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Development of chitosan-based edible biocomposite films incorporated with Kumquat peels extract as food packaging

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Edible films incorporate with various ratio of Kumquat peel extract were prepared by using solvent casting techniques. In order to determine the effect of Kumquat peel concentration, the biofilms have been characterized by physical properties such as moisture content, swelling degree, water solubility, water vapor permeability, color and transparency as their structures were confirmed by Scanning Electron Microscope (SEM). In addition, the mechanical properties have been determined with the tensile strength and elongation in terms of breakage of the prepared films.

It has been observed that the amount of moisture, swelling, and solubility of the films changed between 30.95–22.05%, 177.96–24.8% and 34.58–54.47%, respectively. It has been observed that the amount of moisture and the degree of swelling of the films decreased and the solubility values increased with the increase of Kumquat peel extract. The water vapor permeability, thickness and density range values of the films have been as follows: 1.039 g H_2O Pa^{-1} s^{-1} m^{-1} and 0.989 g H_2O Pa^{-1} s^{-1} m^{-1}, 0.0670 to 0.0554 mm, 0.86 g/cm^3 to 0.79 g/cm^3. It has been determined that the ratio of Kumquat bark extract does not cause a significant change on the water vapor permeability, thickness and density values of the films. With the increasing of the concentration of the Kumquat peel extract in the film structure and the films exhibit a more flexible property and the tensile strength at 33.28–13.5 MPa has been observed to vary between 7.74% and 20.57%. Results indicate that the chitosan-based films incorporated with Kumquat peel extract can be an alternative for food packaging.

Keywords: Chitosan, Kumquat, edible film, biopolymer, food packaging.

Introduction

Biological origin-based polymers which are using for edible films and coatings, are newly undergoing remarkable and prevalent researches[1,2], as a promising alternative for non-biodegradable synthetic products[3], allowing the minimization of waste removal issue. Currently, the edible or biodegradable films are made from natural polymers such as proteins, lipids and polysaccharides. On the other hand, polymer blending is one of the useful methods to obtain new materials with desired functional properties and there has been great scientific and commercial progress made in the area of food applications[4,5].

Packaging plays an important role in reducing food waste because it can improve food preservation and optimize space during handling, shipping, and storage[6]. Nowadays, the largest part of materials used in packaging industries are produced from fossil fuels and are practically un-degradable. For this, packaging materials for foodstuff, like any other short-term storage packaging material, represent a serious global environmental problem[7]. Therefore, innovative edible films derived from agro-food industry wastes and renewable low cost natural resources have been explored as replacement for conventional plastics. Currently, the edible or biodegradable films are made from natural polymers such as proteins, lipids and polysaccharides[8].

Chitosan is a linear polysaccharide consisting of (1,4)-linked-2-amino-deoxy-β-d-glucan; it is obtained through the deacetylation of chitin, which, after cellulose, is the second most abundant polysaccharide in nature[7]. This polysaccharide is widely utilized not only for its film-forming ability but also to its antimicrobial properties. Indeed, the antimicrobial properties of chitosan and its derivate (chitosan-oligo-sac-

charides) have been largely reported in the literature, thereby encouraging its use as potential packaging material[8].

Kumquat is an elliptical shaped fruit, closely related to Citrus[9]. Differently from most Citrus, Kumquat fruits are eaten whole, and they have a strong, sweet start, with a slightly bitter finish[10]. Health benefits of Citrus are well documented; aglycones of flavonoid C-glycosides in Kumquat, such as phloretin and acacetin, exhibit a broad spectrum of biological activities such as antioxidant activity, anti-inflammatory effect, and anticancer effect[11].

Although some studies dealing with chitosan and their composites have been performed, there is no previous report on the chitosan incorporated with Kumquat peal extract films as a packing materials. This work focused on the potential of being edible and biodegradable film that can be used as food packaging with chitosan biopolymer and peel extract of Kumquat fruit has been investigated.

Experimental

Chitosan with the degree of deacetylation of 75% was supplied by Sigma-Aldrich. All the chemicals in this study were of analytical grade. Kumquat, was purchased from a local market. After manual peeling, the separated peels were dried at 60°C for 2 days and were pulverized in a blender.

