Plasticiser Effect on Water Vapour Permeability Properties of Locust bean gum–Based Edible Films

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The barrier properties of edible films prepared from polysaccharide polymer (locust bean gum) and various plasticisers (glycerol, propylene glycol, sorbitol, and polyethylene glycol 200) together with hydrophobic modifiers (stearopten and beeswax) were examined. It was determined that the films containing polyethylene glycol 200 (PEG 200) and sorbitol have the lowest water vapour permeability values and the films containing glycerol have the highest WVP values. It was found that the most reasonable of the studied plasticisers was PEG 200. Polysaccharide–based edible films have higher WVP values than those of lipid– and protein–based edible films. In order to reduce the WVP of locust bean gum (LBG) based edible films they were modified by adding a small amount of stearopten or beeswax to the film structure. It was determined that the WVP values of such modified edible films were always lower than those of unmodified films.

Key Words: Locust bean gum, edible film, water vapour permeability, plasticiser, stearopten, beeswax.

Introduction

Locust bean gum (LBG) is obtained from the seeds of the evergreen tree *Ceratonia siliqua* L. which is indigenous to the Mediterranean region. It is a neutral polysaccharide consisting of linear chains of (1-4)–linked $\beta-$D–mannopyranosyl residues to which are attached (1-6)–linked $\alpha-$D–galactopyranosyl groups as single unit side chains[1]. Due to its high water solution viscosity in a wide range of pHs and temperatures, this polysaccharide polymer can be used in the food industry as a thickener, stabiliser and dispersion agent[2].

Film formation and the properties of several polysaccharide materials such as starch and starch derivatives, cellulose derivatives, alginates, carrageenan, chitosan, pectinates, and various plant and microbial gums have been reviewed by Nisperos-Carriedo[3].

Edible films and coatings can control mass transfer between components within a food product as well as a food and its surrounding atmosphere, thereby improving food quality and extending shelf life.

Because of their ability to associate by hydrogen bonding and, in some cases, electrostatic forces, hydrophilic polymers such as polysaccharides can form strong chain – to – chain interactions which provide

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a good barrier to O_2 and CO_2^{4-7}. However, these interactions are adversely affected by moisture absorption, and so increasing the relative humidity reduces the barrier. On the other hand, the hydrophobic nature of lipid – based edible films provide more effective moisture barrier properties.

The water vapour permeability (WVP) of polysaccharide – based edible films can be improved by the addition of hydrophobic materials such as beeswax (BW), carnauba wax, paraffin wax and oil acids[8−11]. BW, which is one of the most commonly used lipids in the production of edible films with the emulsion technique, mostly consists of long chain hydrocarbons, long chain alcohols and long chain acids[12]. Forming a stable emulsion of lipids within the film forming solution can reduce the WVP of the resultant film. The effectiveness of emulsified lipids in reducing the WVP of whey protein films has been reported[10,13,14]. In these studies, it was shown that BW provides the best moisture barrier in an emulsion film. Another hydrophobic material, stearopten (St), is a by-product of rose absolute production, and similar to BW consists of long chain alcohols, long chain hydrocarbons, long chain acids, and their esters[15]. However, St is more hydrophobic than BW. The presence of the St in rose and rose jams encouraged us to use this material as a modifier in the formation of edible films having relatively lower WVP values. Therefore, in this study the first use of St as a modifier in an edible film has been performed.

When added to the film forming solutions, plasticisers can drastically reduce the intermolecular forces, increase the mobility of the polymer chains, and improve the mechanical properties of the films[3,6,16−25]. However, the addition of plasticisers adversely affects the barrier properties and increases mass transfer through the films. Polyethylene glycol 200 (PEG 200), glycerol (Gly), propylene glycol (PG), and sorbitol (S) are the most commonly used plasticisers in edible film production[26]. Aydinli et al. examined the effects of the amount and molecular weight of PEG on the WVP properties of LBG – based edible films[16]. They found that the WVP values of edible films increased with both the quantity and molecular weight of PEG up to PEG 600.

