Effect of glycerol concentration on physical and texture properties of edible films prepared from karaya gum

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ABSTRACT

This study formulated edible films based on karaya gum in the presence of glycerol. Physical properties of films were investigated by various methods including texture analysis and differential scanning calorimeter (DSC). The obtained results revealed that glycerol acted as a plasticizer contributing to improve the flexibility, water vapor permeability and heat resistance of karaya films. The best value of tensile strength and puncture force for edible films could be achieved by the combination of karaya gum and glycerol at the concentrations of 4% (w/v) and 10% (w/w), respectively.

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1. Introduction

In recent years, plastic utilization has faced social arguments due to its negative effects on the environment. Plastic bags and other synthesized-polymers-based materials takes many years to decompose. In addition, toxic substances released from plastic wastes combustion can leach into soils, water sources and even the air we breathe everyday, leading to serious public health hazards. Though, a considerable amount of researches have been conducted to figure out the new materials which can replace synthetic packaging, and bio-based polymer films have been considered as the promising approach since the 1980s. In comparison with plastic films made from synthetic-materials, edible films still provide a barrier to moisture, oxygen and solute movement while being eco-friendly (Phan et al., 2005). These films are often produced from natural polymers possessing film-forming ability such as pectin, starch, chitosan, xylan, lignin and cellulose nano fibrils (CNF) which can be extracted easily from various agro-byproducts (Vartiainen et al., 2014). Among biopolymers, polysaccharide gums (Karaya gum, gum Arabic, gum ghatti and larch gum) are potential materials for edible films processing but the studies using this kind of material are quite limited especially when comparing with the others such as agar, pectin and methyl cellulose (Nieto, 2009).

Karaya gum, an exudate gum, is plentifully in the trunk and branches of *Sterculia foetida* plants. This gum contains a lot of complex and branched polysaccharides with a high molecular mass ($16x10^6$ Da) (Lujan-medina et al., 2013;

Mortensen et al., 2016). The main chains of karaya gum are structured by α-D-galacturonic acid and L-ramnose while the branches are connected by the linkages between 1,2-β-D-galactose or 1,3-β-D-glucuronic with galacturonic acid (Verbeken et al., 2003). Some researchers stated that the volume of this gum can swell to 60 times when soaking in aqueous medium (Verbeken et al., 2003; Lujan-medina et al., 2013). Similar with most exudate gums, karaya gum is cheap, biodegradable, eco-friendly and considered safe to consumer's health (Mortensen et al., 2016). Based on these advantages, this biopolymer is widely used as additive in food and pharmaceutical industries (Lujan-medina et al., 2013).

However, the application of karaya gum in food packaging is quite limited due to many challenges. Firstly, the low solubility of karaya gum in water results in a very high viscosity solution which causes many difficulties in preparing films (Sarathchandiran, 2014). Secondly, karaya film has weak tensile strength and high brittleness (Lettre, 2010). To improve film properties, the addition of plasticizers as glycerol can be an appropriate method. Glycerol is a popular hydrophilic plasticizer that helps reduce the intermolecular forces between polysaccharide chains to increase their mobility. Many studies proved that the addition of glycerol could improve the physical properties of edible films like flexibility, water vapor and gas permeability (Farahnaky et al., 2013; Sanyang et al. 2015; Saberi et al. 2016). Nieto (2009) explained the slower disintegration of bio-films when glycerol was locked into the matrix structure, leaving the stable film until product consumption.

Therefore, this study aimed to formulate edible films with improved physical properties including water vapor permeability, mechanical resistance and heat stability. The research provides details of karaya-based films and their characteristics, the effect of the plasticizer in various concentrations and the improvement of properties of karaya-based edible films.

2. Materials and Methods

2.1. Raw materials and chemicals

Gum karaya was collected from local suppliers, glycerol (99% of purity were was purchased from Sigma-Aldrich (Canada) and salts (95% of purity) including NaBr, CH_3COOK and KCl) were purchased from Merck (Germany). Raw karaya gum was grounded and classified using a cutting-grinding head (IKA MF10.1, USA) after removing visible impurities. Particles with a size range of 0.5 – 1 mm were collected and stored in vacuum plastic bags for further experiments.

