTIR) was used for the qualitative analysis of the esterified starches. The reaction efficiency of dry method esterified starch reached 92.34%. The dry method esterified starch was blended with polylactic acid (PLA), and the mixture was melted and extruded to produce the esterified starch/polylactic acid (ES/PLA) composites. The degree of crystallinity of the ES/PLA was lower than that of the NS/PLA, indicating that the relative dependence between these two components of starch and polylactic acid was enhanced. Scanning electron microscopy (SEM) indicated that the dry method esterified starch increased the two-phase interface compatibility of the composites, thereby improving the tensile strength, bending strength, and elongation at break of the ES/PLA composite. The introduction of a hydrophobic ester bond and increase in interface compatibility led to an increase in ES/PLA water resistance. Melt index determination results showed that starch esterification modification had improved the melt flow properties of starch/PLA composite material. Strain scanning also showed that the compatibility of ES/PLA was increased. While frequency scanning showed that the storage modulus and complex viscosity of ES/PLA was less than that of NS/PLA.

1. Introduction

Polylactic acid (PLA) is among the most promising biodegradable polymer materials given its compatibility, biodegradability, good physical and mechanical properties, and permeability. Therefore, PLA production has gained attention as an alternative to conventional synthetic polymers [1]. However, PLA has several disadvantages, including poor hydrophilicity, brittleness, a low heat distortion temperature, poor impact resistance, and a difficult-to-control degradation cycle. Its high price, in particular, limits the application of PLA. Starch is a natural polymer with many advantages such as a wide variety of sources, a low price, biodegradability, and renewability. To reduce the cost of using PLA, many scholars have blended PLA with starch. While ensuring that the system is environmentally friendly, the high strength and hydrophobicity of the PLA can offset the deficiencies of starch-based plastics, including their lack of mechanical properties and water resistance, among other factors. However, if the starch and PLA are directly blended, their interfacial adhesion is poor [2]. The brittleness and sensitivity to humidity in the processing products necessitate an in-depth study of the PLA/starch modifications. The most commonly used modification method includes the addition of a plasticizer [3–5] and a compatibilizer [6–8]. As a common reactive compatibilizer, maleic anhydride has been used in starch/PLA blends [9,10] and can significantly improve the interface compatibility of the starch/PLA composites because the starch ester of the maleic anhydride introduces both hydrophilic and lipophilic groups into the starch molecule chain, giving it certain unique properties. Because the main chain of the esterified starch has larger pendant groups on its lateral side, the ester groups within the starch molecule can increase the inner plasticization, reducing the crystalline density of the starch so that small-molecule plasticizers can enter into the starch macromolecules for plasticization. In contrast, the introduction of the hydrophobic ester groups into the esterified starch increases the affinity between the starch and the PLA, improving the blended performance of these two components.

The methods most commonly used to produce maleic anhydride esterified starch are the wet method, an organic solvent method [11], reactive extrusion method [12], and microwave assisted method [13]. The wet method is carried out in an aqueous slurry system. The reaction does not require an organic solvent and is environmentally friendly and uniform. Because the reaction is heterogeneous, combining solid starch particles with a liquid, it must find ways to increase the two-phase affinity to improve the reaction efficiency. In addition, the side reaction involving anhydride hydrolysis cannot be ignored. The organic solvent preparation

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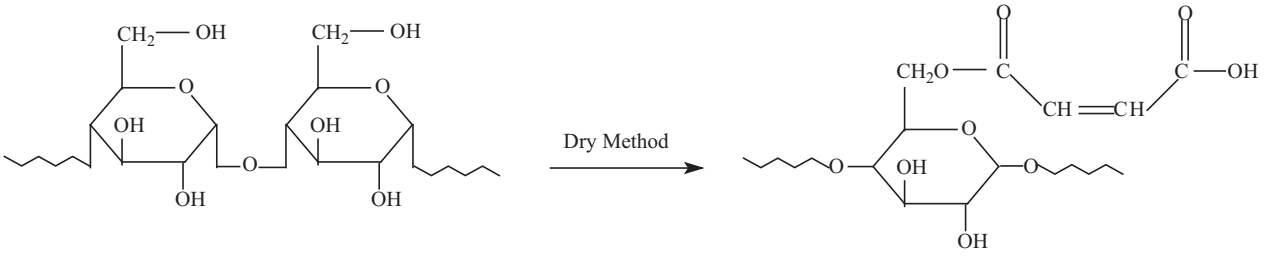
method has the advantage of being uniform but the disadvantages of a low degree of substitution, a high production cost, and the production of environmental pollutants. Reactive extrusion method requires the addition of a plasticizer, which will make the starch occur plasticization and change the granular structure of starch. And microwave assisted method is not suitable for large-scale industrial production; the process is relatively complex, and involves large energy consumption.



