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The effect of plasticizers on the functional properties of biodegradable gelatin-based film: A review

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ABSTRACT

Food packaging derived from a petroleum base represents a serious environmental problem. Finding alternative sustainable solutions is a must. Therefore, the current study has focused on the production of biodegradable food packaging from renewable materials, primarily gelatin. The effect of the biomaterials used on functional properties of the films produced needs thorough investigation. Gelatin represents interesting biomaterials for developing biodegradable food packaging, mainly due to their good film forming properties and abundantly in nature. However, the incorporation of gelatin in biodegradable films for food packaging may give some drawback on certain properties of the film such as tensile strength and water vapour permeability. Thus, addition of plasticizers into the film materials improves the functional properties of films by increasing their extensibility, dispensability, flexibility, elasticity, and rigidity. This study aims to review the current findings on how plasticizers impact the functional properties of biodegradable gelatin-based films. Plasticizers incorporation in the films may affect the continuity of the polymer matrix, leading to physical changes, where the films become more flexible and stretchable. Generally, the plasticization effect of plasticizers strengthens the film structure, in which the tensile strength and elongation of the films are improved and water barrier properties are reduced.

1. Introduction

Packages are used as a marketing tools to communicate with consumers, protect products from the deteriorating effects of the external environment, contain products of various sizes and shapes, and provide the consumer with ease of use and time-saving convenience (Otles & Yalcin, 2008). Food packaging provides a physical barrier between the outside environment and food products, thereby guaranteeing the hygiene and prolong the shelf life of perishable items, especially those prone to microbiological and oxidative deterioration (Gómez-Guillén et al., 2009). The most common materials used for food packaging are plastic, paper, glass, aluminium, fibreboard and steel. Petroleum-based plastics are commonly used as they offer various advantages over other packaging materials in terms of low weight, stability and sturdiness. However, they lead to serious environmental issues because they generate extensive volumes of non-biodegradable waste (Siracusa, Rocculi, Romani, & Rosa, 2008).

New biodegradable films made from biopolymers play a crucial role in lowering the environmental impact of non-biodegradable plastic waste (Soo and Sarbon, 2018). The main biopolymers employed in the development of biodegradable films are protein and polysaccharides. Polysaccharides studied thus far include chitosan (Aider, 2010; Martins, Cerqueira, & Vicente, 2012), carboxymethyl cellulose (Nazmi, Isa, & Sarbon, 2017), and starch (Soo & Sarbon, 2018; Tongdeesoontorn, Mauer, Wongruong, Sriburi, & Rachtanapun, 2011). Commonly studied proteins for developing biodegradable films include soy protein (Guerrero & De la Caba, 2010), milk protein, such as casein and whey protein (Kokoszka, Debeaufort, Lenart, & Voilley, 2010), and gelatin (Hanani & Ross, & Kerry, 2014a; Hanani, O'Mahony, Roos, Oliveira, & Kerry, 2014b; Nor, Nazmi, & Sarbon, 2017).

Gelatin has been studied extensively for its ability to form film, good functional properties, and usefulness as an outer barrier to protect food from drying, exposure to oxygen and light (Bakry, Isa, & Sarbon, 2017). Films composed of gelatin possess good mechanical properties but have been found to be moisture sensitive and exhibit poor barrier properties against water vapour (Gómez-Guillén et al., 2009). This causes negative feedback when applied to high moisture food products because films may dissolve, swell or disintegrate upon contact with water. Therefore, current trends in designing biodegradable materials for food packaging look for optimize film properties by studying the effect of plasticizers.

Plasticizers are molecules of low volatility which are added to biopolymer materials to allow the modification of the functional properties

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of films by increasing their extensibility, dispensability, flexibility, elasticity, rigidity and mechanical properties (Hanani et al., 2014a, 2014b). Polyols have been reported to be particularly efficient in plasticizing hydrophilic polymers (Ghasemlou, Khodaiyan, & Oromiehie, 2011; Tihminlioglu, Atik, & Özen, 2010). For this reason, many recent researchers have focused on the usage of polyols such as glycerol (Li et al., 2011; Muscat, Adhikari, Adhikari, & Chaudhary, 2012), sorbitol (Bakry et al., 2017; Mikus et al., 2014), mannitol (Liew, Tan, & Peh, 2014; Mikus et al., 2014) and xylitol (Tong, Xiao, & Lim, 2013). There are also plasticizers from monosaccharides such as glucose, mannose, fructose, and sucrose (Piermaria et al., 2011; Qiao, Tang, & Sun, 2011). Films have also been produced using fatty acids as plasticizers (Jiménez, Fabra, Talens, & Chiralt, 2012; Limpisophon, Tanaka, & Osako, 2010).

However, plasticizers may also serve as mechanical antiplasticizers at low concentrations (2.5%), resulting stiffer film blends (Chang, Karim, & Seow, 2006). Mechanical antiplasticization has significant effects on physical properties and textural characteristics of edible film (Cheng et al., 2002). Most water compatible diluents (polyols, monosaccharides, disaccharides, oligosaccharides) has been reported to have plasticizing rather than antiplasticizing effects on both physical and mechanical properties of biopolymer-based film (Chang et al., 2006). Therefore, water compatibility diluents are mostly used in film development. However, different types of polymer may respond differently to the low concentration of plasticizers. The absence of antiplasticizing effects may be due to the limited range of diluent concentrations examined, since those plasticizers are usually applied at optimum levels to enhance film flexibility and workability.

