Journal of Analytical and Applied Pyrolysis 115 (2015) 112–124

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Thermochemical conversion of poultry chicken feather fibers of different colors into microporous fibers

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ARTICLE INFO

Article history:
Received 1 October 2014
Received in revised form 8 July 2015
Accepted 10 July 2015
Available online 31 July 2015

Keywords:
Chicken feathers
Microporous materials
Heat treatment
Fourier transform infrared spectroscopy (FTIR)
Thermogravimetric analysis (TGA)
Differential scanning calorimetry (DSC)

ABSTRACT

Thermochemical behavior of the poultry chicken feather fibers (PCFFs) of different colors was studied to gain an insight into their structural changes that were considered when converting them into fibers through pyrolysis process. PCFFs collected from different local farms were categorized according to their color as black, white, and brown. UV light spectroscopy examination revealed that the brown PCFFs were the richest of all in the amount of extractable keratin. Glass transition, melting, and thermal decomposition temperatures of the PCFFs were measured to form the scientific basis for evaluation of the pyrolysis steps. It was revealed that, regardless of color, duration of the heat treatment applied during pyrolysis of the PCFFs at any temperatures below their own crystalline melting peak temperature posed a significant influence on the extent of cleavage of disulfide bonds and the degree of the intermolecular crosslinking achieved. Based on the thermal findings obtained, a-two step pyrolysis method was used to produce the fibers. Scanning electron microscopy (SEM) examination showed that all the resulting fibers were free of etching and preserved their stringy appearance and smoothness when the first and the second steps of pyrolysis were carried out at 230 °C for 24 h and at 450 °C for 1 h, respectively. X-ray diffraction (XRD) and Fourier transformation infrared spectroscopy (FTIR) determinations revealed that the structural changes in the PCFFs subsequent to pyrolysis vary to some extent according to their color. Elemental composition and the specific surface area of the PCFFs were also measured. It was determined that all of the PCFFs after pyrolysis turned into nitrogen containing microporous carbonaceous materials with different oxygen functionalities and surface areas, depending on their color.

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1. Introduction

Tremendous amounts of poultry chicken feathers (PFCs) have been industrially generated and considered as waste materials [1–3]. They are either buried in landfills or end up being recycled into a very low-quality feeds for animals. It is for this reason that a particular emphasis has recently been placed on searching for feasible ways to turn them into more valuable products. Biochemically speaking, PFCs are made up of keratins accompanied with a very small amount of lipids [2,3]. They have thus potential to be a great feedstock for the synthesis of the promising natural and renewable fibers. More specifically, the keratins are biopolymer chains of amino acids with an ability to yield an amide bond (—C (=O) NH—) [4–7]. In addition to this, weak Van der Waals forces keep the linear keratin structure packed, while the crosslinking and hydrogen bonding contribute to the molecule strength [8–20].

There are mainly two types of keratin. One is called: α-keratin that constitutes the majority of the protein in hair, wool, feathers and nails while the other is called: ß-keratin, present in a lot of silk of spiders [6–9]. Biochemically speaking, the keratin content of feathers and its preeminence are considered to be highly dependent on what body parts of birds the feathers are taken from. Generally speaking, the stiff, cylindrical and sharp-pointed of the bird feather is called shaft on which quill (calamus) and rachis are attached together. The slender and parallel side branches arising from two sides of the shaft are called barbs (ramus). Small structures that grow from the barbs of a feather are called barbules that are supposed to give rigidity to feathers. In terms of microstructure and keratin quality, they exhibit different properties than each other. For example, in feather rachis, fraction of α-helix in keratin is higher than the fraction of ß-sheet in keratin, while it is other way around when the feather quill is a matter of subject [4,10]. It was reported that the thermal energy required to perturb the barb

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http://dx.doi.org/10.1016/j.jaap.2015.07.008
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is higher than it is required to perturb the quill [10]. In addition, it was also suggested that the packing within outer quill keratin is less ordered and has a less degree of cross-linking than the packing within barbs and inner quill keratin [11]. Further, it was shown that the modulus of feather rachis is higher in birds capable of flight than in birds incapable of flight [12]. It was determined that mechanical property may vary depending on the type of the feather rachis [13]. Moreover, it was also concluded that elastic modulus may become up to four times higher in swan feather rachis than in ostrich feather rachis. It was also reported in the same study that a gradient occurs in modulus values as a result of different crystal segments across the length of the feather shaft, such that the lowest modulus value is obtained nearby the skin, while the highest modulus is obtained at the tip.

When keratin containing organics are heated, depending on their crystal segments, they may turn into a highly cross-linked structure with a relatively low density. Degree of the cross-linking is highly associated with the major keratin type in the raw feathers and with the heating cycles performed in an oxygen-depleted atmosphere at high temperatures for long periods of time. Physical and chemical changes during pyrolysis of feathers were intensively studied by Senoz et al. [14]. This study includes an–in depth analysis of almost all the possible reactions that may take place during feather pyrolysis under different thermal conditions. It therefore builds a scientific basis on chemically and physically explained experimental facts which the idea of this study was essentially inspired and developed from. In the same study, they obtained industrially-processed chicken feathers (ICFs) from a private company and developed several thermal cycles to explain the structural changes of the ICFs during pyrolysis. As a result, employing a two-step pyrolysis method, they concluded that an intermolecular crosslinking mechanism in the first step of pyrolysis performed at 215 °C for 24 h produced an intact fibrous structure without any trace of melting, and that the second step of the pyrolysis performed at 400–450 °C for 1 h brought about a microporous material with a narrower pore size distribution than commercially available activated carbons [6].

