Carbohydrate Polymers 186 (2018) 236–242

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Electrochemical writing on edible polysaccharide films for intelligent food packaging

Si Wu, Wenqi Wang, Kun Yan, Fuyuan Ding, Xiaowen Shi*, Hongbing Deng, Yumin Du

School of Resource and Environmental Science, Hubei International Scientific and Technological Cooperation Base of Sustainable Resource and Energy, Wuhan University, Wuhan 430079, China

ARTICLE INFO

Keywords:
Chitosan
Agarose
Anthocyanin
Electrochemical writing
Food packaging

ABSTRACT

Polysaccharide films used as intelligent food packaging possess the advantages of renewability, safety and biodegradability. Printing on the polysaccharidic food packaging is challenging due to the high demand for edible-ink and the need for a suitable printing technique. In this work, we propose an electrochemical method for writing on polysaccharide film. Unlike conventional printing, this electrochemical writing process relies on the pH responsive color change of anthocyanin embedded in the chitosan/agarose hydrogel. By biasing a negative potential to a stainless wire (used as a pen) contacting the surface of the chitosan/agarose/ATH hydrogel, the locally generated pH change induced the color change of ATH and wrote programmed information on the hydrogel. We demonstrate the writing can be temporary in the hydrogel but stable when the hydrogel is dried. We further demonstrate that the written film is applicable for the detection of the spoilage of crucian fish. The reported electrochemical writing process provides a novel method for printing information on polysaccharide film and great potential for intelligent food packaging.

1. Introduction

Developing biodegradable packaging from renewable resources is of significance to solving the environmental problems caused by using synthetic plastics. Due to its safety and abundant resources, polysaccharide-based edible food packaging has attracted much attention (Ferreira, Alves, & Coelhoso, 2016). Food packaging made from some polysaccharides has the advantages of transparency and good mechanical properties (Cazon, Velazquez, Ramirez, & Vazquez, 2017). Further, the polysaccharide films can be incorporated with other active materials to give the film additional properties, such as antibacterial, and antioxidant properties and the ability to maintain freshness. The improved properties of polysaccharidic packaging films provided new methods for better food preservation and prolonged shelf life. For instance, Lozano-Navarro et al. (2017) showed that chitosan-starch films with beetroot, cranberry, and blueberry extracts demonstrated enhanced antimicrobial activity against various bacteria and fungi. Badawy, Rabea, El-Nouby, Ismail, and Taktak (2017) found that the chitosan coatings incorporated with gelatin or starch and their combination with geraniol and thymol protected strawberries against fungal decay and prolonged shelf life during storage.

Although much work on food packaging using alginate, chitosan and other polysaccharides has been published, there are few studies on printing on polysaccharide film (Caro et al., 2016), probably due to the high requirement for edible ink and the need for a suitable printing route (Aznar, Domeno, Nerin, & Bosetti, 2015; Huang, Sun, Wei, & Yi, 2014; Zhang, Li, Mou, & Li, 2016). Printing on food packaging can provide important information about the food, such as the manufacture date and storage status of the food. The traditional printing process involves the injection of ink on the package surfaces, and the printing stability relies on the adhesion strength between the ink and the substrate surface. Therefore, developing new techniques for printing on polysaccharide film is highly desirable.

In nature, anthocyanin (ATH) is extracted from plants and flowers, and it is responsible for their coloration. It is non-toxic and used commonly in the food and beverage industry. One unique feature of ATH is that it changes color in response to changes over a wide pH range. It is well-known that pH is one of the important factors for assessing spoilage in many food products. The spoilage of protein-rich foods such as meat and sea foods raises the pH, since these foods produce volatile organic compounds (Wei, Cheng, Ho, Tsai, & Mi, 2017). Moreover, the pH increased significantly during the storage of fruit, due to utilization of organic acids during respiration (Duran et al., 2016). Recently, anthocyanin has been incorporated in polysaccharide films for the detection of food spoilage, which provides a convenient, non-destructive and visual method for food spoilage detection (Choi, Lee, Lacroix, &

* Corresponding author.
E-mail address: shixwwhu@163.com (X. Shi).

https://doi.org/10.1016/j.carbpol.2018.01.058
Received 1 November 2017; Received in revised form 28 December 2017; Accepted 17 January 2018

Han, 2017; Silva-Pereira, Teixeira, Pereira-Junior, & Stefani, 2015).

In this paper, we incorporate ATH in dual responsive chitosan/agarose film for multifunctional food packaging. Chitosan is a cationic polysaccharide from chitin, and it is pH-responsive. The film-forming, antimicrobial and biocompatible features of chitosan make it a favorable material for active food packaging (Al-Naamani, Dobretsov, & Dutta, 2016; Ham-Pichavant, Sebe, Pardon, & Coma, 2005; Siripatrawan & Vitchayakitti, 2016; Zhang et al., 2017). Agarose is a thermally responsive polysaccharide, can form transparent hydrogels at room temperature and has been widely used in biomaterials (Lal, Suraishkumar, & Nair, 2017). The chitosan and agarose films demonstrate excellent compatibility and enhanced mechanical strength due to the formation of hydrogen bonding, demonstrating great potential in food packaging (Cao, Zhang, Chen, Meng, & Liu, 2017; Hu et al., 2016). Our former work demonstrated that by adapting the pH gradient locally generated near the cathode, we can create electrodeposits in chitosan/agarose hydrogel (Yan et al., 2016). Herein, through an electrochemical writing process, varied information can be printed on the chitosan/agarose/ATH film. Specifically, chitosan was blended with agarose at high temperature and cooled to room temperature to produce a red hydrogel. The hydrogel was placed on a conductive surface, which was used an anode, and a stainless steel wire was used as a cathode, contacted the surface of the hydrogel and applied a negative potential. The pH increase near the steeling wire changes the color of the ATH from red to blue. Thus, specific information can be written on the surface of the chitosan/agarose/ATH film, as demonstrated by Scheme 1. Further, we demonstrate that the film can be used as a visualized detection method for the spoilage of fish. Importantly, the information written on the film remained during the whole process, demonstrating the stability of the electrochemical writing and multifunctionality of the ATH-embedded chitosan/agarose film.

