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Effect of Plasticizer Concentration on the Properties of Hydroxypropyl Cellulose (HPC) Film Enhanced with Sodium Dehydroacetate

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In the development of edible films based on hydroxypropyl cellulose (HPC) with sodium dehydroacetate (SD) as an antifungal agent, the effect of various concentrations (20, 30, and 40% based on HPC) of plasticizers (glycerol and sucrose) on the film properties was investigated. The HPC–based film with glycerol showed transparency, while the film with sucrose showed turbid and opaque ($P < 0.05$). The HPC film without plasticizers used as a control had high rigidity and was brittle. This property was improved when glycerol was added to the film ($P < 0.05$). The HPC–glycerol film had low water vapor barrier properties due to its high moisture content, especially when used at high concentrations. The incorporation of sucrose in HPC film had no marked impact on moisture content, water vapor permeability, and mechanical properties compared to control. The rough and heterogeneous morphology of the films was dominant in the film contained sucrose. FTIR spectra showed that the peaks of the glycerol mixed films were shifted to lower wavelengths compared to the control and sucrose mixed films. This is due to the increase of –OH group in the film matrix of HPC film. These results suggest that glycerol is a more promising plasticizer than sucrose to plasticize in the matrix of HPC films. In particular, HPC films containing 20% (w/w of HPC content) glycerol possessed satisfactory film properties and could be formulated as edible films and coatings.

Key words: hydroxypropyl cellulose, glycerol, sucrose, film

INTRODUCTION

Nowadays, the world is faced with environmental issues such as waste management and climate change. One of the causes of these problems is related to the plastics industry and the resistant degradation itself. This led to a search for alternative materials, such as biopolymers to develop as a biomaterial. The goals of "Plastics 2030 Voluntary Commitment" are reduction, recycling, and/or reuse of plastic up to 60% in 2030, and 100% in 2040 (Szabo *et al*., 2020).

The deployment of biopolymer–based edible films and coatings is gaining attention around the world due to their many advantages, such as environmental friendliness, customer acceptance, and excellent functional properties (Umaraw *et al*., 2020). With the increasing use of biopolymers, its global market is expected to grow at around 17% during the forecast period of 2017–2021 and is expected to reach around USD 10 billion by 2021 (Mellinas *et al*., 2020). These biomaterials can be produced from various sources, mainly polysaccharides (e.g., chitosan, cellulose, and cellulose derivatives) (Kan *et al*., 2019), proteins (e.g., whey, collagen, gelatin) (Xiong *et al*., 2020; Pellá *et al*., 2020) and lipids (e.g., wax) (Baswal *et al*., 2020).

Among them, hydroxypropyl methyl cellulose (HPMC) and hydroxypropyl cellulose (HPC) have been extensively studied and applied in many fields such as food (Additives *et al*., 2018), pharmacy (Takeuchi *et al*., 2018), and medicine (Alharbi & Guirguis, 2019), owing to the unique properties such as excellent biocompatibility, plasticity, mechanical properties, edibility, and stability. The addition of antifungal agents can also inhibit microbial growth and extend shelf life of food products. Our previous study the sodium dehydroacetate (SD) showed the best antifungal effect on *Botrytis cinerea* (Kingwascharapong *et al*., 2022). Therefore, in this study, SD, which is classified as generally recognized as safe (GRAS) for use as a food additive by the US FDA, was added to HPC–based films as an antifungal agent. Since HPC is less expensive than HPMC, it is expected to be used more widely in some modifications in place of HPMC. HPC is derived from the substitution of hydroxyl groups of cellulose backbone with propylene oxide by an etherification process (Alharbi & Guirguis, 2019). Although HPC has unique properties, their applications can be broadened by improving some of their properties. In terms of improving the mechanical properties of biomaterials, plasticizers have been implemented. Compatibility and durability are the main factors for considering the proper plasticizers to achieve favorite functional properties in edible films of biopolymers (Razavi *et al*., 2015). Commonly used plasticizers are polyols, mono–, di– and oligosaccharides, which are recognized as the great plasticizing effect on edible films of hydro-

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colloids (Saberi *et al*., 2017).

To our knowledge, there are no existing scientific reports on studying the effect of plasticizer on the properties of HPC–based films with SD. Remarkably, the molecular weight size and the number of OH–groups of the plasticizers influenced the film properties. Therefore, the aim of this study was to investigate the effect of the use of these plasticizers on the visual, microstructural, physical, and mechanical properties of plasticized HPC films. This research will allow us to control various properties of HPC–based coatings and films by adding plasticizers and we will be able to obtain coatings and films suitable for food, pharmacy, medicine and many other applications.

MATERIALS AND METHODS

Materials

HPC with different molecular weights: HPC–SL (MW: 100000), HPC–L (MW: 140000), and HPC–LM (MW: 180000) were provided by Nippon Soda. HPMC was purchased from Thermo Fisher Scientific Company. SD, an antifungal agent, was purchased from Wako Pure Chemical Industry, Ltd. (Japan). Glycerol (MW = 92 g/mol) and sucrose (342 g/mol) used as plasticizers were purchased from Pure Chemical Industry, Ltd. (Japan).

Methods

Viscosity of HPC solutions

The viscosity of HPC solutions was measured using a viscometer (DV2TLVT; Tokisangyo, Tokyo) equipped with a cylinder spindle LV–1 (61) (diameter = 18.90 mm). Each HPC type with different concentrations from 1% to 5% (w/v) was tested. HPMC of 2.5% (w/v) was used as a reference solution because it was known as proper coating material. Since viscosity is one of the most important factors in selecting a base–material, HPC solution with viscosities close to the reference were selected to prepare the filmogenic solution. Viscosity measurements were carried out at a speed of 30 rpm. All measurements were performed at 18–20°C and in four replicates. The results were expressed in centipoise (cP).

pH of HPC solutions

The pH of HPC solutions at different concentrations was tested using a pH meter (LAQUAtwin–pH–22, HORIBA, Ltd., Japan).