The aim of this study was to produce LBG – based edible films with different plasticisers and modifiers in an attempt to develop more effective edible films against water vapour transmission.

Experimental

Materials

PEG 200, Gly, and S were purchased from Sigma Chemical Company. PG and BW were supplied by Fluka Chemie AG and Aldrich Chemical Company, respectively. St was obtained from rose concrete in our laboratories. KCl was used to prepare saturated salt solutions. Carob pods (*Ceratonia siliqua* L.) were supplied from Seryem A.Ş. Antalya, Turkey.

Preparation of LBG

Carob pods (150 g) were crushed mechanically in a blender and sieved to separate the polymer from its outer shell and embryo. The separated polymer was washed with water and then 500 mL of water was added. This mixture was heated for 30 min at 70 °C while spinning at high speed. The obtained solution was added slowly to 2L of ethanol (960 g/L) and mixed for 10 min at room temperature. The precipitated polymer was then filtered using a sieve (0.160mm), separated into small pieces and dried at room temperature. Finally, it was dried in a vacuum oven (Nüve EV 018) at 50 °C and 2666 Pa for 8 h.

Preparation of films

Film – forming solutions were prepared by dissolving 0.7 g of LBG in 75 mL water kept at 70 °C for 2 h using a water bath. The prepared film solutions were homogenised at 13,500 rpm for 2 min with an Ultra–Turrax T 25 homogeniser, and then different plasticisers were added, to the film solution. For each film solution 0.3, 0.6, 0.9, and 1.2 mL plasticisers (Gly, PEG 200 and PG) were added respectively. For S, 0.364 g, 0.728 g, 1.092 g, and 1.456 g were melted and then added, respectively. Then each of these solutions was homogenised at 18,000 rpm for 5 min. In the preparation of modified edible films, after this step, 0.1 g of melted BW and 0.1 g of St were added to the film forming solutions and then each of these solutions was homogenised at 25,000 rpm for 8 min. Due to the high viscosity of the resultant film solutions, removing the dissolved air was not possible under vacuum. Consequently, evaporation was carried out for degassing at 35 °C and under 20 mmHg pressure. During this operation, about 5 mL of water was removed. Solutions were then heated to 40 °C and spread on 20 x 20 cm^2 glass plates by adjusting the hand – operated plate coater of CAMAG thin–layer chromatography. The spread films were dried at 25 ± 5 °C and 60 ± 5 % RH for 1 day.

Thickness measurement

A hand–held Fowler micrometer was used to measure film thickness to an accuracy of 0.001 mm. Five measurements were made at different locations on the film and an average value was calculated.

Water vapour permeability measurement

Water vapour transmissions of films were measured using the ASTM E 96-93 method[27]. All samples were cut from films circularly and mounted using melted paraffin on special glass cups containing 3 g of CaCl$_2$[16,17]. The cups were weighed with their contents and placed in a dessicator containing saturated KCl solution in a beaker at the bottom providing a RH of 0.8434 at 25 ± 0.1 °C. The dessicator was kept in a Sanyo MIR 152 incubator at 25 ± 0.1 °C. Cups were weighed every 24 h until constant weights were achieved. The amount of water vapour transferred through the film was determined from the weight gain of the cup. Steady state conditions were achieved after a period of 6 days. Slopes (changes in weight of the permeation cell over time) were calculated by linear regression. Two replicates for each sample were measured. By dividing the slope of this linear portion with the total area of the film, the total water vapour transmission rate of each film was obtained. Then the permeance and permeability values were calculated using the equations shown below.

$$\text{WVTR} = [\Delta W/(\Delta t.A)] \; kg.s^{-1}.m^{-2} \tag{1}$$

$$\text{Permeance} = [\Delta W/(\Delta t.A.\Delta P)] \cdot kg.s^{-1}.m^{-2}.Pa^{-1} \tag{2}$$

$$\text{Permeability} = [(\Delta W.X)/(\Delta t.A.\Delta P)] \cdot kg.s^{-1}.m^{-1}.Pa^{-1} \tag{3}$$

where $\Delta W/\Delta t$ is the amount of water gain per unit time of transfer, X is the film thickness (m), A is the area exposed to water transfer (m^2), and ΔP is the water vapour pressure difference between both sides of the film (Pa).

