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Thermoplastic films from cyanoethylated chicken feathers

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ABSTRACT

This paper demonstrates that etherification can be used to develop thermoplastic films from chicken feathers. Feathers are inexpensive, abundantly available and renewable resources but have limited applications mainly due to their non-thermoplasticity. However, it has been shown that chemical modifications such as grafting can make feathers thermoplastic. Etherification provides better thermoplasticity to biopolymers compared to chemical modifications such as acetylation. In this research, chicken feathers were etherified using acrylonitrile and various concentrations of catalyst. Even at low weight gain (3.6%), cyanoethylated feathers were thermoplastic and showed a melting peak at 167 °C. Films compression molded from the cyanoethylated feathers had strength ranging from 1.6 to 4.2 MPa and elongation ranging from 5.8 to 14% depending on the extent of cyanoethylation. Feathers modified by cyanoethylation had good thermoplasticity and could be useful to develop various thermoplastics.

1. Introduction

Considerable efforts are being made to utilize biopolymers to develop consumer products, especially disposable thermoplastics and packaging materials [1]. Poultry feathers are inexpensive and abundant resources but do not have any major industrial applications. Most of the feathers generated are disposed in landfills leading to environmental concerns and discarding of a potentially valuable material. Feathers contain more than 90% protein in the form of keratin and are probably the lowest cost proteins available. Feathers have low density (0.9 g/cm^3) and a unique hierarchical structure consisting of the main rachis or quill to which are attached the barbs commonly referred to as "feather fibers" and the tiny barbules that are in-turn attached to the barbs [2]. This hierarchical structure provides the resistance to wind and protection from the environment. In addition, feathers have honey comb shaped hollow centers that make feathers lighter and provide insulation to heat and sound [3,4]. Due to these unique features, attempts have been made to study the potential of using feathers for various applications.

Most of the attempts on using feathers for industrial applications have focused on using feathers in their native form, especially as reinforcement for composites. Whole feathers, feather fibers and feather quills were separately used as reinforcement for light-weight automotive polypropylene composites [3–5]. It was found that feathers provided good sound absorption due to the presence of hollow structures. Whole feathers provided better flexural and tensile properties than feather fibers or feather quill reinforced composites [5]. Feathers were mixed with soybean oil to develop completely biodegradable composites [6]. Similar to using feathers for composites, feather fibers were mixed with low density polyethylene and extruded to form pellets [7,8].

Due to the non-thermoplastic nature of feathers, efforts have been made to use chemical modifications and make feathers thermoplastic. Feathers were grafted with methyl methacrylate and the grafting conditions were optimized [9]. However, the melting behavior or the potential of using the grafted feathers for thermoplastic applications was not studied. We have recently shown that feathers grafted with methyl acrylates can be compression molded into thermoplastic films [10]. Methyl methacrylate grafted feathers had tensile strength ranging from 55 to 206 MPa and breaking elongations ranging from 1.1 to 14% depending on the amount of glycerol used (0 to 30%). The thermoplastic films obtained from methyl methacrylate grafted feathers had better dry and wet tensile properties than films made from feather keratin and also compared to films made from starch acetate and soy proteins [10].

In addition to grafting, esterification (acetylation) and etherification (cyanoethylation) are some of the common approaches used to make biopolymers thermoplastic. Acetylation has been used to modify biopolymers such as cellulose, starch and also proteins for fibers, films and other thermoplastics [11,12]. Recently, we have demonstrated that the carbohydrates and proteins in distillers dried grains (DDG) can be simultaneously acetylated and made into

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thermoplastics [13,14]. Etherification has several advantages over acetylation. Etherification uses relatively milder conditions (low temperatures and pH) than acetylation and therefore will cause lesser damage to polymers, especially proteins that are easily hydrolyzed under high temperatures and strong alkaline or strong acidic conditions. In addition, ethers are more flexible than esters and therefore ethers could provide thermoplastics with better elongation than esters.

We have recently reported that cyanoethylated distillers dried grains with solubles (DDGS) which is a mixture of proteins and carbohydrates can be made into high flexible thermoplastic films [15]. Cyanoethylated DDGS could be compression molded into films without the need for plasticizers. The properties of the films could be controlled by varying the extent of cyanoethylation or compression molding conditions. Films with strength as high as 651 MPa but low elongation or films with high elongation (38%) but with lower strength (14 MPa) were obtained. Cyanoethylated DDGS showed good potential to be useful for thermoplastic applications.

In this research, chicken feathers were cyanoethylated and the cyanoethylation conditions were optimized. Cyanoethylated feathers were characterized for the changes in structure and to confirm cyanoethylation and the potential of converting the cyanoethylated feathers into thermoplastics was evaluated.

2. Experimental section

2.1. Materials

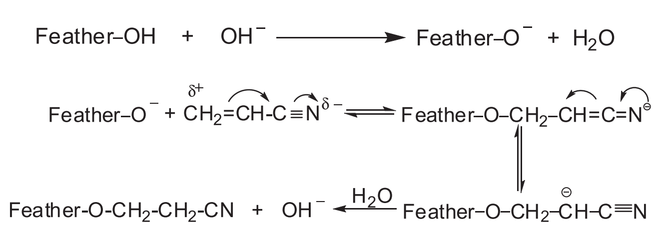
Chicken feathers consisting of quills and barbs were supplied by Feather Fiber Corporation (Nixa, MO). Acrylonitrile required for cyanoethylation and sodium carbonate used as catalyst were reagent grade chemicals purchased from VWR International (Bristol, CT).