However, when it comes to the PCFs, it turns out to be a big challenge in practice to select and separate the most promising ones from the mixed batch of choice. In other words, it is virtually impossible to foresee what PCFs are coming from what body part of the chickens in the prepared batch. Therefore, in this study, a particular attention was paid to categorizing the PCFs collected from different local farms according to their color and to monitoring their alterations during pyrolysis.

In fact, there are a couple of good studies in the literature [6,14,19,20] where the authors suggested a two-step pyrolysis method to stabilize the protein matrix of the ICFs by providing them with a thermally induced crosslinking through isothermal heat treatment below their crystalline melting point, immediate before their crystalline structure are totally destroyed. When compared to those studies, the most significant contribution of this paper is to investigate the pyrolysis of the poultry feather fibers of different colors that were obtained from different local farms. The reason for this lies in finding a more sustainable way to ease the above-mentioned challenges when seeking out a better way of grouping feathers on a common ground. To our best knowledge, in this manner, this study is the first study in the literature that sheds lights on the potential of the PCFs of different colors by evaluating whether to turn them into porous microfibers through pyrolysis. It also seeks an answer to the question of whether or not PCF color plays a pivotal role in evolution of the final product characteristics during and after pyrolysis.

In this study, as the quill of the feather holding the ramus fibers contains β sheets and the barbs are shaped into α-helices, the ramus section of the PCFs that have a theoretically higher modulus value than the quills was named poultry chicken feather fibers (PCFFs). PCFFs obtained were grouped together by color. The extractable keratin amount of the PCFFs was first determined using a UV light spectroscopy. Differential scanning calorimetry (DSC) and Thermal gravimetric analysis (TGA) were systematically conducted to gain more insight into the thermal behavior of the PCFFs at elevated temperatures. The findings of the thermal analysis results were taken into careful account when using a two-step pyrolysis process. Scanning electron microscopy (SEM) was used to examine the surface characteristics of the produced carbon fibers. Elemental composition and surface area of the resulting fibers were also measured. X-ray diffraction (XRD) analysis was performed to evaluate the structural modifications after the PCFFs turned into fibers. Fourier Transform Infrared (FTIR) was used to have a comparison of the chemical alterations of the PCFFs before and after pyrolysis. All the experimental results obtained were then discussed in a concise manner with an emphasis on the effect of PCFF color.

2. Experimental

2.1. Materials

Black, white and brown PCFs collected from different local poultry farms were grouped on the basis of their color and washed with a detergent in distilled water followed by soaking in a mixture of toluene and ethanol for 6 h at room temperature. Having been autoclaved at 121 °C at 15 min, the PCFs were placed in a vacuum oven and allowed to dry overnight at 70 °C. To get the PCFFs, barbs were stripped from the quills by a specially designed and manually operated mechanical device. The samples were vacuum-dried at 105 °C prior to analysis. Sodium sulphide, ammonium sulphate and sodium hydroxide were obtained from Merck and used for determining the extractable keratin amount of the PCFFs. Copper sulphate was obtained from Carlo Erba. It was also used for the extractable keratin content determination.

2.2. Determination of extractable keratin amount from the PCFFs

Sample solutions were prepared by dissolving PCFFs of different colors (10 g for each batch) in 40 ml of 5 M sodium sulphide solution at 30 °C. pH value of the solutions remained constant at about 12.5 during the measurements [15]. A mechanical gadget was used to keep shaking the solution for at least 6 h. The precipitated solid phase was then separated by using a centrifuge (Thermoscientific SL 16) at 10.000 rpm for 15 min. The suspending residue was again centrifuged several times in sequence until the desired phase separation occurs for sure. Ammonium sulphate solution (40 ml and 5 M) was added drop wise to each collected feather filtrate to extract the bulk keratins. The final solution obtained was then centrifuged once again at 10,000 rpm for 5 min and then the bulk part of the solution was extracted followed by adding 20 ml of deionized water for protein purification. The purified proteins were then allowed to dry overnight. The protein obtained from each PCFF was then weighed and dissolved in 10 ml of 2 M sodium hydroxide solution. The 5 ml of the dissolved solution was afterwards mixed with potassium hydroxide (1 wt.%) solution at an equal weight ratio. Furthermore, copper sulphate solution (1 wt.%) was continuously added to the prepared mixture until its color turned to purple. For the purpose of determining the extractable keratin content of the PCFFs, Biuret method was used. First of all a calibration curve of absorbance versus protein concentration is prepared using a series of pure keratin solutions of known concentrations. Absorbance measurements of each solution were then performed using a Cary 100 bio-model Varian UV–visible Spectrophotometer at 540 nm.

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