Studies have shown that the addition of plasticizers in various percentages have improved the mechanical properties of gelatin films (Nor et al., 2017). For instance, the different concentration of glycerol used in film formulation has different effects on the tensile strength values of gelatin films such as glycerol concentration at 10% (108.28 ± 6.38 MPa) (Fakhoury et al., 2012); 20% (1.75 MPa); 25% (1.67 ± 0.12) (Al-Hassan & Norziah, 2012) and 30% (2.91 ± 0.43 MPa) (Soo & Sarbon, 2018). The blend of different plasticizers in film formulation could also improve the functional properties of the gelatin film that was produced (Ghasemlou et al., 2011). For example, the used of the glycerol with sorbitol (Al-Hassan & Norziah, 2012) (1.28–25.03 MPa) and glycerol with Polyethylene glycol (PEG) (33–80 MPa) (Cao, Yang, & Fu, 2009) showed the improvement on tensile strength with concentration increased. As a small hydrophilic molecule, glycerol can be inserted between protein chains, hence acting as a plasticizer. The distance between the protein chains increases and direct interactions are reduced as glycerol become interspaced in a protein network (Guo et al., 2012).

In addition, a study conducted by Rezaei and Motamedzadegan (2015) revealed that the addition of sorbitol to bovine gelatin films with incorporation of clay nanoparticles reduced the Young's modulus (YM) value of the films. There were no significant differences observed when sorbitol concentration increased from 10% up to 25%. However, when sorbitol concentration was raised from 25% to 30%, young's modulus of bovine gelatin films has improved. As for the sago starch/ fish gelatin film with incorporation of 25% sorbitol, showed that the YM value were ranged between 0.91 and 1.71 Pa with varied ratio of blended sago starch and fish gelatin film. The results however, showed higher value when compared to addition of 25% of glycerol into sago starch/fish gelatin film with YM value between 0.12 and 0.20 Pa for different ration of blended sago starch and fish gelatin film (Al-Hassan & Norziah, 2012). To conclude, the study by Rezaei and Motamedzadegan (2015) was in corresponding with findings by Al-Hassan and Norziah (2012) which stated that glycerol has better plasticizing effect than sorbitol with respect to mechanical properties in bovine and fish gelatin film. The results was supported with study by Mali, Sakanaka, Yamashita, and Grossmann (2005) which also mentioned that the lower stress and Young's Modulus values were obtained in films plasticized with glycerol, indicating that glycerol exerted a more effective plasticization.

Falguera, Quintero, Jiménez, Muñoz, and Ibarz (2011) found that food scientists worldwide had developed great interest in recent years in the effects of various types of plasticizers for improving biodegradable film properties. Previous studies on the microstructure, interactions, crystalline structure of gelatin films had been conducted to improve film properties, which include water vapour permeability (Nunez-Flores et al., 2013; Nor et al., 2017), gas permeability (Ninan, Joseph, & Abubacker, 2010), tensile strength (Nor et al., 2017), Fourier transform infrared spectroscopy (Nunez-Flores et al., 2013), X-ray diffraction (Tongdeesoontorn et al., 2011) and light transmission (Ahmad, Benjakul, Prodpran, & Agustini, 2012). Due to growing interest in the study of gelatin biodegradable films, this paper aims to review recent research into the functional properties of gelatin biodegradable film and how they are affected by plasticizers.

2. Biodegradable film packaging

The primary biopolymers used to develop biodegradable films include proteins, lipids, and polysaccharides. Biomaterials or biopolymers are polymers that are bio-based and biodegradable in nature. Polymers were usually produced from renewable feedstock, biomass in general, and had considerable ecological benefits, like decreased carbon dioxide emissions (Imre & Pukánszky, 2013). Biomaterials derived from food ingredients, such as proteins, lipids and polysaccharides, were edible and had a high potential to replace petrochemical-based plastics as edible film packaging (Hanani et al., 2014a, 2014b).

The materials used play an important role in determining the quality of film produced. Biomaterials that could be used for film making included polysaccharides, proteins, lipids and polyesters, or combinations of these materials (Ghanbarzadeh & Almasi, 2011). Biomaterials could stand alone (i.e. single polymers) as films or could be blended with other polymers to improve the characteristics of the film. Single biodegradable films that have been examined include chitosan (Leceta, Guerrero, Ibarburu, Dueñas, & De la Caba, 2013), gelatin (Nor et al., 2017; Nur Hazirah, Isa, & Sarbon, 2016), and starch (Müller, Laurindo, & Yamashita, 2009). The most commonly blended biomaterials include gelatin/ chitosan (Abruzzo et al., 2012), starch/ gelatin (Soo & Sarbon, 2018), gelatin/ carboxymethyl cellulose (Nazmi et al., 2017), pectin/gelatin (Farris et al., 2011), and SPI/ gelatin (Guerrero, Hanani, Kerry, & De la Caba, 2011).

Among all biomaterials, protein is the material commonly studied because of its good functional properties as a food packaging material. Proteins confers a broad range of functional properties, especially a high intermolecular binding potential, due to its unique structure (based on 20 different monomers) (Vieira, Da Silva, Santos, & Beppu, 2011). Protein-based biodegradable films have high potential in forming numerous linkages and could form bonds at different positions (Kokoszka et al., 2010; Vieira et al., 2011). Protein-based films exhibit poor water resistance and lower mechanical strength than that of synthetic films. However, proteins provide films with greater mechanical and barrier properties as compared to polysaccharides (Guilbert, Cuq and Gontard, 1997). Protein-based films possessed better barrier properties for carbon dioxide and oxygen, as well as improved mechanical properties, when compared with polysaccharide films.