2.2. Sample preparation

Karaya solution was formed by dissolving raw material into 250 mL distilled water at ambient temperature. Gum solutions at various concentrations (3, 4 and 5%, w/v) were stirred in 2 h using a magnetic stirrer at 800 rpm in 500 mL erlen flasks. Glycerol was then added into gum solution at the concentration of 10%, 15%, 20% and 25% (w/w) based on the dry weight of karaya gum (DW), the mixtures were gently stirred using a glass stick for 15 min at the room temperature. The bubbles formation should be limited during stirring. The solution was spread on the granite plate which was covered by a polyethylene sheet to prevent adhesion. Those plates were dried for 2 h under a vacuum atmosphere (60 mmHg) for 24 h at 55°C using a convection dryer (Memmert, Germany) before being cooled to room temperature. Film samples were stabilized in desiccators for 48 h at the relative humidity of 57% (using sodium bromide saturated solution). Karaya films were kept in vacuum plastic bags before further analysis.

2.3. Film thickness

The film thickness was measured by using a manual slide micrometer Gauge (The Vernier Caliper) to the nearest value of 0.01 mm. Data were collected at 10 random locations for each film sample and an average value was calculated. The thickness value was used for determining the tensile strength and water vapor transmission.

2.4. Water vapor permeability (WVP)

The water vapor transmission of the film was measured according to the modified ASTM E96-80 method (Phan et al., 2005). In the pretreatment step, all samples were equilibrated in desiccators at 25°C and relative humidity of 22% (using potassium acetate saturated solution) during 48 h. Film samples were set up between two Teflon rings of the glass cell which were placed in the desiccators at 25°C for 15 days. The in-

side and outside relative humidity of glass cells are 84% (using potassium chloride saturated solution) and 22%, respectively. WVP was calculated based on the weight changes ($\Delta m/\Delta t$, g/s) of the cell during measurement time using the following equation 1 (Phan et al., 2005):

$$WVP = \frac{\Delta m \times x}{A \times \Delta t \times \Delta p} (gm^{-1}s^{-1}Pa^{-1}) \quad (1)$$

Where x and A are the film thickness (m) and the exposed surface (m^2), respectively while Δp is the partial water vapor pressure difference between 2 sides of samples (Pa).

2.5. Texture analyzer

Tensile strength test and puncture test were conducted by a texture analyzer (TA.XT plus, Stable microsystem, UK) equipped 5 kN load cell. Film samples were cut into rectangular strips of 15.4 mm width x 100 mm length with a thickness of 0.03 mm before stretching. For the puncture test, the film was fixed in a 52.6 mm diameter cell. Both the force and the deformation at the breaking point of samples were measured using a 3 mm diameter aluminum probe. The puncture deformation was calculated using equation 2 (Gontard et al., 1993):

$$\frac{\Delta t}{\Delta l} = \frac{\sqrt{D^2 + l_0^2} - l_0}{l_0} \quad (2)$$

Tensile strength (TS) at breaking, the puncture force (F) and the displacement of the probe (D) were measured using Exponent software (version 6.0, Stable microsystem, UK). The radius of the measurement cell (26.3 mm) was presented as l_0.

2.6. Thermal characteristic analysis

Heat-resistance of karaya film was analyzed using a different scanning calorimeter (DSC) (Q2000, TA Instrument, USA). Samples (5-10 mg) were sealed into aluminum pans and an empty pan was used as a reference. All samples were heated from ambient temperature to 200°C with a rate of 5°C/min.

2.7. Statistical analysis

The experiment was conducted using 2 full-factorial designs with three replications Analysis of variance (ANOVA) and LSD were applied to compare mean value of film's properties with a significance of 0.05. A significant difference was satisfied at 95% probability. SPSS statistics software (version 20, IBM, USA) was used to evaluate the data.

3. Results and Discussion

3.1. Film formation

Preliminary experiments showed that a good appearance of edible films could be obtained if karaya gum concentration in the formulation was limited under 5%. It took about 2 h for raw material as karaya gum completely dissolved in distilled water before casting. Since the air bubbles can be trapped in high viscosity solutions such as karaya gum solution, the pinholes often form during film formation. Therefore, gum solution needs to be kept in a vacuum dryer at 60 mmHg and 55°C for 2 h to eliminate air bubbles before drying 24 h in a convention dryer at the same temperature. The results were in line with Neito's work, in which he stated that the dried films without glycerol were very adhesive to the casting surface while their tensile strength was too weak and brittle to peel off. The addition of 10% glycerol ensured that karaya films could be removed easily from granite plates. Besides, the flexibility of karaya films increased significantly when adding glycerol in a range of 10 - 25% since this additive was a hydrophilic compounds plasticizer (Phan The et al., 2008; Vieira et al., 2011; Jantrawut et al., 2017). At higher glycerol concentrations, the films were hard to form and also required longer drying time.

