Food Hydrocolloids 80 (2018) 15–23

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Development of a novel on–off type carbon dioxide indicator based on interactions between sodium caseinate and pectin

Inyoung Choi [a], Jaejoon Han [b, *]

[a] Department of Biotechnology, College of Life Sciences and Biotechnology, Korea University, Seoul 136-701, Republic of Korea
[b] Department of Food Bioscience and Technology, College of Life Sciences and Biotechnology, Korea University, Seoul 136-701, Republic of Korea

ARTICLE INFO

Article history:
Received 6 December 2017
Received in revised form
22 January 2018
Accepted 22 January 2018

Keywords:
Sodium caseinate
Pectin
Protein–polysaccharide interaction
CO_2 indicator
Intelligent packaging
Kimchi

ABSTRACT

Intelligent food packaging systems are a new concept and allow real-time monitoring of food conditions using indicators that are clearly visible to consumers. Among intelligent food packaging types, gas indicators detect changes in gas components in headspaces of food packages. This study aimed to develop a carbon dioxide (CO_2) indicator based on reactions of sodium caseinate (NaCas) and pectin. Transparency and pH were measured to confirm the changes in the appearance of the two polymers, and pectin concentrations were optimized for rates of change in transparency. In Fourier transform infrared spectroscopy and confocal laser scanning microscopy analyses, NaCas and pectin suspensions were characterized, and the associations between protein–polysaccharide interactions and pH changes were determined. Subsequently, the developed indicator was applied to kimchi packaging, and changes in pH, titratable acidity, lactic acid bacteria, and CO_2 contents of the kimchi packaging were determined and correlated with changes in transparency and pH of the indicator. The results demonstrated a strong correlation between parameters of kimchi and the indicator and warrant the use of visual CO_2 indicator in food packaging.

1. Introduction

Recently, growing concerns about food safety and quality have driven the design and development of intelligent food packaging systems (Choi, Lee, Lacroix, & Han, 2017). Thus, in addition to traditional packaging functions that contain and protect food and carry labels, intelligent food packaging systems which can monitor food conditions and provide consumers with indicators of food quality have been newly developed (Pereira, de Arruda, & Stefani, 2015). Such systems can be used to decrease food loss and minimize unnecessary transport of spoiled food. Multiple types of intelligent packaging systems have been previously investigated, and these can be classified into two major categories: (i) data carriers such as radio frequency identification tags (RFID) and barcode labels; and (ii) indicators such as pH or gas indicators, time-temperature indicator, and biosensors (Kerry, O'Grady, & Hogan, 2006). These systems generally indicate food quality states according to changes in visual appearance (Zajko & Klimant, 2013). Indirect indicators such as time–temperature indicators were previously commonly used since they were easily produced. Numerous direct indicators of pH and gas have been recently developed to monitor the quality of food products and reportedly provide highly accurate and specific data regarding food quality (Choi et al., 2017; Pourjavaher, Almasi, Meshkini, Pirsa, & Parandi, 2017; Puligundla, Jung, & Ko, 2012; Suh, Meng, & Ko, 2016).

Gas indicators in packaging systems allow monitoring of gas concentrations as a proxy for food conditions and require correlations with food quality indices (Nopwinyuwong, Trevanich, & Suppakul, 2010). Various gases including carbon dioxide (CO_2), carbon monoxide (CO), sulfur dioxide (SO_2) can be produced from food products. Among them, CO_2 is generally produced by microbes in food and accumulates in headspaces of food packaging. Hence, headspace CO_2 contents can indicate food quality changes, particularly those in fermented foods. Pavai, Mihaly, and Paszternak (2015) and Rukchon, Nopwinyuwong, Trevanich, Jinkarn, and Suppakul (2014) developed CO_2 indicators using indicator dyes on films. Other CO_2 indicators have been devised using dyes and biopolymers such as chitosan, which change in size of chitosan nanoparticles to control the indicating performance of the indicator towards CO_2 exposure (Jung, Puligundla, & Ko, 2012; Suh et al., 2016). However, as well as the toxicity of synthetic dyes, the

* Corresponding author.
E-mail addresses: haunlzy@naver.com (I. Choi), jjhan@korea.ac.kr (J. Han).

https://doi.org/10.1016/j.foodhyd.2018.01.028
0268-005X/

migration of natural dyes from indicator to food products can be a problem such as the contamination of food color itself, although the natural dyes such as anthocyanin and curcumin are not harmful to human beings. Thus, the gas indicator composed of biopolymers without dyes is need to be developed to improve the food safety and quality.

Proteins and polysaccharides are commonly found in food stuffs, contributing to structure and stability due to their surface properties and thickening behaviors. Studies of protein–polysaccharide interactions have been implemented, which were widely applicable in studies of protein folding and separation (Joshi, Rawat, & Bohidar, 2018). The formation of complexes from protein–polysaccharide interactions predominantly reflects electrostatic forces between biopolymers. These interactions have also been widely characterized in studies of protein separation and developments of stimuli responsive systems and sensors (Kayitmazer, Seeman, Minsky, Dubin, & Xu, 2013).