Chitosan solution (CH) (2% w/v) was prepared by dissolving into 5% (v/v) acetic acid aqueous solution and after chitosan was dissolved glycerol was added (0.4 g g/g biopolymer) while stirring at 800 rpm for 30 min. Powdered Kumquat peels were extracted with distilled hot water at 80°C for 3 h under 600 rpm then was cooled to room temperature and filtered. Film forming solution were obtained by mixing chitosan solution and Kumquat peel extract (KPE) at 100:0, 95:5, 90:10, 80:20, 60:40 Chitosan:Kumquat peel extracts weight ratio and coded as CH, CHKPE5, CHKPE10, CHKPE20, CHKPE40, respectively. The blends were homogenized with a stirrer at 800 rpm for 1 h. Edible films were produced by casting technique: film forming solutions were poured into 12×12 cm Petri dishes and dried at room temperature for 96 h prior the characterization.

Characterization:

Film thickness was measured using a digital micrometer (Fowler IP54) at five random spots of the film and the mean value was used for the determination of the physical and mechanical properties. The density of the film samples were calculated by using eq. (1).

$$\rho = \frac{m}{A \times \delta} \quad (1)$$

where A is the film area, δ the film thickness (cm), m is the dry mass of film (g) and s is the dry matter density of the film (g/cm^3)[14].

Moisture content (MC) was analyzed gravimetrically by drying equilibrated film sample (2 cm×2 cm) at 110°C to a constant weight[15].

To determine swelling degree (SD) and solubility (S), film pieces (2 cm×2 cm) were dried at 110°C to constant weight to obtain the initial dry mass (W_i). Then, they were immersed deionized water for 24 h. Next, the films were taken out from the water and the weight of films were determined (W_f) after removing the excess water on the films surface using a paper tissue. Swelling degree (SD) and solubility (S) of films were calculated by using following equations[16]:

$$SD = \frac{W_f - W_i}{W_i} \times 100 \quad (2)$$

$$S = \frac{\text{Initial dry weight} - \text{final dry weight}}{\text{Initial dry weight}} \times 100 \quad (3)$$

Water vapor permeability (WVP) tests were conducted according to ASTM method E96-00 (ASTM, 2004) with some modifications. Each film sample was sealed onto a circular permeation cell (permeation area: 7×10^{-2} m^2). To maintain a 75% relative humidity (RH), anhydrous silica (0% RHc) and a saturated NaCl solution (75% RHd) were used. All measurements were made at steady-state conditions. Changes in the weight of the cell were recorded and plotted as a function of time. The slope of each curve ($\Delta m/\Delta t$, g H_2O s^{-1}) was obtained by linear regression and the water vapor transmission rate (WVTR) was calculated from the slope divided by the permeation cell area. WVP was calculated by using eq. (4):

$$WVP = [WVTR/(PV_{H_2O}.(RHd - RHc))].d \quad (4)$$

where WVTR, water vapor transmission rate (g H_2O Pa^{-1} s^{-1}

m^{-1}), PV_{H_2O}: saturation water vapor pressure at test temperature (2339.27 Pa at 20°C), RHd-RHc, relative humidity gradient across the, A, permeation area (m^2) and d, film thickness (m). Each WVP value represents the mean value of three samples taken from different films[17].

The film color was determined using a Miltona colorimeter (CR-300, Japan). The white tile was used as standard during the color measurement. Lightness (L*) and chromaticity parameters a* (red-green) and b* (yellow-blue) were used to characterize the film color in the Hunter Lab scale (CIE Lab scale)[18].

The opacity of the MP films was determined according to a Hunterlab method, with the same equipment used for the color measures, also operating in the reflectance mode. The opacity (Y) of the samples was calculated as the relationship among the opacity of each sample on the black standard (Yb) and the opacity of each sample on the white standard (Yw)[19].

$$\text{Opacity\%} = \frac{\text{Y black packing}}{\text{Y white packing}} \times 100 \quad (5)$$

Zwick Roell (Germany) Universal Testing Instrument was used to measure tensile strength (TS) and percentage elongation at break (%EB) of films. Film sample cut into 1.0×5 cm strips before measurement and the thickness of the film samples was determined using a micrometer at random position. The tensile strength (TS) and elongation at break (%EB) were determined using initial grips separation of 25 mm, load cell 2 kN and cross-head speed of 5 mm/min with the testXpert software. Three sample of each film were evaluated.