Film preparations

Glycerol and sucrose with varying concentrations of 20%, 30% and 40% (w/w) based on HPC concentration were prepared and 0.1% of SD as an antimicrobial agent was added to those solutions. Distilled water was added, and the suspension was stirred at a speed of 500 rpm at 18–20°C for 15 min until it was completely dissolved. The resulting solution was mixed at the selected HPC concentration with gentle pouring for 2 h under the constant magnetic stirring conditions, and the solution was conditioned under vacuum environment using a vacuum chamber (ADP 300, Yamato scientific Co. Ltd., Japan) for 20 min to remove bubbles from the solution. The pH and viscosity of the resulting film–forming solution were analyzed as shown above.

To obtain the films, 5 mL of the film mixture was cast onto a silicone plate (5 × 5 cm^2) and allowed to dry for 24 h at 18–20°C. The dried films were manually peeled off and stored in a desiccator containing a saturated solution of Mg $(NO_3)_2$ (RH. 53 ± 1%) for at least 24 h prior to film characterization (Basiak *et al*., 2018).

Thickness of films

The thickness of films was measured using a digital micrometer. Five locations on three films were measured randomly. Those average value was used as the film thickness.

Color of films

The color of the films was measured according to the method of Kingwascharapong *et al*. (2020) with some modifications. The film samples were cut into rectangular (2 cm × 2 cm) and placed on the surface of a standard white plate of colorimeter. The measurements were performed using a portable colorimeter (CR–20, Konica Minolta Japan Co., Ltd., Japan). Color was expressed in terms of a^* (negative–green; positive–red), b^*(negative–blue; positive–yellow) and L^* (0 = black; 100 = white). The white standard was L^*=94.8, a^*= –0.2, and b^*=4. Color difference (ΔE^*) was calculated using the follow equation:

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

$$whiteness = \sqrt{100 - [(100 - L^*)]^2 + a^{*2} + b^{*2}} \quad (2)$$

where $\Delta L^* = L^* - L_0^*$; $\Delta a^* = a^* - a_0^*$ and $\Delta b^* = b^* - b_0^*$, L_0^*, a_0^* and b_0^* are the values of color of standards, and L^*, a^* and b^* are the film color values (Sun *et al*., 2020).

Light transmission and transparency value of films

After the color measurement was completed, the film was used to measure the light transmission in the visible range (300–800 nm) using a spectrophotometer (V–530, JASCO, Japan) according to the method of Shiku *et al*. (2004). The transparency value of the film was calculated using the following equation:

$$Transparency\ value = \frac{-logT_{600}}{x} \quad (3)$$

where T_{600} is the fractional transmission at 600 nm and is the film thickness (mm). The greater transparency value represents the lower transparency of film.

Moisture content of films

Moisture content was measured according to the standard method D644–99 (ASTM, 1999). The film was cut into rectangular piece (2 cm × 2 cm), and weighed (W_0); after dehydrated in an air circulation oven (EO–300V, AS ONE, Japan) at 105°C for 24 h, the dry samples were weighted (W_1) and the moisture content was calculated as follows:

$$Moisture\ content = \frac{W_0 - W_1}{W_0} \times 100 \quad (4)$$

Mechanical properties of films

The tensile strength, elongation at break and elastic modulus of the films were measured using a motorized force test stands machine (FGS–5E–L, SHIMPO, Japan). The method was based on Abera *et al*. (2020) with slight modification. The films were cut into 1 cm × 5 cm using a cutter. Before testing, the thickness of the film strip was randomly measured using a digital micrometer (Mitutoyo, Japan). The film strip was fixed to the testing machine and the test area was initially set to 3 cm. The elongation speed was set at 10 mm/min. The tensile strength and elongation at break of the film strips were measured five times and the average values were calculated.

ATR FT–TR analysis of films

FTIR analyzes were performed using a spectrometer (FT/IR–620, JASCO, Japan) equipped with an attenuated total reflectance module (ATR, ZnSe crystal, JASCO, Japan). The spectra were recorded as an average of 64 scans in the range of 4000–600 cm^{-1} with a resolution of 4 cm^{-1} (Estevez–Areco *et al*., 2020).

Water vapor permeability (WVP) of films

Water vapor permeability was determined by a gravimetric method in accordance with the JIS Z0208 standard method known as the "cup method". The film was prepared and mounted in a cup with a test area of 3 cm^2. The cup was filled with dried silica gel (0% RH) and placed in an environmental chamber at 25 ± 2°C and 50 ± 5% RH. The weight gain of the cup was plotted against time to determine the water vapor transport. The water vapor transmission rate (WVTR) was calculated from by dividing the slope (g/s) by the transmission area (m^2). The weight of permeation cup was examined at one–hour intervals over a period of 10 h. WVP ($g{\cdot}m^{-1}\ s^{-1}\ Pa^{-1}$) was calculated according to the following Eq. 5:

$$WVP = \frac{WVTR}{\Delta P} L \quad (5)$$

where ΔP is the difference in partial water vapor pressure between two sides of the film specimens (1583.7 Pa at 25°C), and L is the film thickness (m).

Scanning electron microscopy (SEM) of films

The surface and cross–section morphology of the film samples were analyzed using a low vacuum high sensitivity scanning electron microscope (SEM) (SU 3500, Hitachi High Technologies Corporations, Japan). The surface and cross section of films were attached to an aluminum specimen using double–sided conductive adhesive tape (Ted Pella Inc., Redding, CA, USA) and coated with osmium on an ion sputter coated (Denton Vacuum Inc., Moorestown, NJ, USA) for 3 s at 20 mA to make the sample conductive. Photographs were taken at an acceleration voltage of 15 kV. Magnifications of 500× and 3,000× were used to observe the cross section and surface of films, respectively (de Moura *et al*., 2009).

Statistical analysis

The experimental data were expressed as mean ± SD. The mean comparisons were then analyzed through analysis of variance (ANOVA) at a significance level of P–value < 0.05 according to the Tukey–Kramer's multiple range test.

RESULTS AND DISCUSSION

pH of HPC solutions

The pH of HPC solution is shown in Fig. 1A. The pH of all concentrations of HPC is significantly different (P < 0.05). The pH of HPC at all concentrations is a slightly acidic in the range of 5–6. This pH is the natural pH of HPCs reported in the range of 5–8 (Additives *et al*., 2018). Different types of HPCs have different molar substitutions with the hydroxypropyl group of the glucose ring unit of the cellulose backbone, so the pH of their solutions is different. The concentrations of HPC, regardless of the types of HPC, affected the difference in pH by increasing the number of moles.