3.2. Water vapor permeability

Water vapor permeability (WVP) is an important parameter in the evaluation of moisture transmission through barrier of edible films. Various concentrations of the karaya gum and glycerol were investigated to evaluate their effects on WVP of edible films based on karaya gum Two-way ANOVA revealed that both karaya gum and glycerol had significant effects ($P < 0.05$) on the WVP of the films. Generally, a higher concentration of polymer means a denser structure of the film network resulting in a decrease in water vapor transmission. However, WVP of the film with 5% karaya gum was significantly higher than that of films containing 3% and 4% karaya gum at $P =$

Table 1. Physical properties of edible films based on karaya gum and glycerol

Karaya gum (% w/v)	Glycerol (%w/w)	Tensile strength (MPa)	Puncture force (MPa)	Puncture deformation (%)
3	10	46.15 ± 1.80	9.51 ± 2.90	0.72 ± 0.22
	15	37.86 ± 0.26	7.58 ± 0.29	1.07 ± 0.33
	20	16.11 ± 3.25	4.32 ± 1.37	1.98 ± 0.65
4	10	85.89 ± 0.40	10.67 ± 0.47	0.52 ± 0.13
	15	53.59 ± 0.08	10.31 ± 1.27	0.87 ± 0.08
	20	34.61 ± 6.05	4.04 ± 0.20	1.51 ± 0.18
5	10	37.79 ± 0.91	9.66 ± 0.44	2.58 ± 0.30
	15	33.29 ± 1.71	6.67 ± 1.04	5.05 ± 0.09
	20	24.65 ± 1.24	5.68 ± 0.95	5.67 ± 0.10

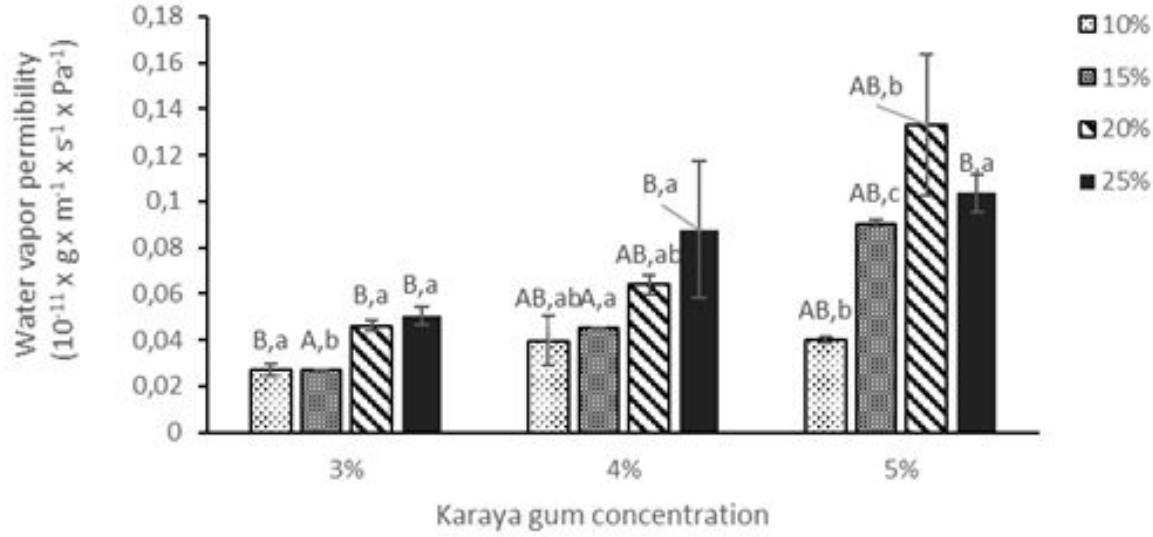

Figure 1. Effect of glycerol concentrations (10, 15, 20 and 25% w/w) on water vapor permeability of karaya films. Different letters are for significantly different groups. The capital letter (A,B) are for comparison of gum content, likewise, lower case (a,b) letters are for comparison of glycerol concentration.