In this study, a simple, low-cost dry method for preparation of the esterified starches was selected that produces little waste water and little waste gas pollution (Eq. (1)). Under anhydrous conditions, the starch was not gelatinized at a temperature above 60 °C, and the melting point of the maleic anhydride was 52.8 °C. Reactions with dry starch at a temperature above the melting temperature can improve the reaction efficiency with little environmental pollution. Maleic anhydride esterified starch prepared via the dry method was blended with PLA to increase the compatibility and improve the mechanical properties and water resistance of the composite material, using glycerol as the plasticizer, starch, glycerol, and PLA together into an extruder for melt extrusion. In this process, starch obtains plasticizing, and then plasticized starch blending with PLA, which can ensure the uniform mixture. A simple of process, high production efficiency and product had good performance.

2. Materials and methods

2.1. Materials

Corn starch, industrial grade, was obtained from Dacheng Corn Development Co., Ltd. (Changchun, Jilin, China), loaded in the vacuum drying oven of 50 °C for 48 h to eliminate moisture before use. PLA, granular, was purchased from Ningbo Huanqiu Plastic Products Co., Ltd. (Ningbo, Zhejiang, China). Maleic anhydride, acetone, and glycerol were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). All chemicals were AR grade.

2.2. *Dry* method ***synthesis of maleic anhydride esterified starches***

Maleic anhydride (1 g) was dissolved in a small volume of acetone, uniformly sprayed onto 100 g cornstarch (dry basis), and mixed until homogeneous. After all acetone had evaporated, the mixture was transferred to a 250 ml conical flask. The flask was put into a heated water bath at a controlled temperature of 80 °C and was stirred intermittently using a glass rod. The reaction was allowed to proceed for 2 h. The heat was then removed. After the reactants had cooled, a certain quantity of acetone was added to dissolve the unreacted maleic anhydride. After brief stirring, the mixture was filtered. Subsequently, the filter cake was washed three times with acetone and was placed in a 50 °C oven for drying until a constant weight was reached [14].

2.3. Preparation of the ES/PLA composites

Glycerol (45 g) was added to 90 g maleic anhydride esterified starch. After mixing, the mixture was sealed and incubated for 18 h to obtain the plasticized esterified starches. Then, 210 g PLA was added to the plasticized esterified starches and the combination was evenly mixed. A twin-screw extruder (length-to-diameter ratio of 40:1) was used to manufacture the granules. The temperatures at each stage were 135-150-165-165-135 °C (from the inlet to the outlet). Finally, a single-screw extruder was used for extrusion molding. A 10 mm-wide, 2 mm-thick strip specimen was obtained. The extrusion temperature program was 150-170-170-130 °C (from the inlet to the outlet).

2.4. Characterization

2.4.1. FTIR characterization

A Magna-IR 560 ESP type Fourier transform infrared spectrometer produced by Thermo Nicolet Corporation had a resolution of 4 cm^{-1} and was used to characterize native starch and esterified starch form 500 to 3800 cm^{-1}. The native starch and esterified starch samples were made up in a potassium bromide press and scanned 40 times using the transmission method.

2.4.2. Calculation of esterification reaction efficiency

1.00 g of dry maleic anhydride esterified starch was weighed accurately and placed in a 250 ml conical flask. Then 10 ml of 75% ethanol solution in deionized water was added, and 10 ml of 0.5 M aqueous sodium hydroxide solution was added. The stoppered conical flask was agitated, warmed to 30 °C, and stirred for 30 min. The excess alkali was back-titrated with a standard 0.5 M aqueous hydrochloric acid solution. A blank titration was carried out using native starch. The degree of substitution (DS) was calculated as follows:

$$W_{MA} = \frac{98c(V_0 - V_1)}{1000 \times 2W} \times 100\%$$

$$DS = \frac{162W_{MA}}{98 \times (100 - W_{MA})}$$

where W_{MA} is the content of maleic anhydride substituted, %; W is the mass of the sample, g; c is the concentration of aqueous hydrochloric acid solution, M; V_0 is the consumed volume of aqueous hydrochloric acid solution by blank sample, ml; V_1 is the consumed volume of aqueous hydrochloric acid solution by esterified starch sample, ml.

Reaction efficiency (RE) was calculated as follows [15]:

$$RE = \frac{DS}{n(MAH)/n((AGU)} \times 100\%$$

where $n(MAH)$ is the molar quantity of maleic anhydride and $n(AGU)$ is the molar quantity of anhydroglucose units in starch.