Viscosity of HPC solutions

The viscosity of a solution is an important parameter that affects the thickness of edible films and coatings. The viscosity of HPC solutions is shown in Fig. 1B. The viscosity of the tested HPC solutions ranged from 4–130 cP. The increasing trends of viscosity was found at the higher concentration used, regardless of types of HPC. The viscosity of HPC–LM at the same concentration is higher than the others. It might be related to the molecular weight of HPC. According to the previous reports, the satisfied viscosity of edible films and coatings applying in the post–harvest field is in the range of 5–150 cP. Cisneros–Zevallos & Krochta (2003) studied the viscosity of two different HPMCs (Mw: 30,000 and 90,000 g/mol) at concentrations ranging from 1 to 4 g /100 g (w/w) and showed viscosity values ranging from 2.3 to 162.6 cP. In the case of the use of high viscosity solutions to make films, gas permeability is completely inhibited, which may adversely affect the crop. As described above, the thickness of the film is related to the viscosity of the solution. To make a film from a highly viscous solution, the concentration needs to be adjusted to a lower level. However, this concentration adjustment affects the solids content in the solution, leading it difficult to prepare the film, and because the solution contains a lot of liquid, evaporation takes a long time, making it impossible to use high–viscosity solutions for coating and film of fruits. Conversely, low–viscosity solutions cannot form a film due to their low solid content and require more concentration to form a film. According to the results, 4% HPC–LM showed an appropriate concentration within the recommended range and the viscosity value was close to reference solution (2.5% HPMC).

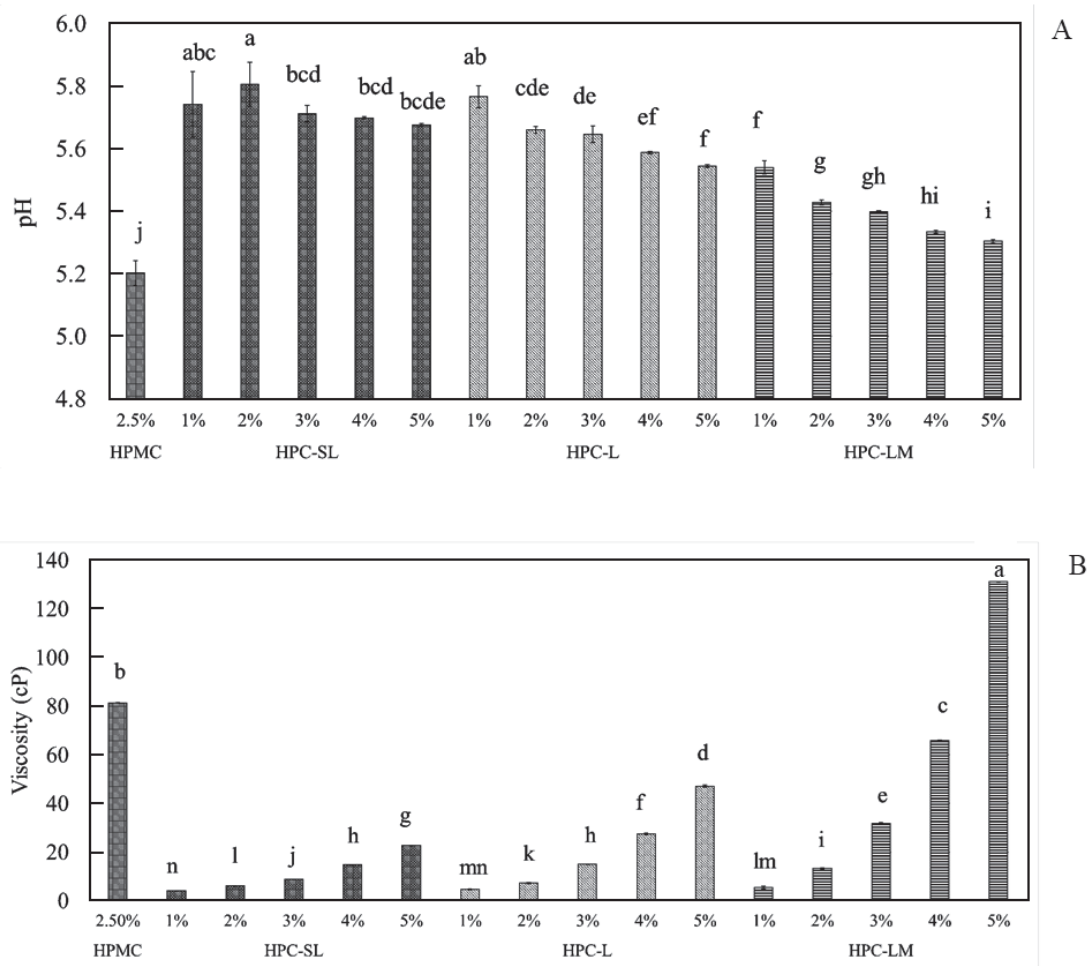

Fig. 1. The pH (A) and viscosity (B) of HPC solutions of different types and concentrations. The different letters on the bars show the significant difference at the 95% confidence intervals.