2. Materials and methods

2.1. Materials

Chitosan (C0831, 200-600 mPa.s) was purchased from Tokyo Chemical Industry (TCI, Shanghai). Low-melting-point agarose (melting point 65. 5 °C, gel strength 250 g cm^{-2} in 1.0% gel and sulfate content < 0.1%) was purchased from Amresco. Anthocyanin was purchased from Qingdao Pengyuan Kanghua Natural Source Co., Ltd. Hydrogen chloride, ammonia and sodium hydroxide were obtained from Sinopharm chemical reagent Co., Ltd. All reagents were of analytical grade and were used without further purification.

2.2. Preparation of chitosan/agarose/ATH hydrogel

An adaptation of previously reported protocols was used in this study (Maciel, Yoshida, & Franco, 2015; Pereira, de Arruda, & Stefani, 2015). Two grams of chitosan was dissolved in 100 mL of hydrochloric acid (0.8%; v/v) under magnetic stirring for 24 h at room temperature (25 °C). The pH of the chitosan was adjusted to 5.5 using 1 M NaOH. One hundred milligrams of ATH was added to the chitosan solution and homogenized by magnetic stirring for 30 min. An agarose solution was prepared by dissolving 2 g of agarose in 100 mL of deionized water at 80 °C for 10 min. Then, the chitosan solution containing ATH was added to the agarose solution under magnetic stirring for 10 min. The mixture was quickly poured into a plastic petri dish and turned into chitosan/agarose/ATH hydrogel as the agarose network formed upon cooling down to room temperature.

2.3. Electrowriting on hydrogel

An anode made of Pt contacted the bottom of chitosan/agarose/ATH hydrogel, while the cathode made of stainless steel (diameter 0.4 mm) touched the upper surface of the hydrogel. A 3D printer moved the cathode on the hydrogel under command of a computer program. When the electrolytic current was set at 2 mA, OH^- was generated around the cathode. Affected by base, the color of ATH was changed to blue, and computer programmed information was left precisely on the hydrogel as it was touched by the moving cathode. Then, the chitosan/agarose/ATH hydrogel was dried in an oven at 45 °C for 12 h to form patterned film.

2.4. Characterization

2.4.1. Film sensitivity to pH

The chitosan/agarose/ATH film was cut into square shapes of 1.5 cm^2 each in area and randomly divided into two groups (n = 5). Group one was put in the headspace of a sealed container saturated with hydrogen chloride gas. Group two was put in the headspace of another sealed container saturated with ammonia gas. The time needed for the color change of each group was recorded.

2.4.2. The stability of the writing

The hydrogel was printed with a letter "A" using the electrowriting method and left at room temperature to observe the color change of the letters. In another study, the hydrogel with the word "fresh" was dried in an oven at 45 °C for 12 h, and then, the film was kept in a desiccator (0% RH at 25 °C or 75% RH at 25 °C) for 16 days. The images of the films were captured every day by an optical scanner (M7600D, Lenovo) and analyzed by Metlab R2015a (Matworks Inc., Natick, MA, USA). The stability of the colorimetric film was defined as the relative color change (Huang et al., 2015; Zhai et al., 2017):

$$\Delta R = |R_0 - R_1|$$

$$\Delta G = |G_0 - G_1|$$

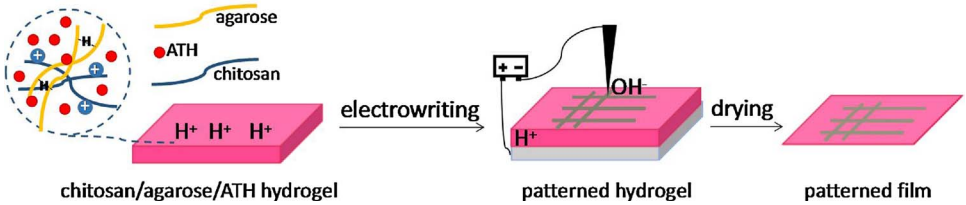
$$\Delta B = |B_0 - B_1|$$

$$S = \frac{\Delta R + \Delta G + \Delta B}{R_0 + G_0 + B_0} \times 100\%$$

where R_0, G_0 and B_0 were the gray values of the red, green and blue in the first day, and R_1, G_1, and B_1 were the gray values of the red, green and blue after storage. S was the relative color change of the R, G and B values.

2.4.3. Fourier transform infrared (FT-IR) spectroscopy

FTIR analysis of the chitosan/agarose/ATH film as well as the chitosan film, agarose film and pure ATH was performed in the range of 4000–400 cm^{-1} using an FT-IR spectrometer (Thermo Scientific, Nicolet 5700 spectrometer, USA) operating in transmission mode with a resolution of 4 cm^{-1}.



Scheme 1. Illustration of electrochemical writing on the chitosan/agarose/ATH hydrogel.