Various types of proteins have been used for the development of edible/biodegradable films, such as soya protein (Guerrero et al., 2011), corn zein (Cho, Lee, & Rhee, 2010), sodium caseinate (Fabra, Talens, & Chiralt, 2010), pea proteins (Kowalczyk & Baraniak, 2011), sunflower protein (Salgado, Ortiz, Petruccelli, & Mauri, 2010) and gelatins (Nor et al., 2017; Nur Hazirah et al., 2016). Among protein films, gelatin-based films likely to have a huge potential for commercial application as green packaging films due to their unique characteristics (Mikkonen et al., 2012). Compared to other materials that had high melting temperatures, gelatin was thermo-reversible and had ability to

'melt-in-the mouth'. It also acts as a gelling and thickening agent, emulsifier and stabilizer, and is easy to handle and use (Johansson et al., 2012; Marsh & Bugusu, 2007).

In addition, single gelatin films have also been combined and blended with other biomaterials in order to improve the functional properties of the film produced. Studies have shown that development of blended gelatin films would improve the physical and mechanical properties of film produced such as gelatin/ corn oil blended films (Wang, Auty, Rau, Kerry, & Kerry, 2009); gelatin/ alginate/corn oil blended films (Liu, Kerry, & Kerry, 2006); gelatin/ chitosan blended films (Celis, Azocar, Enrione, Paez, & Matiacevich, 2011); gelatin/ carrageenan/ gellan gum blended films (Pranoto, Lee, & Park, 2007) and gelatin/ glutaraldehyde blended films (Chiou et al., 2008).

The properties of biodegradable gelatin films depend greatly on the properties of the raw materials obtained from the different animal species, and on the manufacturing and processing conditions of the gelatin. They are also greatly influenced by the addition of plasticizers (Lukasik & Ludescher, 2006) or crosslinking agents (Cao et al., 2009). Guilbert et al. (1997) reported that hydrophilic, low-molecular weight molecules such as glycerol and sorbitol, easily fitted into protein networks and formed hydrogen bonds with reactive groups on amino acid residues, thereby reducing protein-protein interactions. Increasing the concentration of plasticizers in a film-forming solution normally produces film that was less stiff, less rigid, and more stretchable. This is achieved by lowering the biopolymer chains interaction (Arvanitoyannis, 2002). According to Thomazine, Carvalho, and Sobral (2005), glycerol plasticized gelatin films are moisture sensitive and more stretchable than sorbitol plasticized films. Glycerols are often cited as good plasticizers for protein-based materials due to their ability to reduce intermolecular hydrogen bonding while increasing intermolecular spacing. As a small hydrophilic molecule which could be inserted between protein chains, it acts as a plasticizer. As glycerol is interspaced in the protein network, the distance between the protein chains increases and direct interactions are reduced (Guo et al., 2012).

However, a mixture of glycerol and sorbitol produced films that had intermediate mechanical, water vapour barrier, and viscoelastic properties compared to films plasticized with sorbitol or glycerol alone. Other plasticizers such as ethylene glycol, diethylene glycol and propylene glycol have also been found to be compatible with gelatin. However, they are less efficacious than glycerol and are less effective as plasticizers in terms of the resulting functional properties (Vanin, Sobral, Menegalli, Carvalho, & Habitante, 2005). Other plasticizer found to be less efficient to plasticized gelatin film due to their chemical characteristic that is less compatible when plasticized with gelatin film. Glycerol provides films with better functional properties, as it can form more hydrogen and covalent bonds when plasticized with glycerol than that of other plasticizer.

3. Plasticization effect on gelatin film formation

Plasticization refers to a change in the thermal and mechanical properties of a given polymer which involves lowering of rigidity at room temperature, lowering of temperature, at which substantial deformations can be affected with not too large forces, increase of the elongation to break at room temperature (Zhu, Li, Huang, Chen, & Li, 2013). These effects can be achieved by compounding a given polymer with a low molecular weight compound or with another polymer and by introducing into the original polymer a comonomer which reduces crystallizability and increases chain flexibility (Chang et al., 2006).

Plasticizer is commonly defined as desired properties of a given polymer plasticizer system. For films, it defined as a compound that gives shock resistance, flexibility, and enhanced film workability (Vanin et al., 2005). For plastics, it is a compound that offers a preferable degree of flexibility over a wide range of temperatures and reduces the brittle point (Zhang & Rempel, 2012). However, there seems to be no way to characterize plasticizer behavior in terms of certain fundamental properties. This is because the behavior of the plasticizer depends on greatly to the polymer to which it is added (Zhang & Rempel, 2012).

The efficiency of plasticizer greatly depends on its concentration. Study found that the lowering of T_g in films is directly proportional to the concentration and molecular structure of plasticizer in the polymeric material (Bergo, Moraes, & Sobral, 2013). While some researchers have persisted on using molar concentrations, and it was later reported that molar concentration can be used to compare the effectiveness of plasticizers (Sanyang, Sapuan, Jawaid, Ishak, & Sahari, 2016). Generally, with a given polymer such as polyvinyl chloride, for each plasticizer such as the sebacates, adipates, or phthalates, there is a molecular weights range in which the plasticizer effectivity is optimum (Chen & Zhao, 2012). The polarity of plasticizer molecules may also influence the effectiveness of the plasticizer. Polar plasticizers must be used with polymers containing polar groups to achieve good compatibility. There is a higher chance for plasticizer polarity to overcome the forces between the polymer molecules as the distance between the polar groups along the polymer chain gets smaller. However, no plasticization occurs when the molecular forces of the plasticizer become stronger than the plasticizer polymer interactions. It was also agreed that better plasticization occurs if the polar group is located on an aliphatic molecule rather than on an aromatic molecule. This is due to the greater mobility of the aliphatic molecules (Dyson, 2003).