The surface morphologies of the film samples were examined using scanning electron microscopy (Zeiss EVO® LS 10) and analyzed using an accelerating voltage of 10 kV. Prior to the analysis, the film samples were coated with gold under a vacuum.

Results and discussion

Table 1 shows the basic film properties, including film density, thickness, moisture content, solubility, swelling degree, and water vapor permeability.

The thickness of Chitosan:Kumquat peel extract (CH:KPE) based films ranged between 0.0554 and 0.0670 mm while density range between 0.79 and 0.86 g/cm^3. The films thickness is an important characteristic in determining the feasibility of edible films as packaging materials for food products since the thickness of the films affects other characteristics of the films, such as tensile strength, elongation, and water vapor permeability. Incorporating Kumquat peel extract and concentration of KPE did not affect significantly on the film thickness and density and in this study, film thickness and density was controlled in a strait range.

Packaging films should maintain moisture levels within the packaged product. Therefore, the knowledge of moisture content of the films have to be determined for food packaging applications[20].

The MC values of the CH and CH:KPE composite films ranged between 30.95 and 22.05%. The MC values decreased significantly with the increasing KPE concentration. This could be explained by that chitosan is hydrophilic due to stronger interactions between water molecules and its functional groups (-OH, $-NH_2$) by hydrogen bonds[21]. Swelling degree and solubility are both leading property of the edible films, affecting resistance of film to water and storage quality of food[22].

The swelling degree of the films were significantly decreased with incorporating KPE and increasing KPE con-

Table 1. Density, thicknesses, moisture contents (MC), water solubility (S), swelling degree (SD) and water vapor permeability of CH and KPE incorporated CH films

CH:KPE ratio	Density (g/cm^3)	Thickness (mm)	MC%	S%	SD%	WVPx10^{11} (g H_2O Pa^{-1} s^{-1} m^{-1})
CH	0.86±0.13	0.0670±0.001	30.95±0.88	34.58±0.15	177.96±2.55	0.997±0.286
CHKPE5	0.79±0.02	0.0554±0.004	28.43±0.64	42.06±0.60	43.57±1.46	1.099±0.738
CHKPE10	0.86±0.07	0.0612±0.003	27.18±0.59	43.55±0.97	34.9±2.08	1.124±0.397
CHKPE20	0.78±0.06	0.0632±0.004	26.39±0.34	50.25±0.77	25.31±2.94	0.951±0.200
CHKPE40	0.79±0.039	0.0554±0.002	22.05±0.95	54.47±0.94	24.28±7.31	0.951±0.151

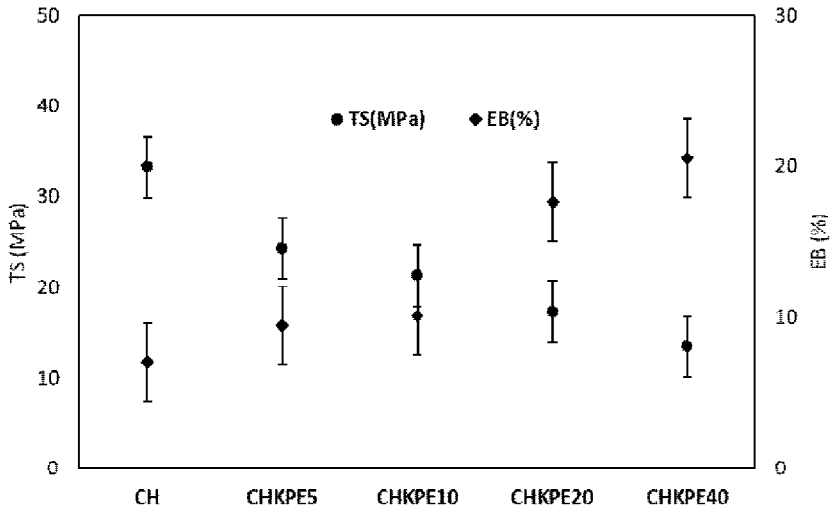


Fig. 1. Tensile strength (TS) and elongation at break (EB)% of CH and KPE incorporated CH films.

centration within the films. The highest SD of pure CH film was around 177.96% which is similar to literature[23]. Although chitosan has hydrophilic groups, such as carboxylic groups, these groups could easily interact with water, resulting in swelling of the films, upon being enriched with the extract intermolecular interaction between chitosan and the extract developed and this resulted in a decrease in the film swelling. In addition, a lower level of swelling could be attributed to the hydrophobic properties of the extract[24].