0.05% (Figure 1). The incorporation of polysaccharide chains of gum with water molecules via the intensive hydrogen bonds produces less effective moisture barriers due to its highly hydrophilic property. On the other hand, the addition of hydrophobic ingredients could contribute to the improved water-resistance of gum films while remain their good mechanical properties (Nieto 2009). Figure 1 also revealed the films with above 20% glycerol (w/w) exhibited the high values of WVP among all films tested ($P < 0.05$). There is no significant difference between samples with 10% (w/w), 15% (w/w) glycerol. The results in agreement with several authors who found that glycerol utilization is for increasing the free volume and chain movement through improving molecular mobility (Xiao et al., 2011; Cerqueira et al., 2012; Jouki et al., 2013). As a consequence, the rigidity was reduced, and more water could diffuse through the film structure. On the contrary, some authors reported an opposite trend of WVP for the composite film prepared from plums gum combined with carboxyl methyl cellulose (Shekarabi et al., 2014). Unlike karaya gum, that mixture did not have a good corporation with glycerol resulting in a reduction of the gum cohesiveness.

3.3. Textural properties

Mechanical properties (including tensile strength, puncture force and deformation) of edible films produced from various concentrations of karaya gum and glycerol were investigated

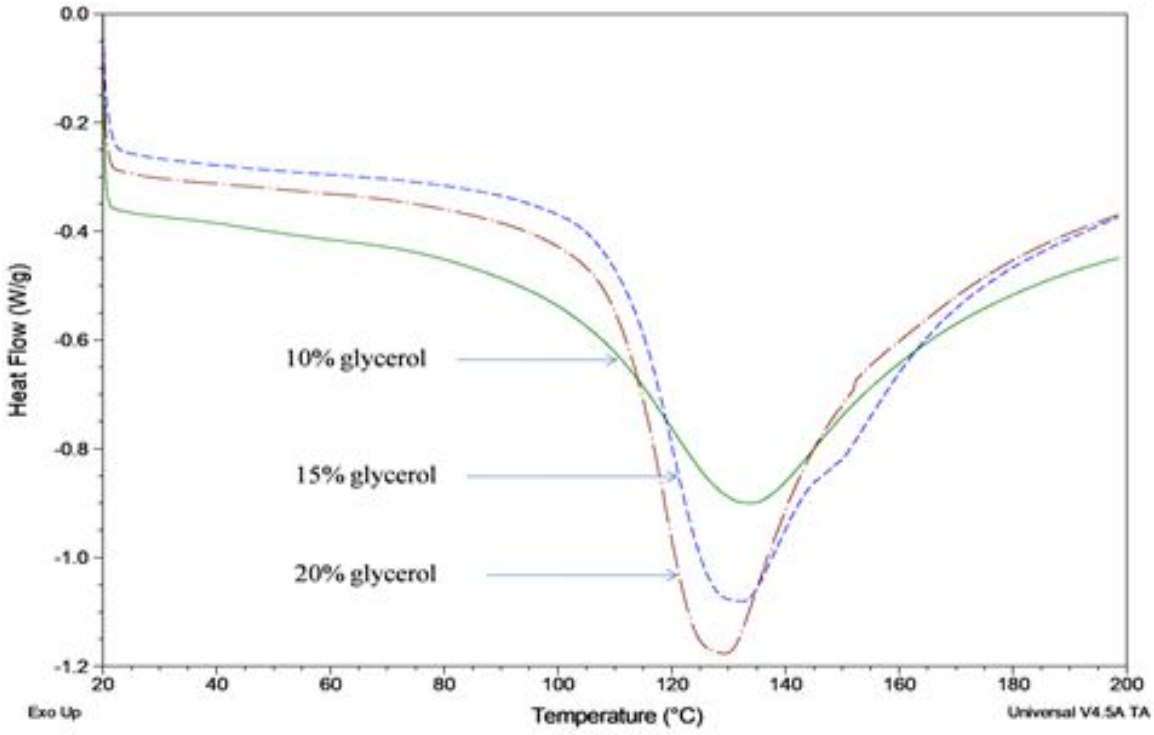

Figure 2. Effect of glycerol concentrations (10, 15 and 20%, w/w) on heat resistance of karaya films (4%, w/v)

and the results are displayed in Table 1. It can be seen that the concentrations of both materials had significant effects on the physical properties of films. According to LSD comparison, 4% karaya gum was the most suitable concentration for producing edible films to obtain the best value of tensile strength and puncture force. A lower concentration of polysaccharide was not enough to stabilize the backbone structure of the films while a higher concentration could increase the brittle.