Numerous studies have reported the plasticization effect of sorbitol and glycerol on various sources of starches in developing biodegradable or edible films (Bakry et al., 2017; Nor et al., 2017; Soo & Sarbon, 2018). A minimum of 20% glycerol or any other suitable plasticizer is required to plasticize gelatin film successfully (Pushpadass, Marx, & Hanna, 2008). With increasing plasticizer amounts, properties like tensile strength, Young's modulus, and glass transition temperature (T_g), decrease, while elongation and gas permeability increase. A gelatin film which contains 25% glycerol is reported to exhibit maximum tensile strength and optimum modulus of elasticity (Pushpadass et al., 2008). Nevertheless, Hanani et al. (2014a, 2014b) found that glycerol molecules can migrate from film matrix when used as a plasticizer alone. Jongjareonrak, Benjakul, Visessanguan, and Tanaka (2008) and Zhong and Xia (2008) also noticed parallel trends with gelatin films plasticized with glycerol only. However, the gelatin film was found to be easily cracked when sorbitol alone is used as plasticizer as reported by Sobral, Monterrey-Q, and Habitante (2002) in the case of bovine gelatin films. Hence, Bergo et al. (2013) described that the incorporation of glycerol-sorbitol as plasticizer in gelatin film produced films with stable film properties rather than using glycerol and sorbitol separately. According to Mali et al. (2005), when mixed plasticizers are used in film matrix, it infers strong plasticizer–plasticizer interactions, which can improve certain film properties. Elsewhere, Al-Hassan and Norziah (2012) also reported the significance of incorporating two plasticizers, especially polyols, at different concentrations to determine their effectiveness in producing gelatin-based films.

4. Plasticizers in gelatin film formation

In biopolymer-based films, plasticizers could be grouped into those that were water soluble and water insoluble (Siepmann, Paeratakul, & Bodmeier, 1998). The amount and the types of plasticizers strongly affected film formation from the dispersions of polymer in aqueous solution (Johnson, Hathaway, Leung, & Franz, 1991). Hydrophilic plasticizers dissolved in the aqueous solution when they were added to polymer, however, if added in high concentrations, it could lead to an increase in water diffusion in the polymer (Hanani et al., 2014a, 2014b). In contrast, hydrophobic plasticizers could close the microvoids in the film, thus decreasing the water uptake. However, water insoluble plasticizers could cause phase separation that lead to loss of flexibility or formation of discontinuity zones during film drying, thus increasing water vapour permeability rates (Vieira et al., 2011).

Table 1
Types of plasticizer used in single and blended gelatin films.

Types of film	Types of plasticizer	References
Single film		
Gelatin	Glycerol	Tongnuanchan, Benjakul, and Prodpran (2013); Ahmad et al. (2012); Nor et al. (2017); Nur Hazirah et al. (2016)
	Sorbitol	Rivero, García, and Pinotti (2010); Peña, De la Caba, Eceiza, Ruseckaite, and Mondragon (2010); Nunez-Flores et al., 2013; Bakry et al. (2017)
Starch	Glycerol	Ghanbarzadeh et al., 2011; Muscat et al. (2012)
	Sorbitol	Abdorreza, Cheng, and Karim (2011)
	Xylitol	Muscat et al. (2012)
Carboxymethyl cellulose (CMC)	Glycerol	Tongdeesoontorn et al. (2011); Ghanbarzadeh et al., 2011; Tong et al. (2013)
	Sorbitol	Ghanbarzadeh et al., 2010; Tongdeesoontorn et al. (2011); Tong et al. (2013)
	Xylitol	Tong et al. (2013)
	Fructose	Tong et al. (2013)
Alginate	Xylitol	Santana et al., 2013
Whey protein isolate	Glycerol, sorbitol, xylitol	Guo et al. (2012)
Blended		
Starch-gelatin	Glycerol, sorbitol	Al-Hassan and Norziah (2012); Fakhoury et al. (2012);
SPI-gelatin	Glycerol	Guerrero et al. (2011)
Pectin-gelatin	Glycerol	Farris et al. (2011)
Chitosan-gelatin	Glycerol	Gomez-Estaca et al., 2009; Hosseini, Rezaei, Zandi, and Ghavi (2013)
Starch-CMC	Glycerol	Ghanbarzadeh et al., 2011
CMC-gelatin	Glycerol	Nazmi et al. (2017)

Hydrophilic plasticizers include polyols, fatty acids, monosaccharides, disaccharides and oligosaccharides. Hydrophobic plasticizers are citrate esters derived from citric acid (Labrecque, Kumar, Dave, Gross, & McCarthy, 1997). Among these plasticizers, hydrophilic plasticizers were found to be particularly efficient in plasticizing gelatin films (Li & Huneault, 2011). Among the hydrophilic plasticizers studied in plasticizing biodegradable single and blended gelatin film was polyols such as glycerol (Nor et al., 2017), ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), polyethylene glycol (PEG), propylene glycol (PG) (Al-Hassan & Norziah, 2012; Santana & Kieckbusch, 2013), sorbitol (Nur Hazirah et al., 2016), mannitol (Liew et al., 2014; Mikus et al., 2014) and xylitol (Tong et al., 2013). Table 1 shows studies that successfully conducted by researchers using various plasticizers in both single and blended gelatin films.