Film thickness

Film thickness is one of the important film properties because it typically affects other film properties such as mechanical properties, water vapor permeability, as well as optical properties (light transmission and transparency) (Pattarasiriroj *et al.*, 2020). The thickness of HPC films incorporating plasticizers was higher than that of control film, regardless of the type and content of plasticizer ($P < 0.05$) (Table 1). Since glycerol and sucrose are hydrophilic plasticizers, the films absorbed more moisture. Hence, these films swelled to a greater extent, resulting in an increase in the thickness of the films. The thickness of all the films tested ranged from 0.11–0.15 mm. There was no significant change in the thickness of HPC films added with different concentrations of sucrose. These results were correlated with

Table 1. Thickness, moisture contents, tensile strength (MPa), elongation at break (%), and WVP of HPC film incorporated with different types and concentrations of plasticizers

Films	Thickness (mm)	Moisture content (%)	Tensile strength (MPa)	Elongation at break (%) (EAB)	WVP x 10^{-11} $gm^{-1}s^{-1}Pa^{-1}$
Control	0.11 ± 0.01 c	7.42 ± 1.39 c	37.69 ± 5.74 a	1.72 ± 0.68 cd	0.49 ± 0.06 d
HPC–20% sucrose	0.14 ± 0.01 ab	7.13 ± 0.73 c	4.02 ± 1.39 cd	1.34 ± 0.59 d	0.47 ± 0.04 d
HPC–30% sucrose	0.14 ± 0.01 ab	5.83 ± 1.45 c	7.15 ± 2.55 c	1.01 ± 0.59 d	0.36 ± 0.03 d
HPC–40% sucrose	0.13 ± 0.01 bc	5.92 ± 0.19 c	18.41 ± 2.95 b	1.09 ± 0.85 d	0.32 ± 0.04 d
HPC–20% glycerol	0.13 ± 0.01 bc	17.22 ± 0.45 b	5.57 ± 0.65 d	6.33 ± 1.73 a	1.26 ± 0.05 c
HPC–30% glycerol	0.14 ± 0.01 ab	23.53 ± 1.52 a	2.30 ± 0.43 d	4.00 ± 1.22 bc	1.86 ± 0.04 b
HPC–40% glycerol	0.15 ± 0.01 a	24.44 ± 2.34 a	1.60 ± 0.34 d	2.90 ± 1.34 c	2.51 ± 0.08 a

Different lowercase letters in the same column indicate the significant difference ($P < 0.05$)

the moisture content results. The result could be postulated that sucrose was composed of bulky ring structures (α–d–glucose and β–d–fructose), and the structure might be difficultly an interaction between sugar ring and starch polymer (Ploypetchara & Gohtani, 2020). It is noteworthy that the addition of different concentrations of glycerol to HPC films significantly affected the thickness of HPC films ($P < 0.05$). The result was in agreement with Thakhiew *et al.* (2010), who found that the thickness of edible chitosan films plasticized with glycerol increased in relation to glycerol. The thickness of gelatin–based films was also dependent on the amount of glycerol added (Vanin *et al.*, 2005). Thus, the addition of glycerol to HPC films could enhance the barrier properties of water absorption.

Optical properties of films

The properties of the films are shown in Fig. 2. The HPC films without glycerol used as a control and with glycerol at any concentrations were transparent and had smooth surfaces without any pores or cracks. As for films containing sucrose, the film became more turbid, brittle, opaque, less elastic, and had a rougher surface. This occurrence could be due to alteration of refractive index across the films and extensive interaction between glycerol and HPC. The white and turbid characteristics of the HPC–sucrose film is probably due to the crystallization of sucrose. During drying of the film on the mold, the evaporation of water might increase the concentration of sucrose in the film, leading to spontaneous nucleation, and possible crystal formation due to rearrangement of randomly bound sugar molecules (Veiga–Santos *et al.*, 2007). Due to the brittle structure of sucrose con-

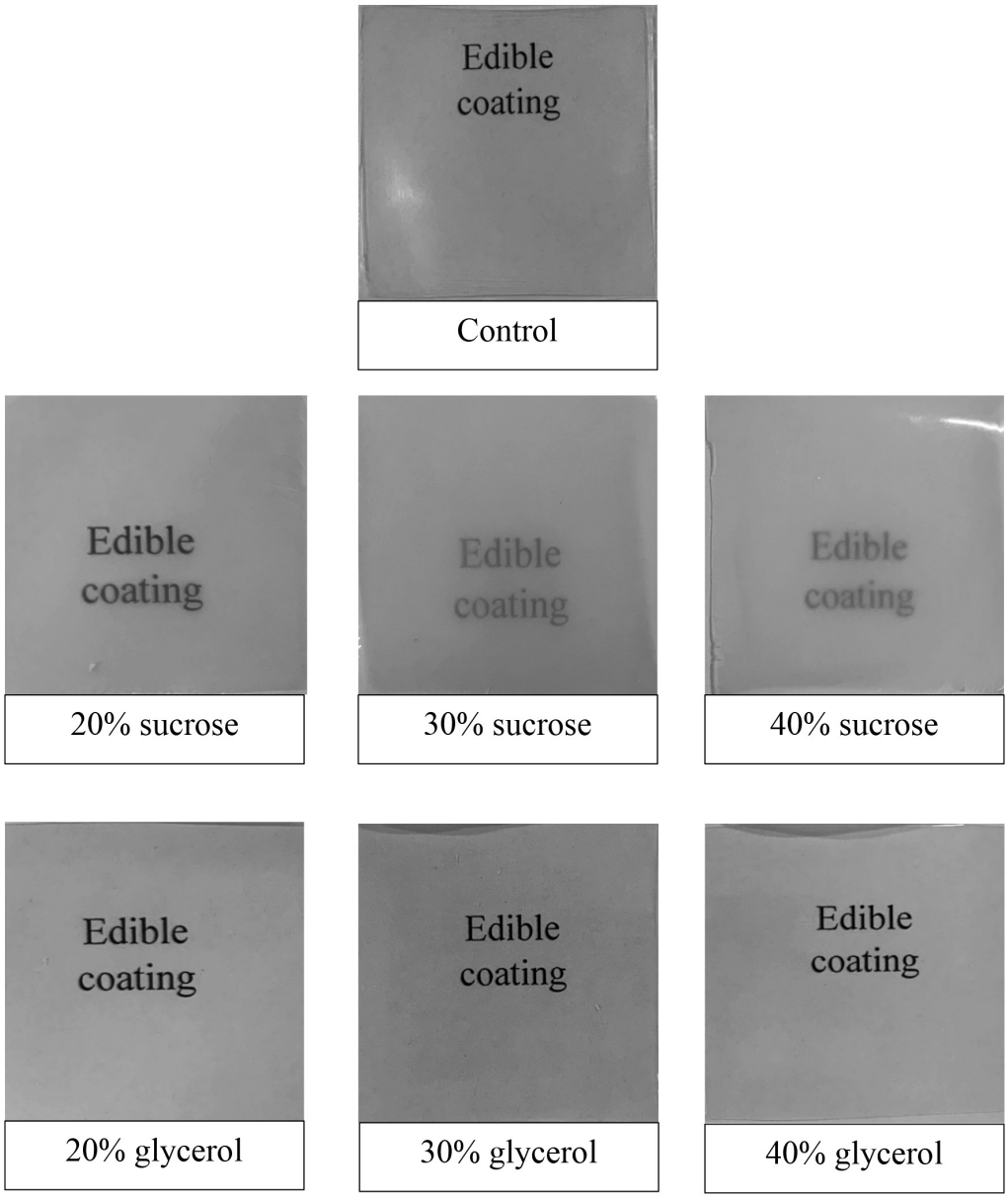

Fig. 2. The optical properties of HPC film contained different types of plasticizers (sucrose and glycerol) at different concentrations (20%, 30%, and 40% w/w of HPC).