Results and discussion

As LBG-based edible films prepared without any plasticiser are too sticky and brittle, it is not possible to remove them from the surface of the glass plate. Therefore, it is necessary to use a plasticiser. The hydrophilic nature of LBG necessitates the use of polar plasticisers for better compatibility, and because of this polar plasticisers (Gly, PG, S, PEG 200) were chosen. All plasticiser–LBG films, except for those 1.092g S/0.7 g LBG, 1.456 g S/0.7 g LBG, and S–BW–LBG, were clear after drying. LBG films containing 1.092 g and 1.456 g S and S–BW had a white residue on the surface. The appearance of a white residue on edible films containing plasticisers has been referred to as "blooming"[28] or "blushing"[23]. This occurs when the plasticiser concentration exceeds its compatibility limit in the polymer causing phase separation and physical exclusion of the plasticiser[28]. The clear appearance of all the other LBG–based edible films indicated that in these films, at the level used, the plasticisers were compatible with LBG.

The WVP values of LBG-based edible films containing different plasticisers (Gly, PG, S and PEG 200) and modifiers (BW and St) are given in the Figure. Film compositions and thickness values are also given in Tables 1, 2 and 3, respectively. In the Figure, the permeability values of the Gly–plasticised unmodified edible films increase as plasticiser amount rise. The high affinity of Gly for water aids the diffusion of water molecules and hence causes significantly large WVP values. As expected, Gly–plasticised films had larger WVP values than those of other films. PG, S and PEG 200 are less effective in reducing intermolecular hydrogen bonding between the polymer chains of LBG compared to Gly. As a result of this, the spacing between polymer chains is decreased, resulting in a reduction in WVP values. In a study by Gontard et al. similar results were found[21]. It was determined that the WVP values of the PG–plasticised films rose slightly with increasing amounts of PG. Testin et al. reported that increasing of the WVP values of methyl cellulose- and hydroxypropyl cellulose–based edible films depends on the increasing amount of PG[7]. Due to the appearance of a white residue on the surface of the films, 1.092 g S/0.7 g LBG and 1.456 g S/0.7 g LBG, almost the same WVP values were obtained for these 2 films. This residue may probably act as an additional barrier to water vapour transmission. The permeability values of PEG 200–plasticised LBG–based edible films were adopted from Aydinli et al. for comparison[16]. In our study, their modified forms were investigated. Aydinli et al. reported that the permeability values of these films did not change with plasticiser concentration[16]. Despite being used in relatively high amounts, permeability values of S–plasticised edible films were higher than those of PEG 200–plasticised films, although they are more hydrophobic.

In order to reduce the relatively high WVP values of these films, they were modified by adding small amounts of hydrophobic materials (BW and St) to the film–forming solutions. In all the experiments, the amount of added modifier was kept constant because of the blooming problems after drying. In addition their amounts must be small enough to produce safe edible films[3]. The WVP values of LBG–based edible emulsion films containing the same plasticisers in the same amounts and 0.1 g of St are given in the Figure. As seen in the results, the WVP values of emulsion films containing Gly slowly rose with increasing amounts of plasticiser and all emulsion films of this type had lower permeability values than those of the unmodified Gly–plasticised films. These results reveal that the addition of even a small amount of St to the film structure can reduce water vapour transmission through LBG–based edible films. The same results were obtained for emulsion films containing PG or S modified by adding 0.1 g of St. It is obvious that the presence of St in the film structure caused a sharp decrease in WVP values. When compared with the permeability values of PEG 200–plasticised emulsion films, it can be observed that the film containing 0.3 mL PEG 200/0.1 g

Table 1. Average thickness values of edible films containing Gly (glycerol), PG (propylene glycol), S (sorbitol), and PEG 200 (polyethylene glycol) of varying concentrations as a plasticiser.

