Developing an intelligent film containing *Vitis amurensis* husk extracts: The effects of pH value of the film-forming solution

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ABSTRACT

Bio-based films have become preferred because of their biodegradability and availability from reproducible resources. *Vitis amurensis* husk is a byproduct of white-wine processing. The colors of *Vitis amurensis* husk extracts vary from red to green as the pH value increases from 2 to 12. A new bio-based intelligent colorimetric film was developed by incorporating *Vitis amurensis* husk extracts into the tara gum/cellulose matrix. The effects of pH value (3, 4, 5, 6, and 7) of the film-forming solution on the color, transparency, morphology, mechanical properties, barrier properties, and moisture uptake properties of the films were investigated. The color of the film changed from pink to yellow-green as the pH value of the film-forming solution increased from 3 to 7. The scanning electron microscope results showed that the cross sections of the film formed at pH of 3, 6 and 7 showed a wrinkled appearance. The reduction of the tensile strength and oxygen permeability were related to the wrinkle appearance. The resulting films changed in color after immersion in solutions with different pH values. Similar color changes occurred, and there was an apparent difference in the monitoring test for fish products. The film formed at pH 6 changed to green in 48 h, and the other film at pH 3, 4, and 5 changed in 60 h, indicating that it had a better sensitivity. This study showed that an intelligent colorimetric film can be utilized as a visual indicator for food quality assurance.

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1. Introduction

The functions of traditional food packaging are generally protection, communication, convenience, and containment (Yam et al., 2005). Food packaging materials are used to protect the product against adverse external environment, as a marketing tool for communicating with the consumer, to provide convenience and greater ease of use, and to contain other product information. However, these functions cannot meet consumers' need because of the increasing demand for high-quality, safe, and fresh food. These demands have accelerated the development of smart packaging or intelligent food packaging. Different from traditional packaging, intelligent packaging aims to convey information about the status of the food and environmental conditions (Restuccia et al., 2010).

For example, an intelligent packaging system can show whether the food product is fresh or has expired (Ghaani et al., 2016). Undoubtedly, this feature can decrease food loss and waste and minimize expenditures due to transport and logistics throughout the food supply chain (Pourjavaher et al., 2017).

Normally, intelligent packaging contains an intelligent device, for example, a data carrier such as a barcode label and radio-frequency identification tag, as well as a package indicator such as a time-temperature indicator, a gas indicator, or a pH indicator (Kerry et al., 2006). Because a pH change usually accompanies the process of spoilage, pH indicators have gained much popularity. A pH sensor generally contains a dye that changes in color according to pH conditions (Golasz et al., 2013). Compared with synthetic dyes, natural dyes are advantageous because of their safety and eco-friendly feature. Anthocyanin, a known flavonoid, is one of the six common subgroups of plant pigments. Most fruits, vegetables, flowers, and some cereal grains are rich in orange, red, purple and blue pigments. It is a dietary antioxidant that can prevent neuronal diseases, cardiovascular illnesses, cancer, diabetes, inflammation,

and many other diseases (Yousuf et al., 2016). Importantly, anthocyanin is sensitive to pH conditions because of its conjugated structure. There are some reports on the use of anthocyanin as natural pH indicators, for example, anthocyanin extracted from red cabbage (Pereira et al., 2015), black bean seed coat (Prietto et al., 2017), and *Bauhinia blakeana* Dunn (Zhang et al., 2014). *Vitis amurensis* husk, which is one of the sources of anthocyanin for food coloring and a byproduct of white-wine processing, is commonly used to brew wines. *V. amurensis* is abundant in northeast China, Korea, Russia, among others. Thus, anthocyanin from *V. amurensis* husk is easily obtained at low cost.

Bio-based films have become preferred because of efforts to prevent "white pollution". Tara gum is a polysaccharide extracted from the seeds of *Caesalpinia spinosa* tree (Pizato et al., 2013). It consists of a linear chain of mannopyranose units attached to galactopyranose and is used in food industry as a thickener and stabilizer (Sittikijyothin et al., 2007). Tara-gum-based films have good mechanical properties and oxygen barrier properties, but they exhibit poor barrier permeability to water vapor due to its hydrophilicity (Antoniou et al., 2014). Cellulose nanocrystals (CNCs) were used as nano-filler in tara gum film to obtain desirable properties (Ma et al., 2016). In our laboratory, we previously incorporated grape skin extracts into tara gum/CNCs films to confer intelligent properties, and our results showed that the film could respond to pH conditions. We found that the pH value of the film-forming solution affected the physical properties and pH sensitivity of the films. The corresponding studies have not been reported. In the present study, *V. amurensis* husk extracts (VAHE) were used to prepare intelligent colorimetric pH-sensitive films. The effect of pH value of the film-forming solution on the mechanical properties, oxygen barrier properties, moisture uptake, and color-response efficiency of the films was studied. The prepared films were also used as an intelligent indicator for monitoring the quality of a fish product.

