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# Water resistance, mechanical properties and biodegradability of methylated-cornstarch/poly(vinyl alcohol) blend film

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**Abstract**

The main shortcomings of biodegradable starch/poly(vinyl alcohol) (PVA) film are hydrophilicity and poor mechanical properties. With an aim to overcome these disadvantages, cornstarch was methylated and blend films were prepared by mixing methylated-cornstarch (MCS) with PVA. The mechanical properties, water resistance and biodegradability of the MCS/PVA film were investigated. It was found that MCS/PVA film had higher water resistance than the native starch/PVA film. However, the water resistance of MCS/PVA films did not have significant difference with the increase in the degree of substitution (DS) of the methylated starch from 0.096 to 0.864. Enzymatic, microbiological and soil burial biodegradation results indicated that the biodegradability of the MCS/PVA film strongly depended on the starch proportion in the film matrix. The degradation rate of starch in the starch/PVA film was hindered by blending starch with PVA. Both tensile strength and percent elongation at break of the MCS/PVA film were improved as DS of the methylated starch increased. Conversely, increasing the methylated starch proportion in film matrix deteriorated both tensile strength and percent elongation at break of the film.

*Keywords:* Methylated-cornstarch (MCS); Poly(vinyl alcohol) (PVA); Mechanical properties; Water resistance; Biodegradability

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## 1. Introduction

Synthetic plastics, such as polystyrene, polypropylene and polyethylene, are used widely in daily life, in food industry, biomedical field and agriculture. A heavy environmental pollution accompanies their uses, because they need hundreds of years to degrade, and the disposal of waste plastics has become a serious problem [1]. Therefore, in the past two decades, biodegradable materials have been paid attention as alternatives to the petroleum-derived plastics [1–9]. Natural biopolymers including starch, cellulose and chitosan were tested, alone or combined with synthetic polymers, for the possibility to form a fully or partially biodegradable film [1]. Of these materials, starch is the most attractive candidate because of its low cost, easy availability and high production from annually renewable resources [7]. However, the low water resistance and high brittleness of starch films limited their extensive application [6,8,10]. Therefore, many attempts have been made to overcome these problems by blending starch with synthetic polymers. However, the biodegradability of starch film decreased with addition of the non-degradable synthetic polymers. Therefore, much interest lies in blending starch with biodegradable synthetic polymers.

Poly(vinyl alcohol) (PVA) is a hydrophilic biodegradable polymer which is mainly composed of C–C

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bonds [6]. However, its water solubility is related to its degree of hydrolysis, molecular weight, and the modification while blending with other processing additives [11], with a maximum value at the degree of hydrolysis of 88% [12]. From the cost and practicality points, it is preferable that the blend contains as much starch as possible. However, the properties of the blend films deteriorated as starch proportion in the film formulation increased. This might result from a poor compatibility between starch and PVA [13] and phase separation during film preparation [14]. Moreover, the water resistance of the native starch/PVA film deteriorated compared to that of the PVA film.

The techniques for increasing the compatibility between starch and synthetic polymers include adding a compatibiliser to the blends [15], chemical modifications of the synthetic polymers [1,16] and starch. They have been proved as effective measures to improve the properties of film. A number of methods are available in starch modification including esterification, oxidation, etherification and cross-linking [2,4,7,8,10,17–19]. Of these methods, methylation, as one etherification method, was used widely in elucidating the structure of polysaccharides and the substitution pattern in polymer chains [20–23]. Theoretically, methylation is an effective way to increase the hydrophobicity of the starch and to improve the compatibility between starch and PVA (hydrolysis degree 99.5%). However, no information was available on the methylated starch-based film. Therefore, the objective of this work was to methylate starch and to prepare blend film by mixing methylated starch with PVA. Water absorption capacity, mechanical properties and biodegradability of the blended films were evaluated.

## 2. Experimental

### 2.1. Materials

The raw materials used in our experiments are available as commercial products. The cornstarch, a white fine powder with 10 wt% moisture content containing 30 wt% amylose and 70 wt% amylopectin, was purchased from Tuoketuohua Starch Company (Neimeng, China). PVA, with a hydrolysis degree of 99.5% and the polymerisation degree of 1700, was obtained from Weilun Company (Changshou, Chongqing, China). α-Amylase ($5.0 \times 10^4$ U/g) and β-amylase ($2.0 \times 10^3$ U/g) were supplied by Xingda Bioengineering Company (Wuxi, Jiangsu, China). *Bacillus subtilis* and *Aspergillus oryzae* were maintained in our laboratory. *Pseudomonas aeruginosa* (CICC10204) and *Aspergillus niger* (CICC2089) were purchased from China Centre of Industrial Culture Collection (CICC).

### 2.2. Preparation of methylated-cornstarch

Cornstarch was methylated by dispersing starch granules in an aqueous suspension at pH 10 and using dimethyl sulfate as methylating reagent. After modification, the reaction mixture was neutralized, dialyzed and dried. Samples with different DS values were obtained by varying the reaction parameters (Table 1).

### 2.3. Degree of substitution

DS indicates the average number of substituted groups (methyl) per anhydroglucose unit in methylated starch. Since three free hydroxyl groups are available in each anhydroglucose unit of native starch, the maximum DS is 3. DS values were determined by the Morgan–Zeisel method [23]. The Morgan–Zeisel assay was based on ether-cleavage by hydrogen iodide resulting in the formation of iodomethane, which was led by a nitrogen flow into a trap solution of Ag(I)–ethanol to form Ag(I) solid. Dried methylated starch (25 mg) and 0.5 ml of phenol were added into a conical flask, followed by the addition of 0.2 ml of propionic anhydride (AR grade) in a drop-wise manner. After the starch was dispersed fully, the flask was cooled in an ice bath, and 5 ml of hydrogen iodide was added. Dried nitrogen was introduced into the solution through the needle with a rate of 60–70 bubbles per minute. The flask was heated to 90 °C for 2 h to completely convert the methyl group to iodomethane. The resulting iodomethane was driven out of the flask and absorbed by 0.05 M $AgNO_3$–alcohol solution to give an Ag(I) solid. A reflux-condenser also was used to prevent the loss of iodomethane. The DS values were calculated on the weight basis of the Ag(I) produced.

### 2.4. Characterization by Fourier transform infrared spectrophotometry

Changes in the chemical structure of the starch molecules were confirmed with a Fourier transform infrared spectrophotometer (FT-IR) (model 2000, Perkin–Elmer, USA). After drying in the vacuum oven at 60 °C overnight, samples (2 mg) were prepared in the form of KBr (10 mg) pellets. The spectra were recorded over the wavenumber from 450 $cm^{-1}$ to 4000 $cm^{-1}$, operating with a 4 $cm^{-1}$ resolution.

Table 1
Degree of substitution as a function of reaction parameters

| Temperature (°C) | Concentration of starch slurry (%) | Dimethyl sulphate addition (g/g starch) | Time (h) | DS |
|---|---|---|---|---|
| 45 | 20 | 0.4 | 1.0 | 0.096 |
| 50 | 15 | 0.4 | 2.5 | 0.275 |
| 50 | 15 | 0.8 | 1.5 | 0.581 |
| 50 | 15 | 0.8 | 2.0 | 0.864 |