Hydrophobic plasticizers such as citrate esters which derived from citric acid has been used in the pharmaceutical field for the production of biodegradable materials, but not commonly used in the films formulations (Labrecque et al., 1997). Citrate esters which showed fast biodegradability did not present sign of toxicity and were legally used as additives in plastics for medical applications, personal care products and as food packaging materials (Rahman & Brazel, 2004). Hydrophobic plasticizers such as tributyl citrate, acetyltributyl citrate, triethyl citrate and acetyltriethyl citrate were used in the production of polyvinyl alcohol films and resulted in the increase of the flexibility of the films, which reached elongations above 600%. However, increasing concentration of plasticizers caused a reduction of tensile strength up to 80%, also reduced the glass transition temperature of the resulting films (Labrecque et al., 1997), similar to the behavior observed in biodegradable and edible films plasticized with polyols (Sobral, Menegalli, Hubinger, & Roques, 2001). In addition, study by Andreuccetti, Carvalho, and Grosso (2010) found that, gelatin-based films containing hydrophobic plasticizers (ATB, TB and ATC) and the saponin extracted from Y. schidigera (yucca) as surfactant, showed good mechanical resistance (TS), low values of water vapour permeability and reduced drying times.

4.1. Functional properties of gelatin film affected by plasticizers

Recent research has focused on developing new biodegradable food packaging materials using gelatin because of its total biodegradable nature. Gelatin has also gained much interest because of its excellent filmogenic properties, good ability to form film, and its usefulness as an primary packaging film that protects food from drying and from exposure to oxygen and light (Arvanitoyannis and Stratakos, 2012). Different sources of gelatin have also been used to make biodegradable films. For example, gelatin from tuna skin (Gómez-Estaca, Bravo, Gómez-Guillén, Alemán, & Montero, 2009), Nile perch skin (Muyonga, Cole, & Duodu, 2004), pigskin (Sobral et al., 2001), bovine bone (Cao et al., 2009), bovine hide (Rivero et al., 2010), and chicken skin (Nor et al., 2017) have been used in developing film packaging. Gelatin had been deliberated as the most assuring materials for film production. However, they presented poor mechanical properties due to their fragility and brittleness during film formation, which limits their potential for such applications (Falguera et al., 2011). Findings relating to the functional properties of gelatin film and how they are affected by different plasticizers are shown in Table 2.

4.1.1. Mechanical strength

Sufficient mechanical strength and flexibility are necessary for packaging film to endure external stress, as well as to maintain its integrity and barrier properties during packaging (Rao, Kanatt, Chawla, & Sharma, 2010). The tensile strength, elongation at break and puncture test values for gelatin-polyols plasticized film are shown in Table 2. These range from 0.99 to 38.79 MPa, 1.25–294.5% and 2.44–54.8 N, respectively. The ranged included gelatin-glycerol (Hosseini et al., 2013; Nor et al., 2017), gelatin-sorbitol (Bakry et al., 2017), gelatin-polyethylene glycol (Pranoto et al., 2007), and gelatin-mannitol (Pranoto et al., 2007). The value for gelatin-monosaccharides plasticized film were in the range of 0.59–17.94 MPa, which included gelatin-sucrose (Giménez, De Lacey, Pérez-Santín, López-Caballero, & Montero, 2013) while for gelatin-lipid plasticized film the value ranged from 0.95 to 14.71 MPa (Tongnuanchan et al., 2013). Higher mechanical strength resulted in stronger films (Vanin et al., 2005). It may thus be concluded that film plasticized with glycerol has good mechanical strength. Su, Huang, Yuan, Wang, and Li (2010) concluded that glycerol with a small size molecule plasticizer penetrates between the polymer chains, weakening the interaction between polymer materials as in polysaccharides and proteins film and increasing its flexibility and extensibility. Sothornvit (2014) demonstrated that hygroscopic nature of glycerol contributed more plasticization effect compared to any other plasticizer, thus increasing the mobility of polymer chains and leading to increased stretchability and flexibility of films.

4.1.2. Water vapour permeability (WVP)

It is necessary to have an understanding of a film's permeability characteristics and moisture content to use it in food packaging. One of

Table 2
Functional properties of gelatin films as plasticized by different types of plasticizer.

Types of film	Plasticizer	Functional properties						References
		Thickness (mm)	TS (MPa)	EAB (%)	Puncture test (N)	WVP (g.mm/m^2 h Pa) × 10^{-4}	Light transmission (%)	
Gelatin-starch	Glycerol, sorbitol	0.05–0.09	1.28–25.03	4.33–102.31	–	1.30–3.97	0.86–2.12	Al-Hassan and Norziah (2012)
Gelatin	Glycerol	0.02–0.05	1.75–3.49	2.54–3.46	2.44–5.22	4.0–4.8	–	Nor et al. (2017); Nur Hazirah et al. (2016)
Gelatin	Polyethylene glycol (PEG)	0.02–0.03	33–80	3.50–5.90	–	0.2–2.3	–	Cao et al. (2009)
Gelatin-tea extract	Glycerol	0.01–0.02	15.20–23.40	30.80–62.80	–	1.81–2.63	0.04–0.57	Li, Miao, Wu, Chen, and Zhang (2014)
Gelatin-manioc starch	Glycerol, sorbitol	0.03–0.07	64.29–166.32	3.89–9.94	–	4.17–6.40	–	Fakhoury et al. (2012)
Gelatin-glutaraldehyde	Glycerol	0.02–0.07	2.70–4.40	1.25–1.72	–	0.22–0.31	7.4–17.6	Kavoosi, Dadfar, and Purfard (2013)
Gelatin-alginate-WPI	Glycerol	0.02–0.05	7.09–10.77	12.55–29.42	11.56–32.63	4.80–7.58	8.0–40.0	Wang et al. (2009)
Tilapia skin gelatin	Glycerol	0.03–0.05	35.3–63.5	4.7–8.81	–	1.70–3.13	1.44–18.38	Nagarajan, Benjakul, Prodpran, and Songtipya (2014)
Gelatin-citrus oil	Glycerol	0.04–0.05	25.87–42.86	9.61–62.79	–	2.81–4.07	2.14–5.66	Tongnuanchan et al. (2013)
Pig hide gelatin	Tributyl citrate, acetyl-tributyl citrate,	0.04–0.06	9.30–30.71	3.06–12.24	–	0.17–0.32	16.9–33.9	Andreuccetti, Carvalho, and Grosso (2009)
Red snapper gelatin	Glycerol	0.02–0.04	7.97–58.10	3.40–95.04	–	1.31–2.61	0.3–13.1	Jonjareonrak et al., 2006
Bovine gelatin	Glycerol	0.02–0.05	0.15–19.62	–	–	3.21–3.87	–	Rivero et al. (2010)
Cuttlefish gelatin	Glycerol	0.03–0.04	11.64–45.63	2.45–5.39	–	0.66–1.18	1.33–1.40	Hoque et al., 2011
Gelatin	Sorbitol	0.05–0.07	–	–	5.8–15.7	2.2–3.9	–	Sobral et al. (2001)
Gelatin	Glycerol	0.04–0.06	1.26–29.1	4.1–30.8	–	0.7–2.6	–	Thomazine et al. (2005)