taining HPC films, it is not recommend to use this formulation for edible film and coating applications if the surface color of the fruit itself is important. However, opacity may be useful when light may degrade the quality of products. The opacity of HCP–based film can be controlled by selecting the type of plasticizer.

Color of films

The appearance of the film, particularly color, is a very crucial parameter as it relates to the consumer's preference. The color parameters of HPC films with plasticizers are shown in Table 2. The L^* and b^* values of HPC films incorporated with sucrose were higher than those of glycerol added and control films at all concentration. These results correlated with the whiteness values, which were higher for HPC film containing sucrose regardless of concentration. HPC films mixed with sucrose had a whitish and opaque appearance, especially when used at high concentrations, while films mixed with glycerol were brighter and more transparent (Figure 2). It might be due to the crystallization of sucrose, which refracts light from the film, as a result, the film appears whiter and has a larger L^* value. Sucrose molecules can form crystals and affect the film–forming matrix (Nindjin *et al*., 2015; Zhang *et al*., 2019). Crystallinity, fractal and morphological structures have been described as the main factors affecting the change in whiteness of the films. When glycerol was formulated in HPC films at different concentrations, the L^* and b^* values were found to decrease and a^* increased compared to others. The whiteness of the HPC film formulated with glycerol was lower than that of the control. It might be due to the localization of glycerol in the film matrix and the retention of water within the HPC structure, which resulted in a lower light scattering effect.

Light transmission and Transparency of films

The light transmittance and transparency of HPC film with plasticizer in the visible range of 300–800 nm are shown in Table 3. The film with plasticizer can protect the light transmission of the HPC film at all wavelengths as can be indicated by the lowering transmission values compared to control, regardless of types and concentration of plasticizer. These barriers became more pronounced as the concentration of plasticizer increased. The plasticizer dispersed throughout the film might obstruct the light transmit through the film. Differences in the molecular weight, composition, size, nature, and some properties of the plasticizers affected the light transmission (Saberi *et al*., 2017). HPC films formulated with sucrose are more likely to protect visible light from penetrating the film than those formulated with glycerol. This was associated with the opaqueness of HPC films containing sucrose.

For the transparency value, the lower transparency value, the higher the transparency of the film (Nilsuwan

Table 2. Color (L^*, a^* and b^*), ΔE, and whiteness of HPC film incorporated with different types and concentrations of plasticizers

Films	L^*	a^*	b^*	ΔE	Whiteness
Control	93.23 ± 0.11 b	–0.20 ± 0.00 a	4.03 ± 0.13 bc	1.58 ± 0.10 de	92.12 ± 0.16 ab
HPC–20% sucrose	93.25 ± 0.17 b	–0.53 ± 0.04 d	4.70 ± 0.14 a	1.74 ± 0.18 cd	91.76 ± 0.19 bc
HPC–30% sucrose	93.65 ± 0.21 ab	–0.50 ± 0.00 d	4.20 ± 0.07 bc	1.21 ± 0.21 ef	92.37 ± 0.21 a
HPC–40% sucrose	93.78 ± 0.13 a	–0.40 ± 0.00 c	4.25 ± 0.05 b	1.08 ± 0.12 f	92.24 ± 0.11 a
HPC–20% glycerol	92.65 ± 0.21 c	–0.20 ± 0.00 a	4.15 ± 0.05 bc	2.16 ± 0.21 bc	91.56 ± 0.20 cd
HPC–30% glycerol	92.35 ± 0.17 cd	–0.25 ± 0.05 ab	4.13 ± 0.04 bc	2.45 ± 0.17 ab	91.30 ± 0.14 de
HPC–40% glycerol	91.95 ± 0.17 d	–0.33 ± 0.04 bc	4.00 ± 0.07 c	2.85 ± 0.17 a	91.00 ± 0.14 e

Different lowercase letters in the same column indicate the significant difference ($P < 0.05$)

Table 3. Light transmittance and transparency value of HPC film incorporated with different types and concentrations of plasticizers

Film	Light transmission (%) at different wavenumbers (nm)						Transparency value
	300	400	500	600	700	800	
Control	0.55	82.26	89.45	89.95	90.04	90.49	0.40 ± 0.00 e
HPC–20% sucrose	0.31	28.65	49.99	56.21	61.55	65.60	1.85 ± 0.01 c
HPC–30% sucrose	0.22	16.83	40.00	47.72	55.21	61.09	2.38 ± 0.07 b
HPC–40% sucrose	0.19	12.44	36.26	41.725	36.095	56.81	2.62 ± 0.03 a
HPC–20% glycerol	83.75	83.39	85.38	86.58	87.93	88.48	0.46 ± 0.01 e
HPC–30% glycerol	74.60	78.67	83.07	85.14	87.26	88.36	0.56 ± 0.00 d
HPC–40% glycerol	74.82	79.205	80.86	84.58	87.14	88.63	0.58 ± 0.01 d

Different lowercase letters in the same column indicate the significant difference ($P < 0.05$)

et al., 2016). In general, the HPC films showed high transparency (Figure 2). Among all the films tested, the HPC mixed with glycerol showed higher transparency values. This could be attributed to the fact that glycerol, being a small molecule, dispersed well in the HPC structure through hydrogen bonds, increasing the swelling structure and compromising the compactness of the film. Thus, it was found that the light transmittance and transparency of the films varied with the addition of different types and levels of plasticizers to the HPC films. Since the addition of sucrose to the HPC film resulted in water loss, causing cracking and brittleness of the film surface, transparency decreased with increasing the concentration of sucrose. It had the potential to prevent light–induced quality degradation of coated or packaged products.