2. Materials and methods

2.1. Materials

Tara gum (TG) was obtained from Dymatic Fine Chemical Co., Ltd. (Guangzhou, China) with a molecular weight of 1000 kDa measured by gel permeation chromatography (GPC). Microcrystalline cellulose (MCC, degree of polymerization (DP) = 200) was purchased from Shanghai Shenmei Pharmaceutical Technology Co., Ltd. (Shanghai, China). *Vitis amurensis* was purchased from local market. Glycerol was analytical reagent grade purchased from Yongda chemical Reagent Co. Ltd. (Tianjin, China).

2.2. Preparation of VAHE

V. amurensis was first peeled after washing. The husk was then dried at ambient temperature and powdered. The powder obtained was macerated in ethanol–water solution (7:3, v/v) at a pH value of 2.0 (Ma and Wang, 2016). Subsequently, the solution was stored in a refrigerator for 24 h, and protected from light with tinfoil. After this period, the solution was centrifuged at 3000 rpm for 5 min to remove the impurities. The solvent was then removed from the supernatant using a rotary evaporator at 50 °C. Finally, the resulting paste was transferred to a volumetric flask for the preparation of the films.

2.3. Preparation of the intelligent films

CNCs were obtained by sulfuric acid hydrolysis (55 wt%) at 42 °C for 96 min. After acid hydrolysis, the suspension was diluted with

2 L of distilled water to quench the reaction. The resulting suspension was centrifuged at 10,000 rpm for 10 min to remove the excess acid. The precipitate obtained was dialyzed for 7 days until the pH 7 was reached. Finally, ultrasonic treatment (1000 W for 20 min) was performed in an ice bath, and the suspension was stored in a refrigerator until further use.

Tara gum solution (1 wt%) was prepared by dissolving tara gum at 45 °C for 3 h. On the basis of our previous study, optimum proportions of 6% CNCs (w/w, tara gum basis) and 30% glycerol (w/w, tara gum basis) were added (Ma et al., 2016). The solution was then stirred for 15 min, and VAHE was added to a proportion of 10% (w/w, tara gum basis). The film-forming solution was adjusted with NaOH/HCl (1 mol/L) to pH values of 3.0, 4.0, 5.0, 6.0, and 7.0, cast onto a Plexiglass plate (26 cm × 26 cm × 4 cm) after removal of bubbles, and then dried at 60 °C for 24 h in a vacuum-drying oven. Dried films were conditioned in desiccators before other tests. The obtained films, Fp3, Fp4, Fp5, Fp6 and Fp7, were coded according to the pH value of the film-forming solution (i.e., 3.0, 4.0, 5.0, 6.0, and 7.0, respectively).

2.4. Characterization

2.4.1. Colorimetric analysis

The color parameters of the films were measured by a portable colorimeter (Xrite2600d, MI, 101, USA). L (lightness), a (redness-greenness), b (yellowness-blueness) were measured to evaluate the color difference of the films. Three measurements were taken on each film. The total color difference (ΔE) was calculated as shown in Eq. (1).

The sensitivity of the films to acid and alkali solution was measured in aqueous solution (pH = 1, 2, 4, 6, 8, 10 and 12). The films were first cut into rectangles and immerged into the aqueous solution for 5 s. After removing the solutions, each film was placed on a white plate and its color was noted without drying. The color change was also recorded by using a portable colorimeter.

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \qquad (1)$$

where $\Delta L^* = L-L_0^*$; $\Delta a^* = a-a_0^*$; $\Delta b^* = b-b_0^*$, L_0^*, a_0^* and b_0^* are color values of the reference.

2.4.2. UV–vis spectra measurement

The UV–vis spectra of VAHE in different pH solutions and the transparency of the films (Fp3, Fp4, Fp5, Fp6 and Fp7) were measured by an ultraviolet–visible (UV–vis) spectrophotometer (UV-2600, Shimadzu, Kyoto, Japan) operating in the range of 200–800 nm.

2.4.3. SEM observation

Micrographs of the samples were examined under a Quanta 200 scanning electron microscope (Philips-FEI Co., AMS, The Netherlands) with an accelerating voltage of 5 kV. The cross sections and the surface of films were coated with a thin gold layer prior to observation.

2.4.4. Moisture sorption isotherms

The film specimens (15 mm × 15 mm) were pre-dried in a drying oven for several days and accurately weighed. The films were then stored in separate desiccators at specific humidities (11%, 22%, 33%, 53%, 75%, 84%, and 90%) at ambient temperature for at least ten days to attain equilibrium. The changes in weight of the films were measured to determine the extent of moisture adsorption. The Guggenheim Anderson de Boer (GAB) model was used to predict the moisture adsorption of the films. The GAB isotherm model is expressed as follows (Teodoro et al., 2015):