Although karaya gum has been considered an inappropriate material to form edible films (Nieto, 2009), the result of the current study showed that a combination of karaya gum and glycerol helped form the films with excellent physical properties to possibly apply in packaging technology. Two-way ANOVA and LSD comparison revealed that both tensile strength and puncture force decreased with the increase of glycerol concentration ($P < 0.05$). Similar trends were reported in the previous studies which using glycerol to modify biopolymer films (Bourtoom, 2008; Jouki et al., 2013; Sanyang et al., 2015). As a plasticizer, glycerol was responsible for the decrease of interactions between polysaccharide molecules and the formation of new hydrogen bonds. For examples, glycerol could weaken the macromolecules forces between agar particles (Arham et al., 2016) or increase the free volume between rice starch and chitosan (Sobral et al., 2001). In our study, the addition of glycerol improved the puncture deformation of karaya films. For films containing 4% karaya gum, the deformation could be enhanced to 300% (Table 1) as increasing glycerol concentration from 10 to 20% (w/w). Therefore, it can be confirmed that glycerol contributed to improving the flexibility of karaya films.

3.4. Thermal properties

Thermal analysis was applied to evaluate the heat resistance of edible films based on karaya gum (4% w/v). In all samples, the thermo-curves (Figure 2) showed a major melting peak in a range of 120 - 140°C which should be represented to the release of water in heating. It means that edible films based on karaya gum were thermal-stable below 100°C and hence can be applied as commercial plastic films in food packaging. This

result was in line with the previous study which suggested that the decomposition temperature of raw karaya gum was around 316°C and the water loss occurred around 60°C (Sarathchandiran, 2014). In the current study, it was observed that glycerol played an important role in the water holding capacity of karaya films. For example, the water loss of films adding glycerol only occurred above 100°C instead of 60°C as raw gum. Figure 2 indicated that films with minimum glycerol concentration transform apparently to a viscous rubbery state at a lower temperature than others. Glycerol in karaya films made films more hydrophilic and maintained a high moisture content. The result in this study showed the agreement with Shekarabi's research , in which he reported that the glass transition value of edible films increased sharply with higher glycerol content since new linkages between the polymer chains required more energy to break up and release the aqueous phase (Shekarabi et al., 2014).

4. Conclusions

This work was successful to produce edible films based on karaya gum with a concentration in a range of 3 - 5% (w/v). As expected, the addition of glycerol contributed to improve the water vapor permeability, the flexibility and the textural properties of those films. A combination of 4% karaya gum and 10% glycerol (w/w) was the appropriate ratio to obtain films having the highest values of tensile strength and puncture force while remaining folding ability. Edible films produced from those materials were thermal stable below 100°C and could be applied in food packaging. Further studies can combine karaya gum with other materials such as lignin, chitosan, or pectin to formulate new edible films or improve the physicochemical properties of films.

Conflict of interest declaration

We do not have any conflict of interest.

This study does not involve any human or animal testing.

References

Arham, R., Mulyati, M. T., Metusalach, M., & Salengke, S. (2016). Physical and mechanical properties of agar based edible film with glycerol plasticizer. *International Food Research Journal* 23(4), 1669-1675.

Bourtoom, T. (2008). Plasticizer effect on the properties of biodegradable blend from rice starch-chitosan. *Songklanakarin Journal of Science and Technology* 30(SUPPL. 1), 149-155.

Cerqueira, M. A., Souza, B. W. S., Teixeira, J. A., & Vicente, A. A. (2012). Effect of glycerol and corn oil on physicochemical properties of polysaccharide films - A comparative study. *Food Hydrocolloids* 27(1), 175-184.

Farahnaky, A., Saberi, B., & Majzoobi, M. (2013). Effect of glycerol on physical and mechanical properties of wheat starch edible films. *Journal of Texture Studies* 44(3), 176-186.

Gontard, N., Guilbert, S., & Cuq, J. L. (1993). Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten film. *Journal of Food Science* 58(1), 206-211.

