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The structure, tensile properties and water resistance of hydrolyzed feather keratin-based bioplastics☆

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ABSTRACT

Feather, as a by-product of the poultry industry, has long been treated as a solid waste, which causes environmental and economic problems. In this work, the hydrolyzed feather keratin (HFK) was extracted from the chicken feather using a cost-effective method of alkali-extraction and acid-precipitation by applying urea and sodium sulfide. The aim was development and characterization of the eco-friendly films based on the HFK with variable glycerol contents by a thermoplastic process. The thermal analysis showed that high temperature and high pressure improved the compatibility between the glycerol and the HFK molecules. Also it was shown that the addition of water is necessary in the hot-pressing process of films. The FT-IR analysis indicated that the formation of the new hydrogen bonds between HFK and glycerol. By increasing the glycerol content, the film tensile strength (σ_b) decreases from 10.5 MPa to 5.7 MPa and the solubility increases from 15.3% to 20.9%, while the elongation at break (ε_b) achieves the maximum value of 63.8% for the film with 35% glycerol. The swelling was just below 16.9% at 25 °C for 24 h, suggesting a good stability of the films in water. The water vapor permeability (WVP) varied between $3.02 \times 10^{-10} \text{ g} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and $4.11 \times 10^{-10} \text{ g} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ for the films with 20% and 40% glycerol, respectively. The HFK film was uniform, translucent and tough, which could be used in packaging and agricultural field.

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1. Introduction

There is currently a surge in research on biodegradable materials obtained from renewable materials such as proteins, polysaccharides and lipids [1,2]. Application of biodegradable materials is considered as the most effective solution for a number of the environmental pollution problems caused by synthetic polymers. Feather is one of the most important potential resources to produce biodegradable materials. More than 90% of feather is a protein called keratin, which is abundantly available in the poultry industry [3]. It is estimated that 3–4 billion lbs of feather are generated as the by-product of the poultry industry in the United States [4], and more than 1.5 billion lbs in China [5]. Although feather is cheap, renewable, biodegradable and abundantly available, it is almost useless in industry applications. Except for applications in animal feed, duvet and down coat, feather is mostly disposed in the landfills as the solid wastes, causing environmental and economic issues

[4]. In addition, the abandoned duvet and down coat could result in a secondary pollution. To solve the solid waste pollution, several research groups are working on developing potential materials from feather.

The use of hydrolyzed feather keratin solution to produce films by casting (wet process) has been reported [1,6–9]. However, due to the high cost of preparation from the solution, most of the investigations on the protein-based films are focused on the thermo-mechanical processing (dry process), such as hot-pressing and extrusion [10–12]. As native chicken feathers are non-thermoplastic, some studies have been done to convert native feathers into films by thermal processing via chemical modifications, such as plasticization, grafting or crosslink. The poultry feather fiber was hot-pressed into films at 160 °C using a variable amount of glycerol (15%–50%) as a plasticizer. The values of film tensile strength and elongation at break were 6–15 MPa and 8%–50%, respectively [10]. Native chicken feathers were cyanoethylated using acrylonitrile and sodium carbonate. Cyanoethylated feathers showed a melting peak at 167 °C and could be hot-pressed into thermoplastic films at 180 °C using glycerol (20%) as the plasticizer [13]. Poultry feathers were partly hydrolyzed by the alkaline agent and cross-linked by citric acid, and then hot-pressed into films plasticized with glycerol (20%). Cross-linking with a citric acid concentration of 2% resulted in the strength and elongation values of 5.2 MPa and 13.5%, respectively [14]. In addition, S-sulfo keratin powder was extracted from wool by

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using sodium disulfite and sodium dodecyl sulfate (SDS). The powder was then mixed with ethanol/water and hot-pressed into the films with tensile strength of 27.7 MPa and elongation at break of 4.7%. The film supported the adhesion and proliferation of fibroblast cell, and the film swelling was 53.4% at pH 7 [15].

Above reports show that the films developed from the native feather using a chemical modification by hot-pressing are opaque and nonuniform and still contain some feather fibers [4,13]. The type and extent of grafting may also decrease the biodegradability of the feather. Besides, the hot-pressed S-sulfo keratin films showed a relatively low flexibility and high moisture sensitivity. At the best of our knowledge, little information is available on the thermal processing of the hydrolyzed keratin films. The aim of this work is to produce plasticized hydrolyzed feather keratin films by hot-pressing. The film properties were controlled by addition of glycerol as an effective plasticizer for protein-based materials (glycerol has low molecular weight and can easily diffuse into the protein molecule to interact with polar groups). Furthermore, the hydrolyzed feather keratin was extracted from the chicken feathers using a reducing agent, sodium sulfide, which is cheaper and more effective than other reducing agents [16].

This work is focused on the evaluation of the processability, thermal properties, structure, tensile properties, micromorphology, water resistance and water vapor permeability (WVP) of the HFK films produced by hot-pressing.

2. Materials and Methods

2.1. Materials

The chicken feathers used in this study were collected from farmer's markets. Urea, sodium sulfide nonahydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$), sodium dodecyl sulfate (SDS), hydrochloric acid and glycerol were purchased from a local company (Guangzhou Chemical Reagent Factory, Guangzhou, China).