Mechanical properties of films

The mechanical properties of HPC films blended with different types and concentrations of plasticizers, expressed in terms of tensile strength (TS) and elongation at break (EAB), are shown in Table 1. The highest TS was observed for the control sample (HPC only). It might be due to the molecule's interaction of the HPC; the addition of glycerol to the HPC film generally decreased the tensile strength in correlation with the concentration used. The decrease in tensile strength of polysaccharides–based films with increasing plasticizer concentration could be explained by the role of the plasticizers in interrupting the intramolecular cross–linking between polysaccharide chain structures and inducing the formation of hydrogen bonds between plasticizer and polysaccharide chains (Sanyang *et al*., 2015). Contrary to the case of sucrose addition, the tensile strength is likely to increase with increasing concentration. This might be due to the inability of the structure and size of sucrose to localize in the film matrix, resulting in aggregation of the polymer chains. The mechanical properties of polymer films depend on the configuration, molecular size, and total number of functional hydroxyl groups of the plasticizer along with its compatibility with the polymer (Saberi *et al*., 2017). Nindjin *et al*. (2015) reported that sucrose (ring chain) was more difficult to distribute uniformly in the polymeric chains compared to straight chains of other plasticizers (glycerol and sorbitol).

The film elongation of the sucrose added film (EAB) was not significantly different at all concentrations. However, the elongation of HPC films with glycerol significantly decreased with increasing concentration. This result was in agreement with Sanyang *et al*. (2015) who reported that the elongation of sugar palm starch significantly decreased from 61.63% to 28.39% and 46% to 34.27% when glycerol increased from 30% to 45%, respectively. This might be due to the anti–plasticization behavior or phase separation of the highly plasticized starch films.

ATR–FTIR analysis of films

The FTIR spectra of HPC film with plasticizer are shown in Fig. 3. The FTIR spectra of the control film showed peaks at 3413, 2876, 1374 and 1048 cm^{-1}. In general, the HPC spectra had dominant peaks at 3334 cm^{-1} and 1058 cm^{-1} assigned to –OH stretching, 2960 cm^{-1} assigned to $–CH_2–O–CH_2$ stretching, and 2870 cm^{-1}, assigned to $–CH_2–O–CH_2$ stretching, respectively (Chen *et al*., 2014). The FTIR spectra of the control film and sucrose doped films showed similar major characteristic peaks, but the amplitudes of the peaks were different. Similar results were also suggested by Saberi *et al*. (2017). The IR spectra of the glycerol incorporated film showed a notable change in the wavenumber, decreasing from 3413 to 3394–3398 cm^{-1} compared to the control film. The shift to lower wavenumbers suggested that hydrogen bonds (cross–links) were strongly formed in the films (Saberi *et al*., 2017). Abera *et al*. (2020) found that starch films plasticized with glycerol and sorbitol had a reduced signal from 3310 cm^{-1} to 3290 cm^{-1}. They found that the lower wavenumber

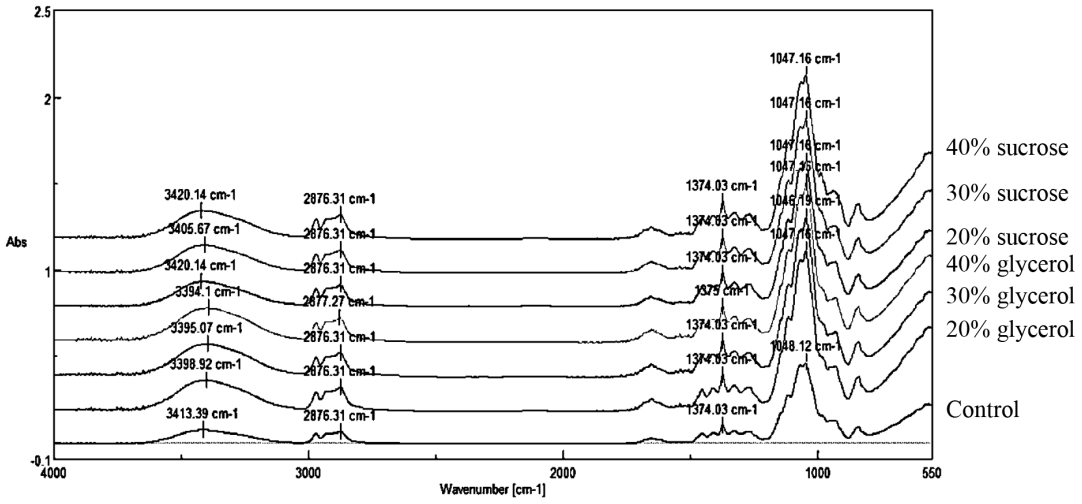

Fig. 3. ATR–FTIR spectra of HPC film incorporated with different plasticizers and concentration from 4000–400 cm^{-1}.

was obviously observed when incorporating glycerol to pea starch and guar gum film compared to ethylene glycol (EG) and propylene glycol (PG) (Saberi *et al*., 2017). Therefore, the incorporation of glycerol could affect or modify the functional groups of resulting films.

Moisture content of films

The moisture content is an important factor affecting the film properties, mainly mechanical properties (Pattarasiriroj *et al*., 2020). The results of moisture content of film samples are shown in Table 1. The addition of glycerol significantly increased the moisture content of the HPC films from 19–25%, while the addition of sucrose did not change the moisture content with respect to the gelatin films. Glycerol induces network formation between HPC molecules and can be localized inside them. Furthermore, glycerol could plasticize to water, resulting in water being retained in the HPC structure via hydrogen bonding (Pattarasiriroj *et al*., 2020). In contrast, there was no significant difference in the moisture content of HPC films with sucrose at all concentrations tested. There are several possible explanations for these results, particularly the effect of the molecular weight size of the plasticizer. This is agreed with Saberi *et al*. (2017) who reported that the higher moisture content of pea starch and guar gum films, the higher the plasticizer content in the order of glycerol > ethylene glycol > propylene glycol > xylitol > fructose > galactose > glucose > sorbitol > mannitol > sucrose > maltitol. In general, high moisture content of films is not a preferable property as it promotes microbial growth and prevents water loss from food (Rawdkuen *et al*., 2020). These issues can be solved by the addition of hydrophobic materials, such as essential oils (Mohammadi *et al*., 2021a; Mohammadi *et al*., 2021b; Tran *et al*., 2021; Wardana *et al*., 2021).