The solubility values of the CH and CH:KPE films ranged between 34.58 and 54.47% which were very closed to reported by Rodriquez-Nunez *et al.*[25]. The lowest S values of pure chitosan films was observed 34.58%. The results showed that incorporating KPE and increasing KPE concentration into the chitosan films, significantly increased in water solubility. The reduction of the solubility was not observed indicating that the interaction between chitosan and the extracts was not hydrophobic. A similar phenomenon was also observed by Souza *et al.*[26] for chitosan films incorporated with natural antioxidants.

WVP controls the transfer of water from the food to its environment and to keep foods fresh, the WVP value should be maintained as low as possible. As shown in Table 1, incorporating KPE did not significantly influence the WVP values of pure chitosan film which remain around 10^{11} g H_2O Pa^{-1} s^{-1} m^{-1}. This results could be associated with the density of the CH:KPE films.

The values of L, a, b and opacity are shown in Table 2. It is clear that all the parameters were observed to be affected by KPE. After the addition of KPE, the opacity and a* values were significantly increased, while the L value decreased, indicating a tendency towards redness and darkness. This may help to protect the packaged foods from visible and ultraviolet light that lead to nutrient losses, discoloration and off-flavour[27].

Table 2. Color parameters including L, a, b and opacity of CH and KPE incorporated CH films

CH:KPE ratio	L	a	b	Opacity %
CH	93.2±0.33	0.31±0.16	5.45±0.42	10.45±0.49
CHKPE5	90.5±1.25	1.08±0.23	16.3±1.72	13.22±0.40
CHKPE10	86.84±0.97	1.25±0.25	31.52±0.35	16.45±0.28
CHKPE20	84.62±0.90	3.26±1.32	44.67±2.36	20.39±0.76
CHKPE40	81.8±0.95	6.46±0.40	53.88±0.81	26.14±1.37

Tensile strength is the ability of a material to resist under tensile stress until it breaks and is one of the most important and widely measured properties of materials used in structural applications. Elongation-at-break of a material is the percentage increase in length that occurs before it breaks under tension. As shown in Fig. 1, TS values decreased while EB values increased with the increasing KPE concentration within the CH film. The results indicate that CH:KPE film more flexible compare to pure CH films. These behaviors suggest

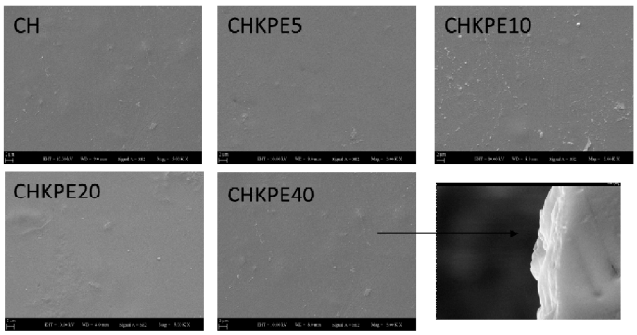


Fig. 2. SEM images of CH and KPE incorporated CH films.

that pectin content of KPE, acted as a plasticizer for CH:KPE films due to the its low molecular weight[28].

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The SEM images of CH, CH-KPE and cross-section of CHKPE40 films are depicted in Fig. 2. All films showed compact and homogeneous surface without pores and cracks and this indicated that KPE was dispersed in composite film structure.

Conclusions

In this study, chitosan-based edible biocomposite films incorporating KPE as food packaging materials were successfully fabricated. The effect of KPE on the physical and mechanical properties of CH based films were revealed. Among physical properties, moisture content, solubility and swelling degree of CH based films were significantly improved by KPE incorporation. The improved mechanical properties were associated with the intermolecular interactions between CS chains and KPE molecules. SEM images displayed that the films have homogeneous surface without pores and cracks. In future, the applications of CH-KPE films as active packaging materials in food industry can be conducted.

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