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Films based on κ-carrageenan incorporated with curcumin for freshness monitoring

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ABSTRACT

Novel films based on κ-carrageenan (Car) incorporated with curcumin (Cur) were developed for freshness monitoring of foods. Cur and Car were interacted by hydrogen bonds. A low amount of Cur (no higher than 3%) could be well-dispersed in Car matrix. These characteristics significantly improved the film barrier and tensile strength, besides the enhancement of thermal stability. Hence, the Car film with 3% Cur exhibited the best performance. The films showed a good release control of Cur and a predominant Fickian diffusion release mechanism, which was favorable to sustainable pH change sensing. The Car-Cur films demonstrated a strong redness-shift under alkaline condition. This characteristic was successfully used to monitor the spoilage of pork and shrimp during storage. As a pH colorimetric indicator, the Cur incorporated Car films may have a great potential in the freshness monitoring of foods.

1. Introduction

Recently, there is a growing interest in developing intelligent or smart packaging capable of providing information, enhancing safety, and improving quality of the packaged food during storage, transportation and distribution (Kuswandi, JayusRestyana, Abdullah, Heng, & Ahmad, 2012; Niponsak, Laohakunjit, Kerdchoechuen, & Wongsawadee, 2016). Owing to the microbial spoilage, it is likely to establish the relationship between the food freshness and pH value. On basis of the color change characteristic towards acidic or basic environments, pH colorimetric indicators have exhibited a great potential use in the freshness monitoring of foods such as fish (Kuswandi et al., 2012; Silva-Pereira, Teixeira, Pereira-Júnior, & Stefani, 2015; Zhai et al., 2017) and fresh pork sausages (Salinas et al., 2014). In general, pH colorimetric indicators are composed of a solid support incorporated with a pH sensing dye.

As an appropriate solid matrix for the incorporation of pH sensing dye, the safety of the matrix must be considered. Many valuable research works have been done with some natural polysaccharide polymers including chitosan (Yoshida, Maciel, Mendonça, & Franco, 2014; Zhang, Lu, & Chen, 2014), starch (Luchese, Sperotto, Spada, & Tessaro, 2017), gellan gum (Wei, Cheng, Ho, Tsai, & Mi, 2017), and tara gum (Ma, Ren, Gu, & Wang, 2017; Ma & Wang, 2016). Differently, our interest is focused on κ-carrageenan, an abundant natural hydrocolloid extracted from red seaweeds, which consists of alternating 3-linked β-d-galactose 4 sulfate and 4-linked 3, 6-anhydro α-d-galactose (Fouda et al., 2015). Besides the good film-forming ability, κ-carrageenan tends to form a stronger and more rigid gel than l- and i-carrageenan due to the characteristic of negative charge per disaccharide (Park, Lee, Jung, & Park, 2001). Furthermore, films from κ-carrageenan have a good barrier against oxygen, which is favorable to restrain the lipid oxidation (Varela & Fiszman, 2011). Apart from pH colorimetric indicator, κ-carrageenan has been successfully employed to fabricate κ-carrageenan-based active food packaging with plant essential oils (Shojaee-Aliabadi, Hosseini, et al., 2014; Shojaee-Aliabadi, Mohammadifar, et al., 2014). Due to the safety and easy preparation, interest in pH colorimetric indicators for freshness monitoring has been focused on the applications of natural dyes from plant tissues, such as roselle anthocyanin (Zhai et al., 2017), extracts from red cabbage (Silva-Pereira et al., 2015), and *Vitis amurensis* husk for

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fish (Ma, Ren, et al., 2017), purple sweet potato anthocyanin for pork (Choi, Lee, Lacroix, & Han, 2017), and extracts from grape skins for milk (Ma & Wang, 2016). As is well known, curcumin is a polyphenol extracted from herbaceous turmeric and curcuma rhizomes, which possesses anticancer, anti-inflammatory, antioxidant, and antimicrobial activities (Liu, Cai, Jiang, Wu, & Le, 2016; Mahady, Pendland, Yun, & Lu, 2002; Sonkaew, Sane, & Suppakul, 2012). To the best of our knowledge, few literature has been reported on the usage of curcumin as pH colorimetric indicator: curcumin incorporated in tara gum/polyvinyl alcohol non-edible film (Ma, Du, & Wang, 2017) and curcumin incorporated in a gelatin edible film (Musso, Salgado, & Mauri, 2017).

Different from the abovementioned, we aim to develop a pH colorimetric indicator based on κ-carrageenan incorporated with curcumin to monitor the freshness of foods (pork and shrimp, two typical easily spoiled spoilage protein foods). Attentions were focused on pH sensing characteristics of the films. The curcumin release behavior was evaluated emphatically for the sustainable pH change sensing. Thermal stability, tensile strength, barrier properties, and the microstructure of the films were investigated.