Water vapor barrier (WVP) of films

WVP is an important parameter for food packaging because it is strongly related to the commercial application of food preservation. The desired property of food packaging is to retard the moisture transfer between the

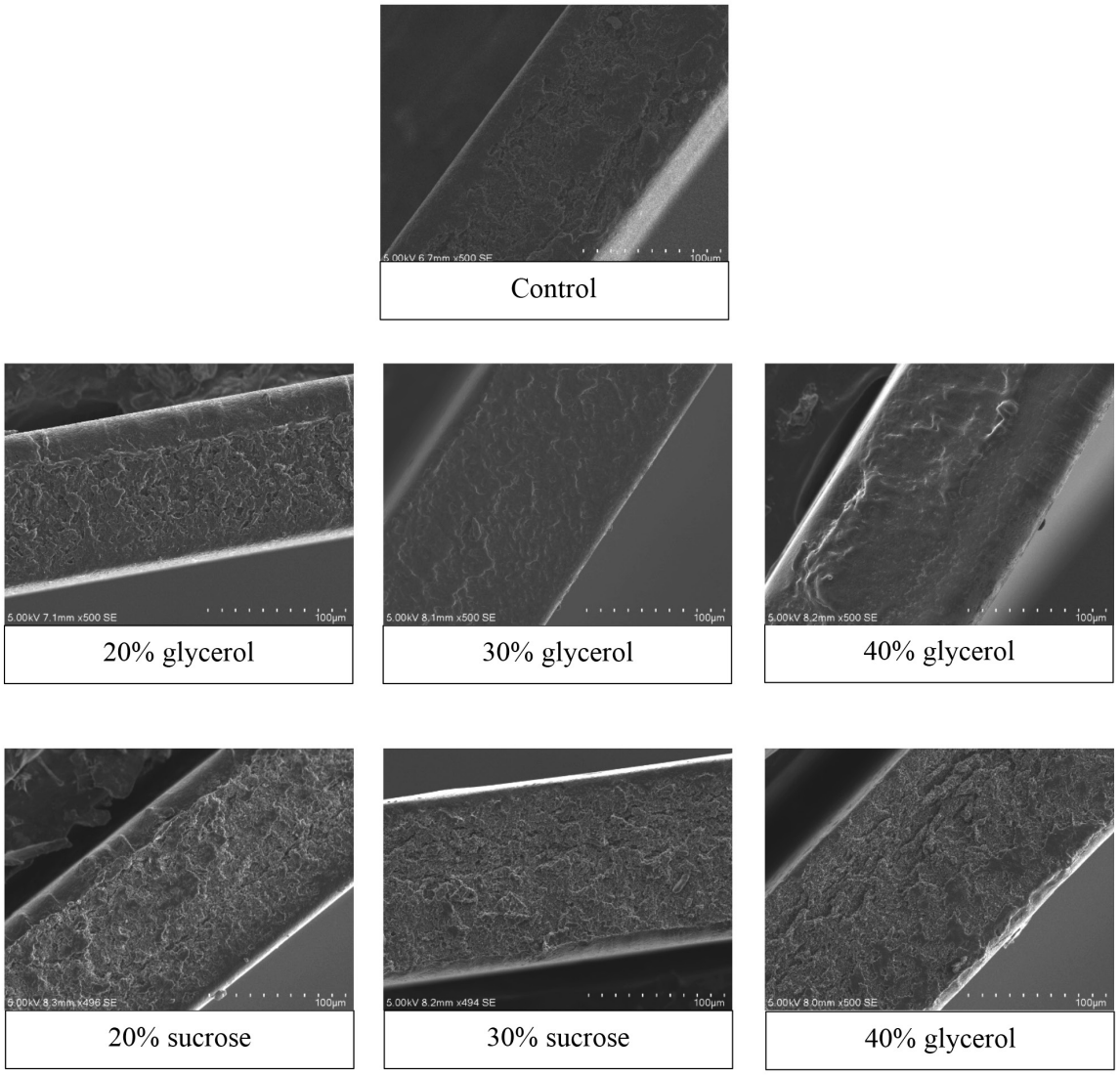

Fig. 4. The SEM of cross section of HPC film contained different types of plasticizers (sucrose and glycerol) at different concentrations (20%, 30%, and 40% w/w of HPC). Magnification 500x

inside and outside of the packaging (Rawdkuen *et al*., 2020). The effect of plasticizer type and concentration on the WVP of HPC films is shown in Table 1. The highest WVP was found for films containing glycerol, and it is more pronounced with the higher concentrations used ($P < 0.05$). It might be noticeable that low molecular weight and hydrophilic nature of glycerol, which allows it to be easily dispersed in the film matrix and to bond with the hydroxyl groups of water molecules by hydrogen bonding, resulting in higher WVP. The lower levels usage of glycerol, a commonly used plasticizer in biopolymer–based films, tends to improve the water barrier properties due to its hydrophilic nature (Hoque *et al*., 2011). Films plasticized with sucrose showed lower WVP values ($P > 0.05$), especially at higher concentrations, due to the higher molecular weight of sucrose. These results suggest that HPC films containing high concentrations of glycerol are not suitable for application in edible films and coatings due to their high WVP. This property can be improved by adding hydrophobic materials such as lipids.