Abbreviations: TS = tensile strength; EAB = elongation at break; WVP = water vapour permeability.

the permeability characteristics had been water vapour permeability (WVP). The barrier properties for water vapour of packaged products, and the related physical or chemical deterioration of the products, was related to its equilibrium moisture content, and was of great importance in maintaining or extending its shelf life (Siracusa et al., 2008). Table 2 demonstrated the WVP values of single and blended from different gelatin source with single and blended plasticizers used. Combination of two type's polyols plasticizer in gelatin films resulted in better WVP values as compared to the single polyols plasticizer used in film production. The water vapour permeability value for plasticized gelatin film with polyols were in the ranged of $1.32 - 6.78 \times 10^{-8}$ (g mm/ Pa h cm^2), and included gelatin-glycerol (Nor et al., 2017), gelatin-sorbitol (Bakry et al., 2017), gelatin–polyethylene glycol (Pranoto et al., 2007), and gelatin-diethylene glycol (Núñez-Flores et al., 2013). For plasticized gelatin films with monosaccharides, the range was $1.73 - 18.6 \times 10^{-8}$ (g.mm/ Pa.h.cm^2), which included gelatin-glucose (Vanin et al., 2005): the plasticizers used in this study were: GLY—-glycerol, PPG—propylene glycol, ETG—ethylene glycol, DTG— diethylene glycol. Overall, gelatin-polyols plasticized film showed the lowest range of WVP compared to gelatin-monosaccharides plasticized films. As shown in Table 2, the gelatin film plasticized with Tributyl citrate and PEG showed significantly lower WVP. This is because Tributyl citrate and PEG possess hydrophobic character in which it will limits the amount of water vapour passing through the film membrane, thus lowering the WVP. Lower WVP values indicated good water vapour barrier properties of the films. Single gelatin films with a higher concentration of protein blot more water from the surrounding environment due to the existence of hydrophilic amino acids in the gelatin. Therefore, the presence of polysaccharide in the film enhanced the cross-linking of gelatin and lowered the free volume of the polymeric matrix, thus lowering the rate of water molecules passing through the film membranes and resulting in lower WVP (Hosseini et al., 2013).

4.1.3. Crystalline and structure analysis

Film structure was an important characteristic in film production because it contributed to the physicochemical properties and industrial applications of the film. An X-ray diffraction analysis was performed to quantify the crystalline and amorphous structure of polymers in film materials. The diffractogram acquired on the gelatin films plasticized with polyols were typical of a partially crystalline gelatin with peak ranges at $2\theta = 7.8^{\circ} - 20.5^{\circ}$ that included gelatin-glycerol (Nor et al., 2017; Soo & Sarbon, 2018) and gelatin-sorbitol (Bakry et al., 2017). Gelatin films plasticized with lipid and monosaccharides showed about the same peak ranges as film plasticized with polyols. These characteristic peaks were usually assigned to the triple-helical crystalline structure in collagen and gelatin (Peña et al., 2010). On the other hand, Bigi, Panzavolta, and Rubini (2004) demonstrated that the diffraction peak at $2\theta = 8^{\circ}$ was directly proportional to the diameter of the triple helix of gelatin and its intensity would be associated with the triple-helix content of the films. It was also found that the addition of polyols, such as glycerol, decreased the intensity of the peak ($2\theta = 8^{\circ}$). This structural change could be attributed to glycerol properties, both its high water affinity, as well as its interference in polymer interaction (Rivero et al., 2010).

4.1.4. Thermal properties

The thermal properties of the film depend on the state of the polymer (i.e. rubbery or glassy); it was therefore essential to investigate the glass transition temperature (T_g) of the film. This was an important parameter for the selection of storage and processing conditions of the film, also for film applications (Langmaier, Mokrejs, Kolomaznik, & Mládek, 2008). A few methods had been applied to study semi-crystalline materials, among them was differential scanning calorimetry (DSC). DSC was broadly used to certify the glass transition temperature of materials. Patil, Mark, Apostolov, Vassileva, and Fakirov (2000) reported that the strong tendency of decreased T_g in gelatin films upon

water uptake, similar trends had also been observed in biopolymer films plasticized with different plasticizers, such as Nile-tilapia protein (Sobral et al., 2001), methylcellulose and chemically crosslinked methylcellulose (Park, Whiteside, & Cho, 2008), wheat gluten protein (Irissin-Mangata, Bauduin, Boutevin, & Gontard, 2001), hydroxypropyl starch and gelatin (Arvanitoyannis & Stratakos, 2012), chitosan and gelatin (Rivero et al., 2010), gelatin (Sobral et al., 2001), and myofibrillar proteins (Guilbert, Gontard, & Gorris, 1996).