2. Materials and methods

2.1. Materials

Powders of κ-carrageenan (Car, CAS number 11114-20-8) and glycerol (≥99.5%, CAS number 56-81-5) were purchased from Aladdin (Shanghai, China). Curcumin (Cur, CAS number 458-37-7, appearance: yellowish-orange powder), absolute ethanol (≥99.5%), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were provided by Sinopharm (Shanghai, China). The Milli-Q water used in experiment was from a Millipore purification system (Bedford, MA, USA). All chemicals were of analytical grade. Pork and shrimp were purchased from local market (Hefei, China).

2.2. Film preparation

A series of Car solutions were prepared by dissolving 2 g Car powders in 100 mL Milli-Q water containing 2 mL glycerol with vigorously stirring at 90 °C for 30 min. After then, a set of ethanol solutions (10 mL, ethanol/water = 4/1, w/w) containing Cur with weight of 0, 1, 3, 5, and 7% of Car were prepared with stirring at room temperature for 10 min and added to solutions. After another stirring of 10 min at 90 °C, the mixtures were subjected to an ultrasonic treatment of 3 min for the removal of bubbles. The final film-forming solutions were spread on glass plates with a diameter of 15 cm and dried at 60 °C for 48 h. The corresponding dried films (coded as Car-Cur0, 1, 3, 5, and 7) were peeled from the plates and stored in desiccators until further testing.

2.3. UV–vis measurement and colorimetric analysis

UV–vis spectra of Cur solutions and films were measured by UV-754PC spectrophotometer (Shanghai, China). Before measurement in the range of 250–600 nm, the solutions were adjusted to the desired pH values (pH 3.0–10.0) with 0.1 mol/L HCl or NaOH solutions. The solution without Cur was used as blank. For film transmittance testing, each sample (4 cm × 1 cm) was placed directly in the spectrophotometer cell and measured in the range of 400–800 nm. Measurement was performed with air as a reference for transparency.

The color of films was determined by CR-300 colorimeter (Minolta, Japan), using the values of L, a, and b for the evaluation of the film colors. The films were determined on the surface of white standard plate ($L^* = 97.48$, $a^* = -0.48$ and $b^* = 2.15$). The total color difference (ΔE) was calculated by eq (1).

$$\Delta E = \left[(L - L^*)^2 + (a - a^*)^2 + (b - b^*)^2 \right]^{0.5} \quad (1)$$

2.4. Film morphology and structure

Micrographs of the films were visualized using SU8020 scanning electron microscopy (SEM, Hitachi, Japan) and each specimen was sputtered with gold. The microstructure and morphology of Cur powders were observed with JEM-2100 transmission electron microscopy (TEM, JEOL, Japan). The Cur suspension (0.1%) was dropped onto a thin carbon film supported by a copper grid before the observation. Fourier transform infrared (FTIR) spectra were carried out on a Nicolet 6700 spectrometer (Madison, WI, USA) to determine the interaction between Car and Cur. The crystal phase of samples was characterized by X-ray diffraction (XRD) recorded on a D/MAX2500V diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 0.15418 nm).

2.5. Thermal stability

Thermal stability of samples was evaluated by Q2000 differential scanning calorimetry (DSC, TA Instruments, New Castle, USA) and the temperature was ranged from 40 to 230 °C (10 °C/min, under nitrogen).

2.6. Mechanical properties

The tensile strength (TS) and elongation at break (EB) of specimens were tested with TA-XTPlus Texture Analyzer (Stable Micro Systems, Co., UK) according to ASTM D882-91. Five measurements were taken on each specimen (1 cm × 10 cm) to calculate the average. During the testing, an initial grip separation of 50 mm and a crosshead speed of 0.5 mm/s were employed. The values of TS and EB of the specimens were determined from stress-strain curves, from which the corresponding values of Young's modulus could be calculated by the slope of the initial linear portion.

2.7. Barrier properties

Oxygen permeability (OP) and water vapor permeability (WVP) were used to assess the barrier properties of the films. Oxygen gas transmission rate (OTR) was detected at room temperature (0% RH) with an N500 gas permeameter (Guangzhou, China). According to OTR ($cm^3\ m^{-2}\ d^{-1}\ atm^{-1}$), OP was calculated by eq (2).

$$OP = OTR \times thickness \quad (2)$$

WVP of the films was measured briefly as follows: the testing films were fixed on the top of beakers which contained silica gel (0% RH) and then placed in a BIC 250 artificial climate incubator (Shanghai, China) at 25 °C and 75% RH. The moisture absorption was measured by weighing beakers at an interval of 6 h within 5 d and WVP ($g\ m\ m^{-2}\ s^{-1}\ atm^{-1}$) was calculated by eq (3).

$$WVP = (w \times x)/(A \times t \times \Delta P) \quad (3)$$

where w (g) stands for beaker weight gain, x (m) thickness and A (m^2) exposed area of the films, t (s) the weight gain time, and ΔP (atm) the water vapor partial pressure difference across both sides