Morphological characteristics of films: microstructure

The surface and cross–section of HPC film supplemented with plasticizers are shown in Fig. 4. These results showed that the control HPC film had a compact, smooth, and continuous surface. The smooth surface was also observed for the film containing glycerol, regardless of the glycerol content (Fig. 5). Nevertheless, the surface of the HPC film with sucrose was found to be discontinuous, uneven, and rough, with the presence of grooves and pores (Fig. 2). For cross–section, the control film and the glycerol added films showed a smooth and compact structure. When sucrose was added, the cross–section of film became rougher than that of the control film and the glycerol added film. The reason why the structure of HPC sucrose films was not compact and large pores and cracks occurred might be related to the rate of moisture loss in the film (Ploypetchara &

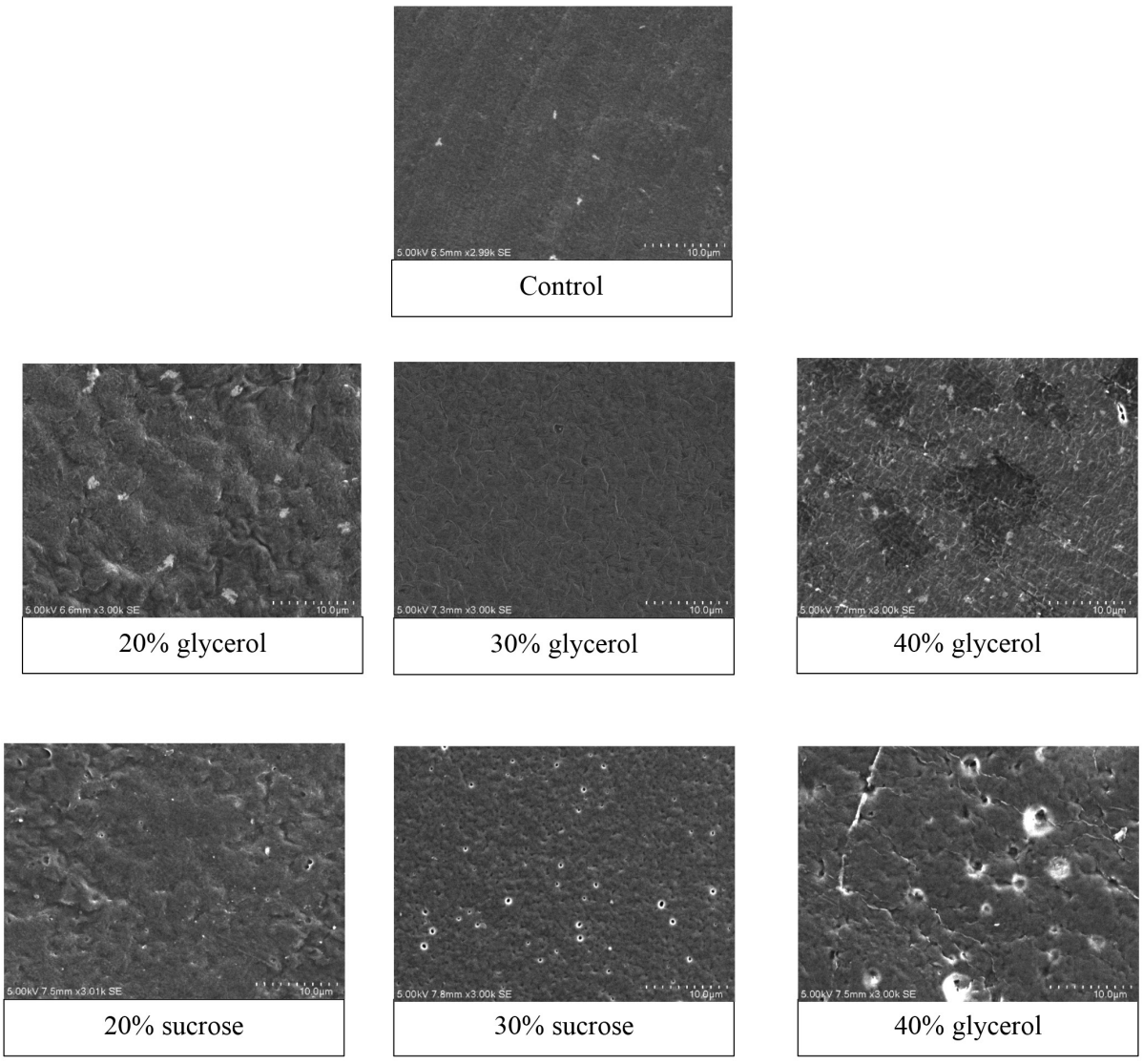

Fig. 5. The SEM of surface of HPC film contained different types of plasticizers (sucrose and glycerol) at different concentrations (20%, 30%, and 40% w/w of HPC). Magnification 3000x

Gohtani, 2020) and the large size of plasticizers that are not compatible with the film matrix (Saberi *et al*., 2017). Pea starch–guar gum films plasticized with polyethylene glycol and sucrose were rougher than those made with glucose due to their molecular weight structure (Saberi *et al*., 2017). Ploypetchara & Gohtani (2018) reported that films developed from different starch sources (normal corn, normal rice, waxy corn, and waxy rice) with D–allulose showed smoother surface than those mixed with sucrose. Thus, it is possible that the film structure containing the plasticizer might be related to the film properties.

CONCLUSIONS

The incorporation of plasticizers into HPC–based films with SD affected the mechanical properties, moisture, water vapor permeability, color, and optical properties of films. In particular, the films formulated with glycerol were more transparent and higher elongation at break than those formulated with sucrose, regardless of the concentration. The glycerol films had lower water vapor barrier properties and tensile strength than those of the base film and sucrose–added film. These were mostly related to the hydrophilic nature of glycerol; the addition of sucrose to the HPC films resulted in water loss, causing cracking and brittleness of the film surface; however, it had the potential to prevent light–induced quality degradation of coated or packaged products. It is clear that the properties of HPC films can be modified by selecting the type and concentration of plasticizers, so that the properties can be controlled to the application.

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AUTHOR CONTRIBUTIONS

Passakorn Kingwascharapong: Conceptualization; Data curation; Investigation; Methodology; Resources; Writing–original draft. Arisa Koga: Data curation; Investigation. Supatra Karnjanapratum: Writing–review & editing. Fumina Tanaka: Project administration; Writing–review & editing. Fumihiko Tanaka: Supervision; Writing–review & editing.

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