Polyols have been commonly cited as effective plasticizers for protein-based materials (Audic & Chaufer, 2005). The T_g value for gelatin-polyols plasticized film were in the range of 136.41–188.16 °C, and included gelatin-glycerol (Nor et al., 2017), gelatin-sorbitol (Bakry et al., 2017) and gelatin-mannitol (Sionkowska, Wisniewski, Skopinska, Kennedy, & Wess, 2004). The differences in values for each type of plasticizer are due to the differences in polyol concentration used for each study. In which the higher the concentration of polyols used showed the decreased of the T*g* values of gelatin films. This finding may due to the saturation of the protein matrix and consequently the slight decreasing of films miscibility between glycerol and gelatin as polyols concentration increased. While for gelatin-lipid plasticized films, the range was 67.85–113.46 °C (Tongnuanchan et al., 2013). The low T*g* values for gelatin-lipid plasticized films as compared to gelatin-polyols plasticized films was due to its hydrophobicity properties. Hydrophobic plasticizers may close the micro-voids in the film, leading to a decrease in water uptake. However, water insoluble plasticizers may cause phase separation, leading to flexibility losses or the formation of discontinuity zones during film drying (Vieira et al., 2011). As a consequence, water vapour permeability rates are increased due, resulting in low T*g* values. Among polyols, glycerol is the most widely used (Audic & Chaufer, 2005). Most literature cited described the effects of glycerol addition in low and middle concentrations, which is between 0% and 50%, on gelatin films (Langmaier et al., 2008). The middle concentrations of glycerol generally decreased the process temperatures, reduced moulds sticking and enhanced wetting. Glycerol also increases the temperature range of treatment, increases film toughness, and lowers glass transition temperatures (Sothornvit, 2014).

4.1.5. Functional group of gelatin-based films

The FTIR spectrum is crucial in film production as it determines the potential functional groups that perform specific functions in the gelatin film properties, such as tensile strength and water vapour permeability (Al-Hassan & Norziah, 2012). FTIR was used to study the molecular interaction in gelatin films as plasticized by different types of plasticizers. The important functional groups that correlated with gelatin films plasticized with polyols, lipid and monosaccharides were the hydroxyl group at wavelengths ranging from (3000–3500 cm^{-1}), amide I (1640–1650 cm^{-1}), amide II (1539–1550 cm^{-1}), and amide III (1033–11035 cm^{-1}) (Altiok, Altiok, & Tihminlioglu, 2010; Nor et al., 2017).

Amide-I vibration mode is basically a C=O stretching vibration conjoin with the CN stretch, in plane NH bending modes and CCN deformation (Bandekar, 1992). The spectral differences in amide-I region between different film samples were largely indicated to different orientation and conformation of polypeptide chains as was affected by the addition of gelatin. The shifting of the amide-I peak to a lower wavenumbers of gelatin films is due to the conformational changes that cause a decrease in molecular order (Altiok et al., 2010). The change in molecular order is due to the gelatin concentration incorporated and intermolecular interaction arose during the film drying process. These results associated with decreased tensile ability as the gelatin concentration incorporated in the films increased.

Amide-II vibration modes are associated with out-of-plane combination of the CN stretching vibration and the NH in plane bend with smaller contributions from the CC and NC stretching vibrations as well as the CO in plane bends (Jackson & Mantsch, 1995). The shifting of amide-II to lower wavenumbers leads to intermolecular interactions between plasticizers and gelatin molecules (Cheng et al., 2002). In addition, amide-III may be attributed to the combination peaks between N–H deformation and C–N stretching vibrations from amide linkages, as well as arising absorptions from fluctuating vibrations from CH_2 groups from the proline side-chains and glycine backbone of gelatin molecules (Jackson & Mantsch, 1995). A study conducted by Nor et al. (2017) the increased of glycerol concentration caused the displacements with increased intensity and wider, sharper peaks. Such displacements may be related to additional interactions arising between glycerol and film structure. This also reflects the presence of free water. These same peak amplitudes increased with more glycerol content, thus increasing the amount of free water (Bergo & Sobral, 2007).

However, new peaks aliphatic group have been observed in the range of 1030–1070 cm^{-1} when gelatin films were plasticized with glycerol; this peak corresponds with the glycerol, which increased intensity with the increase of glycerol content (Nor et al., 2017). These results have confirmed that the loss of film elasticity and flexibility was due to the lower concentration of glycerol used in the films. The present of aliphatic group indicates that the content of glycerol in gelatin films at the highest glycerol concentration is high enough to exhibit a signal in an infrared spectrum (Nor et al., 2017).

The interactions between the plasticizer and the polymer depend on the molecular size, configuration, and total number of functional hydroxide groups of the plasticizer, as well as its compatibility with the polymer (Wittaya, 2013). Sorbitol is comparably less effective than glycerol among three due to its larger molecular size (not readily insert between polymer chains), higher molecular weight (less number of –OH functional groups per mole), as well as the presence of ring molecular conformation that sterically hinder insertion between the protein chains, leading to less efficient interchain interruptions (Wittaya, 2013).