2.2. Extraction of the hydrolyzed feather keratin (HFK)

HFK was extracted by an amended technique reported in [16]. The sterilized chicken feathers were soaked in $7 \text{ mol}\cdot\text{L}^{-1}$ urea solution (1:15, mass ratio) at $50\text{ }^\circ\text{C}$ for 24 h. Then, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (40 wt% of the feather mass) and SDS (1 wt% of the feather mass) were added to the mixture and extraction was carried out at $50\text{ }^\circ\text{C}$ for 30 min under continuous stirring. The extracted solution was then centrifuged at $1000 \text{ r}\cdot\text{min}^{-1}$ for 15 min, and pH of the supernatant was adjusted to 4.7 (isoelectric point of keratin) using a $1 \text{ mol}\cdot\text{L}^{-1}$ hydrochloric acid solution to obtain the HFK, followed by vacuum-drying at room temperature for 24 h. The protein content calculated after nitrogen analysis was 96.51 wt% (dry matter basis), using Kjeldahl nitrogen determination method with the conversion factor, 6.25 (K-314, BUCHI).

2.3. HFK film preparation

The HFK powder was mixed with water (15 wt%) and glycerol (20 wt%–40 wt%). The amount of the each reagent was chosen based on the weight of the HFK. To obtain a uniform HFK/glycerol mixture, glycerol was first dissolved in water. The mixture was ground using a mortar and then was added into a kitchen mixer to ensure the uniform mixing. The mixture was stored at $25\text{ }^\circ\text{C}$ for 24 h and then was compress-molded into the films in a press at $130\text{ }^\circ\text{C}$ for 6 min under 10 MPa of pressure. The compression molding was controlled and watered-cooled to $40\text{ }^\circ\text{C}$ in 10 min to obtain a semitransparent smooth brown film.

2.4. Characterization

The effect of water and glycerol thermal processing was assessed using a DSC (METTLER Instruments 910s). Aluminum pans were used as the sample containers. The DSC analysis of the HFK powder or feather was performed from $25\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ [17]. The HFK/glycerol mixtures and films were first heated from 25 to $105\text{ }^\circ\text{C}$ at a heating rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, holding for 5 min, and then cooled from 100 to $-60\text{ }^\circ\text{C}$ at a rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The second heating step was from $-60\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

FTIR spectra of the samples were analyzed using a FTIR spectrometer (spectrum 100, Perkin-Elmer) with ATR attachment. An average of 8 scans was used for the analysis.

The tensile strength (σ_b) and breaking elongation (ε_b) of the samples were measured on a universal testing machine (CMT6503, Shenzhen MTS Test Machine Company Ltd., China) according to ASTM standard D638 with a rate of $10 \text{ mm}\cdot\text{min}^{-1}$. HFK films were conditioned at $25\text{ }^\circ\text{C}$ and 55% relative humidity for 24 h before tensile testing. Films were cut to size of $75 \text{ mm}\times 10 \text{ mm}$. Thickness of the samples was measured by a micrometer and ranged from 0.20 to 0.40 mm for the various conditions studied. The results were averaged from three samples.

Micrographs of the films were obtained using a Quanta 400 SEM (Oxford, England). To perform the SEM tests, the samples were coated with a thin layer of gold. All the samples were examined using an accelerating voltage of 20 kV.

The water resistance of the HFK film was expressed by the swelling and solubility. The rectangular specimens ($40 \text{ mm}\times 10 \text{ mm}$) were preconditioned by drying in an air oven at $70\text{ }^\circ\text{C}$ for 12 h, followed by a cooling in a desiccator for a few minutes and immediate weighing (W_1). The preconditioned specimens were immersed in distilled water at $(25\pm 1)\text{ }^\circ\text{C}$ for 24 h under shaking. The specimens were removed, wiped with a filter paper to remove the water on the surface of the films and immediately weighed (W_2). The as-prepared wet specimens were dried again in an oven at $70\text{ }^\circ\text{C}$ for 24 h followed by a cooling in a desiccator and immediate weighing (W_3). Each film was tested 3 times. The swelling and solubility of the films were calculated using the following Eqs. (1)–(2):

$$\text{Film swelling} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

$$\text{Film solubility} = \frac{W_1 - W_3}{W_1} \times 100\% \quad (2)$$

Water vapor permeability (WVP) of the films was measured using a water vapor transmittance tester (Perme W3/030, Labthink Ltd, CHN) at $38\text{ }^\circ\text{C}$ with a gradient of 90% relative humidity (RH) to 0% RH (dry air) across the film.

3. Results and Discussion

3.1. Thermal properties

Thermal analysis of the HFK powder depends on the moisture content (0, 5.5 wt% and 9.8 wt%), see Fig. 1. All of the four curves show two endothermic peaks. A broad, low-temperature peak was observed at around $100\text{ }^\circ\text{C}$, which is attributed to the evaporation of bound water in the protein structure (could be regarded as the glass transition– T_g), as previously reported. The second peak is observed at around $210\text{--}240\text{ }^\circ\text{C}$, which is assigned to the crystalline melting [15, 18–20]. Following extraction with sodium sulfide, the temperature and the area under the peak of the crystalline melting peak decreased significantly. This could be due to the transition of the α -form crystallites to β -pleated sheet structures, similar to those in wool [21]. The

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