Jantrawut, P., Chaiwarit, T., Jantanasakulwong, K., Brachais, C. H., & Chambin, O. (2017). Effect of plasticizer type on tensile property and in vitro indomethacin release of thin films based on low-methoxyl pectin. *Polymers* 9(7), 289.

Jouki, M., Khazaei, N., Ghasemlou, M., & Hadinezhad, M. (2013). Effect of glycerol concentration on edible film production from cress seed carbohydrate gum. *Carbohydrate Polymers* 96(1), 39-46.

Lettre, D. P. (2010). Applications of gum karaya in drug delivery systems: A review on recent research. *Cosmetics* 2(5), 39-48.

Lujan-Medina, G. A., Ventura, J., Ceniceros, A. C. L., Ascacio, J. A., Valdés, D. B. V., & Aguilar, C. N. (2013). Karaya gum: General topics and applications. *Macromolecules Indian* 9(4), 111-116. *text* Mortensen, A., Aguilar, F., Crebelli, R., Domenico, A. D., Frutos, M. J., Galtier, P., Gott, D., Gundert-Remy, U., Lambre, L., Leblanc, J. C., Lindtner, O., Moldeus, P., Mosesso, P., Oskarsson, A., Parent-Massin, D., Stankovic, I., Waalkens-Berendsen, I., Woutersen, R. A., Wright, M., Younes, M., Brimer, L., Peters, P., Wiesner, J., Christodoulidou, A., Lodi, F., Tard, A., & Dusemund, B. (2016). Re-evaluation of karaya gum (E 416) as a food additive. *EFSA Journal* 14(12), 4598.

Nieto, M. B. (2009). *Edible films and coatings for food applications* (1st ed.). New York, USA: Springer.

Phan, T. D., Debeaufort, F., Luu, D., & Voilley, A. (2005). Functional properties of edible agar-based and starch-based films for food quality preservation. *Journal of Agricultural and Food Chemistry* 53(4), 973-981.

Phan The, D., Debeaufort, F., Luu, D., & Voilley, A. (2008). Moisture barrier, wetting and mechanical properties of shellac/agar or shellac/cassava starch bilayer bio-membrane for food applications. *Journal of Membrane Science* 325(1), 277-283.

Saberi, B., Vuong, Q. V., Chockchaisawasdee, S., Golding, J. B., Scarlett, C. J., & Stathopoulos, C. E. (2016). Mechanical and physical properties of pea starch edible films in the presence of glycerol. *Journal of Food Processing and Preservation* 40(6), 1339-1351.

Sanyang, M. L., Sapuan, S. M., Jawaid, M., Ishak, M. R., & Sahari, J. (2015). Effect of glycerol and sorbitol plasticizers on physical and thermal properties of sugar palm starch based films. *13th International Conference on Environment, Ecosystems and Development* (157-162). Kuala Lumpur, Malaysia: WSEAS Press.

Sarathchandiran, S. K. (2014). Characterization and standardization of gum karaya. *International Journal of Biopharmaceutics* 5(2), 142-151.

Shekarabi, A. S., Oroiehie, A. R., Vaziri, A., Ardjmand, M., & Safekordi, A. A. (2014). Effect of glycerol concentration on physical properties of composite edible films prepared from plums gum and carboxy methyl cellulose. *Indian Journal of Fundamental and Applied Life Sciences* 4(Cmc), 1241-1248.

Sobral, P. J. A., Menegalli, F. C., Hubinger, M. D., & Roques, M. A. (2001). Mechanical, water vapor barrier and thermal properties of gelatin-based edible films. *Food Hydrocolloids* 15(4-6), 423-432.

Vartiainen, J., Vähä-Nissi, M., & Harlin, A. (2014). Biopolymer films and coatings in packaging applications—A review of recent developments. *Materials Sciences and Applications* 5(10), 708-718.

Verbeken, D., Dierckx, S., & Dewettinck, K. (2003). Exudate gums: Occurrence, production, and applications. *Applied Microbiology and Biotechnology* 63(1), 10-21.

Vieira, M. G. A., Da Silva, M. A., Dos Santos, L. O., & Beppu, M. M. (2011). Natural-based plasticizers and biopolymer films: A review. *European Polymer Journal* 47(3), 254-263.

Xiao, G., Zhu, Y., Wang, L., You, Q., Huo, P., & You, Y. (2011). Production and storage of edible film using gellan gum. *Procedia Environmental Sciences* 8, 756-763.