4.1.6. Light barrier properties (optical properties)

The optical barrier property is a crucial attribute which influenced suitability, appearance and marketability of the films for various applications. Luminous edible films are habitually desirable with higher acceptability and applicability in food packaging systems (Ahmad et al., 2012). One of the functions of food packaging films is to protect foods from the effects of light, especially from UV radiation (Li et al., 2014). Films with a lower UV light transmission value possessed a better barrier of UV penetration through the film. The UV light transmission of gelatin films plasticized with polyols is in the range of 0.04–33% light transmission at wavelengths of about 200–280 nm and 2.9–33% at wavelengths of about 280 nm and includes gelatin-glycerol (Nor et al., 2017), gelatin-sorbitol (Bakry et al., 2017) and gelatin-xylitol (Núñez-Flores et al., 2013). For gelatin-lipid plasticized films, the UV light transmission exhibited a range of 0.35–8.31% light transmission at wavelengths of about 280 nm (Hoque, Benjakul, & Prodpran, 2010). Within the UV range of 200–280 nm, gelatin-monosaccharides plasticized films allow lower UV light penetration on the films that caused the oxidative deterioration of food products, and which led to rancidity, off-flavours, nutrient losses and discoloration (Martins et al., 2012). Overall, lowering transmission was observed when concentrations of gelatin increased. The results indicate that gelatin, especially at higher concentrations and higher light transmission barriers, is more likely to exhibit limited film light transmissions at visible range. When glycerol is incorporated, films became more transparent. Essential oil such as virgin coconut oil, rosemary oil and argan oil, which are clear and transparent in nature, may contribute to the transparency of the films to some extent. The optical properties of plasticized materials are related to the plasticizer type and concentration used (Chang & Nickerson, 2014). The light transmission of UV and visible light increases with increasing glycerol content (Nilsuwan, Benjakul, & Prodpran, 2016; Nor et al., 2017). It is due to the effect of glycerol added to reduce the compactness of the film matrix, thus allowing higher light transmission of the films. As the glycerol concentration increase, the transparency

values tend to increase (Nor et al., 2017). Higher transparency values indicate a more opaque film, which may be due to the higher polymer chain compaction that modifies the refractive index and restrict the light passage through the film matrix (Ortega-Toro, Jiménez, Talens, & Chiralt, 2014).

4.1.7. Film microstructure

Apprehension of film microstructure is of great importance as it determines the mechanical, physicochemical and barrier properties of the film, and also conditioned its application. Scanning electron microscopy (SEM) was conducted to study the microstructural changes in gelatin films and to obtain the surface and cross-section topography of the films. SEM shows that the internal structure of gelatin films plasticized with polyols contained the presence of discontinuous zones that were characterized by horizontal cracks randomly distributed along the networks (Vanin et al., 2005). The addition of plasticizers leads to the disruption of the smooth and homogeneous structure of the parent gelatin film, which may be attributed to the formation of preferential channel during the drying process of the filmogenic solution (Hanani et al., 2014a, 2014b). The addition of lipids as plasticizers has been found to modify the internal structure of fish gelatin films, and the lipids eliminates the present cracks, which resulted in compact and dense appearances (Falguera et al., 2011). Lipids could initiate some linkages between the fibrillary zones of the fish gelatin through polyelectrolytes association with the gelatin. Differing from those added with lipids, the addition of polyols, especially glycerol, showed a light modified internal structure of the fish gelatin films (Gómez-Guillén et al., 2009; Rivero et al., 2010). However, both levels result the cracks in the film matrices remaining. The microstructure observations also explains the for improvements in tensile strength and WVP properties of modified fish gelatin films, as polyols were found to modify the film matrix more distinctly than either lipids or monosaccharides.

5. Current and future trends

Synthetic packaging materials are gradually being replaced by biopolymer especially those derived from protein. More than the origin, the chemical structure of a biopolymer determines its ability to degrade naturally. It has been observed that the use of such green packaging will strengthen the economic potential of agricultural processors and farmers. Extended research on multicomponent and bilayer films resembling synthetic packaging materials with excellent mechanical and barrier properties must be encouraged. The plasticizing, either enzymatically or chemically, of the various plasticizers is yet another appeal of value in developing biodegradable films. Recently, the use of nanotechnology food packaging has been a major focus on packaging to prevent food spoilage, increase shelf life, and provide quality and safety to the consumers as well as to ensure food reaches them in a wholesome form. Nanotechnology solutions focus on food safety by controlling pathogenic microbial growth, improving tamper visibility, delaying oxidation, and convenience. The use of nano-based packaging materials in food packaging films has also raised a number of environmental, ethical, safety, and regulatory issues. However, nanotechnology is expected to play an important role, taking into consideration all additional safety measures and the present packaging needs of the food industry.

6. Conclusion

Glycerol has been found to be particularly effective in plasticizing gelatin films due to the hydrophilic nature of the film produce, thus resulting in high environmental susceptibility. Other polyols plasticizers also produce gelatin film with good functional properties under certain condition. However, different types, blending and concentration of plasticizers use different mechanisms when plasticizing gelatin film. There have been few studies conducted on the quality properties of plasticized gelatin films. However, one study resulted in a unified phase diagram of gelatin films plasticized by hydrogen bonded liquids. More research is needed to provide information about the properties of the gelatin film when plasticized with different plasticizers with different types, blends, and concentrations. The molecular mechanisms which control functionality in gelatin films, such as physical cross-links of water and glycerol that involve in gelatin films formation, especially on its hydrogen-bonding molecules, call for more exploration. Reaching an understanding of the plasticizing effects of water and glycerol will be broadly useful in gelatin film pharmaceutical capsule production.

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