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Preparation and properties of biodegradable stearic acid-modified gelatin films

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Abstract

Gelatin was modified by various amounts of stearic acid using different reaction times in aqueous media at 60 °C and pH of 5.5. By casting the modified gelatin solutions, slightly yellow films were formed. It was found that all modified gelatin films had longer drying time, lower tensile strength, lower % moisture absorption, and better biodegradability than unmodified ones. Their oil resistance was comparable. It was also found that the amount of stearic acid and the reaction time significantly affected these properties. As the amount of stearic acid increased, the films exhibited longer drying time, lower tensile strength and lower moisture absorption. With increasing the reaction time, the films exhibited shorter drying time, higher tensile strength and lower moisture absorption. The results suggest that the film prepared from 15% stearic acid-modified gelatin using the reaction time of 8 h had highest potential for applications in environmental friendly packaging.

Keywords: Gelatin; Stearic acid; Modification; Biodegradable

1. Introduction

Currently, the idea of replacing commonly used plastics prepared from synthetic polymers with biodegradable plastics prepared from natural polymers is increasingly interesting. Gelatin is one of the natural polymers which is now widely studied. It is a high molecular weight polypeptide composing of amino acids mainly glycine (27%), hydroxyproline and proline (25%) [1]. Because its molecules are tightly bound with hydrogen bonds, pure gelatin films are normally brittle. Furthermore, the polar groups present in its structure cause a gelatin film to have high moisture absorption. Due to these disadvantages, pure gelatin films are not suitable for many applications. Therefore, gelatin is generally blended or copolymerised with other synthetic polymers [2–7]. Blending is easy to handle but may encounter the incompatibility between hydrophilic gelatin and hydrophobic synthetic polymers. Copolymerisation overcomes the incompatibility problem but the technique is usually more complex and more difficult to handle than blending. Therefore, more effective methods to prepare such plastics from gelatin should be developed.

Previous studies indicated that gelatin plasticised with a plasticiser such as sorbitol or chemically modified with suitable modifying agents such as formaldehyde, glyoxal, glutaraldehyde, hexamethylene diisocyanate, butadiene diepoxide and maleic anhydride can be used to prepare fully biodegradable plastics [8–10]. In addition to those chemicals above, stearic acid also has the potential to be used in gelatin modification. Besides esterification between carboxylic groups of stearic acid and hydroxyl groups of hydroxyproline in gelatin

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molecules as was reported by Djagmy and coworkers [11], the long chain hydrocarbon segments of stearic acid may act as a plasticiser for the system. This suggests that stearic acid functions as both modifying agent and plasticiser.

The possibility of preparation of biodegradable plastic films from gelatin modified with other modifying agents such as formaldehyde, glyoxal, glutaraldehyde, hexamethylene diisocyanate and butadiene diepoxide was studied [8] whereas the use of stearic acid-modified gelatin in such films has not been investigated. Since stearic acid is natural product, the films prepared from gelatin modified by stearic acid are more environmental friendly than those prepared from synthesized chemicals. Therefore, in this research, stearic acid-modified gelatin films were prepared using various reaction conditions and their properties were characterized in order to determine the suitable reaction conditions for preparing such films which can be used for packaging applications.

2. Experimental

2.1. Materials

Gelatin (commercial grade) was purchased from Suksapanpanich, Kurusapa Business Organization, Thailand. Stearic acid (analytical grade) and 37% hydrochloric acid (analytical grade) were purchased from Lab-Scan. Sodium hydroxide (analytical grade) was purchased from Merck. All materials were used as obtained without further purification.

2.2. Methods

Twenty-five grams of gelatin was dissolved in 475 g of distilled water in 600 ml beaker at 60 °C for 15 min. The pH of gelatin solution was adjusted to 5.5 using hydrochloric acid solution. After that, the desired amount of stearic acid was added and the mixture was continuously stirred at 60 °C for the desired reaction time. The solution was then neutralized by sodium hydroxide solution. The abbreviations of modified gelatins prepared at different conditions are presented as G-X-Y where X indicates the reaction time and Y indicates the amount of stearic acid (% by weight of gelatin). For example, G-2-5 means that this modified gelatin was prepared using the reaction time of 2 h and the amount of stearic acid 5% by weight of gelatin.

The modified gelatin solutions were poured into plastic moulds. The samples were left to dry at room temperature. Drying time to hard dry state of modified gelatin films was determined based on ASTM D 1640-95. Their chemical structures were characterized using FT-IR Spectrometer Model Nicolet-Impact 400.

Tensile strength of these gelatin films was determined based on ASTM D 882-01 using a universal tensile testing machine.

For determination of moisture absorption, samples with the size of 1×3 in. were dried in a desiccator until their weights became constant (W_0). These samples were then placed in moisture saturated atmosphere for 7 days. After that, the samples were weighed (W_1). Moisture absorption ($\%M$) can be calculated from the following equation:

$$\%M = (W_1 - W_0)/W_0 \times 100$$

Biodegradation testing was based on a soil burial method. The samples with the size of 1×2 cm were dried in a desiccator until their weights became constant (W_2). These samples were then buried in soil for 5, 7, 10, 12, and 15 days. After that, the samples were dried until their weights became constant (W_3). % Weight loss ($\%W$) can be calculated from the following equation:

$$\%W = (W_2 - W_3)/W_2 \times 100$$

Oil resistance of these films was tested using Thailand Industrial Products Standard 654-2529. In this method, a film was cut into five test samples with a size of 100 mm × 100 mm. Each sample was placed on a white paper. A tube with 25 mm in diameter and more than 25 mm in height was placed over each sample. Then 4.9–5.1 g of sand was poured into the tube. After that, 1.1 cm^3 of pine oil was dropped to the sand and the tube was then covered with a glass lid. After 1 day, the sample along with the tube was moved to another area of the paper and the oil stain at the previous area was observed. This process was repeated every day. If no oil stain was present after 5 days, this means that the oil resistance of the film is as required. This test method must be performed at 25–29 °C and 60–70% relative humidity.

3. Results and discussion

Non-treated, unmodified and modified gelatin films were prepared in this research. The drying time of non-treated gelatin film was found to be 48 h while the drying times of both unmodified and modified gelatin films were shorter. In the case of unmodified ones, an evaporation of water during heating process resulted in lower water content in these films when compared to non-treated film. Consequently, the drying time of the former was shorter than that of the latter. In the case of modified ones, the presence of hydrocarbon segments of stearic acid increased the rate of water evaporation due to their hydrophobic characteristic; therefore, the drying time of modified gelatin films was shorter than that that of non-treated gelatin film.