2.2. Methods

2.2.1. Cyanoethylation of chicken feather

Cyanoethylation of the chicken feathers was carried out using acrylonitrile and sodium carbonate as both the swelling agent and catalyst. The reaction between the hydroxyl groups in the proteins in chicken feather and acrylonitrile in the presence of sodium carbonate is believed to be a typical nucleophilic addition reaction. The possible mechanism of the reactions between acrylonitrile and the hydroxyl groups in the feathers is given in Scheme 1. The reaction between the acrylonitrile and the hydroxyl groups in chicken feather results in the formation of the cyanoethylated chicken feather.

To perform the cyanoethylation, chicken feather was mixed with equal amounts of various concentrations 5, 10, 15, and 20% (w/w) of aqueous sodium carbonate for 15 min at room temperature. Later, acrylonitrile was added into the feathers at an acrylonitrile to feather weight ratio of 8:1 under constant mixing until the temperature reached 40 °C. The cyanoethylation was completed by heating the mixture containing chicken feather, acrylonitrile and sodium carbonate for 2 h at 40 °C. At the end of the reaction, the products formed were added into 50% ethanol to ensure complete removal of



Scheme 1. Possible reaction between acrylonitrile and the hydroxyl groups in chicken feather under alkaline conditions. Feather-OH represents the hydroxyl groups in the proteins in chicken feather.

acrylonitrile and the products obtained were later neutralized with acetic acid (20% w/w). The precipitate obtained was first washed with ethanol, then thoroughly with distilled water at 50 °C for 30 min and repeated five times, followed by absolute ethanol and finally dried in an oven at 50 °C for 12 h. To exclude the effect of alkali on the thermoplasticity of the feathers, the reaction was performed under the same conditions (40 °C, 2 h) using 20% sodium carbonate but without acrylonitrile.

The amount of acrylonitrile consumed by the feathers was determined by titrating the double bonds in acrylonitrile using potassium bromate. Based on the differences in the double bonds in acrylonitrile before and after the reaction, it was found that less than 2% of the acrylonitrile was consumed and the remaining acrylonitrile could be reused for etherification. Therefore, the cost of etherification will be low even though relatively high ratio of acrylonitrile to feathers was used for the reaction.

2.2.2. Percent weight gain

In order to quantitatively determine the efficiency of cyanoethylation of chicken feathers, percent weight gain values which describe the percent increase in the weight of cyanoethylated chicken feather compared to the weight of unmodified chicken feather used for the reaction were determined. Before determining the % weight gain, the cyanoethylated feather was thoroughly washed in 50 °C water for 30 min under constant stirring 5 times to ensure complete removal of unreacted chemicals and soluble impurities. The feathers were later dried in an oven at 50 °C until constant weight was obtained. The percent weight gain values were calculated according to the formula

$$\text{Percent Weight Gain} = ((W_{mod} - W_{unmod}) / W_{unmod}) \times 100$$

Where W_{unmod} was the initial oven-dried weight of the chicken feather before chemical modification and W_{mod} was the oven-dried weight of the cyanoethylated chicken feathers.

2.2.3. Fourier transform infrared (FTIR) spectrum analysis

Samples for FTIR spectroscopy of unmodified and cyanoethylated chicken feather were thoroughly washed in distilled water to remove any chemicals prior to mixing with KBr. Samples in the form of thin films were placed in the FTIR-cell at room temperature. FTIR spectra were recorded on a Nicolet NEXUS 670 (Thermo-Nicolet, Waltham, MA) FTIR spectrometer. Each sample was measured from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans were collected. The FTIR spectrums obtained were analyzed using OMNIC software (Thermo Electron Corp).

2.2.4. Nuclear magnetic resonance studies

^{1}H NMR spectroscopy studies were conducted to understand the changes in the modified chicken feather. The unmodified and cyanoethylated feather samples were dissolved in DMSO-d_6 and the concentration of product was adjusted to 20–30 mg/mL for the ^{1}H NMR measurements. ^{1}H NMR spectra were recorded at 295 K using a Bruker Advance DRX-400 (Bruker, Billerica, MA) spectrometer operating at a proton frequency of 400.13 MHz. Typically, 64 scans were collected into 64 K data points over a spectra width of 11990 Hz with a relaxation delay of 6 s, an acquisition time of 2.7 s, and 90° flip angle. All free induction decays (FID) were multiplied by an exponential function with a 1 Hz line broadening factor prior to Fourier transformation (FT). The spectra were phase corrected interactively using TOPSPIN. Baseline correction was carried out manually each time using the appropriate factors. Chemical shifts were reported using DMSO-d_6 (δ_H 2.50) as an internal reference.

2.2.5. Pyrolysis–gas chromatography–mass spectrometry studies

Mass spectrometer was also used to confirm the cyanoethylation of feathers using a Chemical Data Systems Pyroprobe 120 pyrolyzer