Among proteins with potential indicator properties, sodium caseinate (NaCas) is a soluble form of milk casein and comprises four principle proteins (α_{s1}-, α_{s2}-, β-, and k-caseins). These proteins tend to associate with each other and form casein micelles (casein aggregates) depending on pH (Chu, Zhou, Wu, & Farrell, 1995). Moreover, many studies have been performed to prevent sedimentation of casein micelles in acidic milk drinks; the addition of polysaccharides into the system reportedly stabilizes pH-dependent phase changes. Among these, pectin is an anionic polysaccharide from plant cell walls which has negative charges owing to ionized carboxylic groups on its backbone structure of D-galacturonic acid units (Thakur, Singh, Handa, & Rao, 1997). Thus, pectin and its derivatives are commonly used as gelling, thickening, and stabilizing agents in food products. Several studies show that casein/pectin interactions improve the stability of capsules, gel networks, and acidified milk drinks (Chang et al., 2017; Matia-Merino, Lau, & Dickinson, 2004; Tholstrup Sejersen et al., 2007) and are used to facilitate film fabrication (Zhuang, Sterr, Kulozik, & Gebhardt, 2015). However, to our knowledge, no previous studies exploited casein–pectin interactions in food quality sensors.

Here the pH stability of NaCas suspensions was determined to assess their potential as an indicator material based on changes in transparency. NaCas–pectin complex solutions were also prepared to investigate the effect of pectin on the stability of NaCas suspensions with CO_2-mediated changes in pH. Finally, we developed an on–off type of CO_2 indicator that comprised NaCas and pectin and demonstrated its application as a food quality indicator in kimchi packages by correlating changes in food quality and indicator transparency.

2. Materials and methods

2.1. Materials

Sodium caseinate (NaCas) from bovine milk and pectin from citrus fruits were purchased from Sigma-Aldrich (St. Louis, MO, USA), and 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) were purchased from Daejung Chemicals & Metals Co. Ltd (Shiheung, Korea) and Yakuri Pure Chemicals Co. Ltd (Kyoto, Japan), respectively. Rhodamine B for fluorescence was obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Preparation of NaCas solutions

NaCas powder samples of 0.175, 0.25, 0.5, 0.75, and 1.0 g were added to 100 mL of distilled water and were stirred for 3 h until the NaCas solutions became transparent. After totally dissolved, the pH of the solutions was adjusted to 6.5 using 0.1 M HCl and 0.1 M NaOH. The NaCas solutions were maintained under magnetic stirring for 30 min until the pH was stable at 6.5.

2.3. Measurements of changes in transparency and pH of NaCas solutions

In brief, 3-mL aliquots of NaCas solutions were placed in 35-mm Petri dishes in an airtight container (135 mm × 135 mm × 75 mm) to adjust CO_2 concentrations. CO_2 was then injected into the airtight container until headspace CO_2 was approximately 95%. After exposing NaCas solutions to 95% CO_2 condition for 30 min, changes in transparency were measured using a UV–vis spectrophotometer (UV mini-1240, Shimadzu, Kyoto, Japan) at 650 nm. Finally, pH changes of the solutions were measured using a digital pH meter (Accumet AB15, Fisher Scientific, Pittsburgh, PA, USA).

2.4. Determinations of zeta potentials and stability

NaCas and pectin solutions were prepared by adding 0.75 g of respective powder samples to 100-mL aliquots of distilled water. The solutions were continuously stirred for 3 h to achieve complete dissolution, and pH values were then adjusted to 6.5 by adding 0.1 M HCl and 0.1 M NaOH solutions. Zeta potentials of NaCas and pectin solutions were then measured at different pH values (3.5, 4.0, 4.5, 5.0, 5.5, 6.0, and 6.5) after 10-fold dilution in distilled water using a Brookhaven instrument 90 plus (Holtsville, NY, USA). Subsequently, zeta potentials of various ratios of mixed NaCas and pectin solutions (%, v/v) were determined at pH 4.0 to investigate the effects of pectin on NaCas solution. All measurements were performed in triplicate at 20 °C.

In further experiments, aggregation of NaCas suspensions with varying pectin contents was determined to investigate stability of the solutions. NaCas and pectin solutions were blended at ratios of 9:1, 8:2, and 7:3, and pH values were adjusted from 6.5 to 3.5 using 0.1 M HCl and 0.1 M NaOH. Physical stability of the NaCas suspensions was visually assessed according to aggregation and sedimentation at each pH value.

2.5. Confocal laser scanning microscopy (CLSM)

Rhodamine B (0.01%, g/ml) was added to suspensions of NaCas and pectin to identify the casein protein before acidification. After adjusting the pH of the suspensions to 6.0 and 4.5 with stirring, single solution droplet was placed onto glass slides and was covered with glass coverslips. Then, it was examined using a Zeiss LSM 700 confocal microscope (Carl Zeiss MicroImaging GmbH, Jena, Germany) in fluorescence mode. Rhodamine B-labeled proteins were excited using laser at 555 nm, and images were captured through a 20 × objective.

2.6. Measurements of changes in transparency and pH in NaCas solutions with pectin

To investigate the effects of pectin on the indicator properties of NaCas solutions, changes in transparency and pH were analyzed after adding pectin. In brief, NaCas and pectin solutions were prepared by dissolving NaCas (0.175 g) and pectin (0.5 g) powder in distilled water (100 mL) and stirring for 3 h. The solutions were then blended together at ratios of 9.9:0.1, 9.875:0.125, 9.85:0.15, 9.825:0.175, 9.8:0.2, 9.775:0.225, and 9.75:0.25 for 1 h. Subsequently, pH values of mixed solutions were adjusted to 6.5, and the solutions were placed in airtight containers and were exposed to 95% CO_2 condition for 30 min. Transparency and pH values of each solution were investigated using the UV–vis spectrophotometer (UV mini-1240, Shimadzu) at 650 nm and the digital pH meter