Composition	Average film thickness (m)
Gly(mL):LBG(g)	
Gly:LBG (0.3:0.7)	2.0×10^{-5}
Gly:LBG (0.6:0.7)	2.8×10^{-5}
Gly:LBG (0.9:0.7)	2.7×10^{-5}
Gly:LBG (1.2:0.7)	2.4×10^{-5}
PG(mL):LBG(g)	
PG:LBG (0.3:0.7)	1.8×10^{-5}
PG:LBG (0.6:0.7)	1.8×10^{-5}
PG:LBG (0.9:0.7)	1.9×10^{-5}
PG:LBG (1.2:0.7)	1.8×10^{-5}
S(g):LBG(g)*	
S:LBG (0.346:0.7)	1.6×10^{-5}
S:LBG (0.728:0.7)	2.2×10^{-5}
S:LBG (1.092:0.7)	2.2×10^{-5}
S:LBG (1.456:0.7)	2.3×10^{-5}
PEG 200(mL):LBG(g)**	
PEG200:LBG (0.3:0.7)	1.6×10^{-5}
PEG200:LBG (0.6:0.7)	1.8×10^{-5}
PEG200:LBG (0.9:0.7)	1.7×10^{-5}
PEG200:LBG (1.2:0.7)	2.2×10^{-5}

*S is solid at room temperature, and for this reason the amount of S was taken in grams. ** Values were adopted from Aydinli et al. [16].

Table 2. Average thickness values of modified edible films containing 0.1 g of St and Gly, PG, S and PEG 200 of varying concentrations as a plasticiser

Composition	Average film thickness (m)
Gly(mL):St(g):LBG(g)	
Gly:St:LBG (0.3:0.1:0.7)	2.2×10^{-5}
Gly:St:LBG (0.6:0.1:0.7)	2.2×10^{-5}
Gly:St:LBG (0.9:0.1:0.7)	2.2×10^{-5}
Gly:St:LBG (1.2:0.1:0.7)	2.2×10^{-5}
PG(mL):St(g):LBG(g)	
PG:St:LBG (0.3:0.1:0.7)	1.2×10^{-5}
PG:St:LBG (0.6:0.1:0.7)	1.2×10^{-5}
PG:St:LBG (0.9:0.1:0.7)	1.3×10^{-5}
PG:St:LBG (1.2:0.1:0.7)	1.3×10^{-5}
S(g):St(g):LBG(g)	
S:St:LBG (0.346:0.1:0.7)	2.2×10^{-5}
S:St:LBG (0.728:0.1:0.7)	2.2×10^{-5}
S:St:LBG (1.092:0.1:0.7)	2.2×10^{-5}
S:St:LBG (1.456:0.1:0.7)	2.2×10^{-5}
PEG 200(mL): St(g):LBG(g)	
PEG200:St:LBG (0.3:0.1:0.7)	2.1×10^{-5}
PEG200:St:LBG (0.6:0.1:0.7)	2.0×10^{-5}
PEG200:St:LBG (0.9:0.1:0.7)	2.2×10^{-5}
PEG200:St:LBG (1.2:0.1:0.7)	2.0×10^{-5}

St/0.7 g LBG had the highest permeability value. The high value of permeability for the film containing 0.9 mL PEG 200/0.1 g St/0.7 g LBG resulted from the thickness of that film.

Table 3. Average thickness values of modified edible films containing 0.1 g of BW and Gly, PG, S, and PEG 200 of varying concentrations as a plasticiser

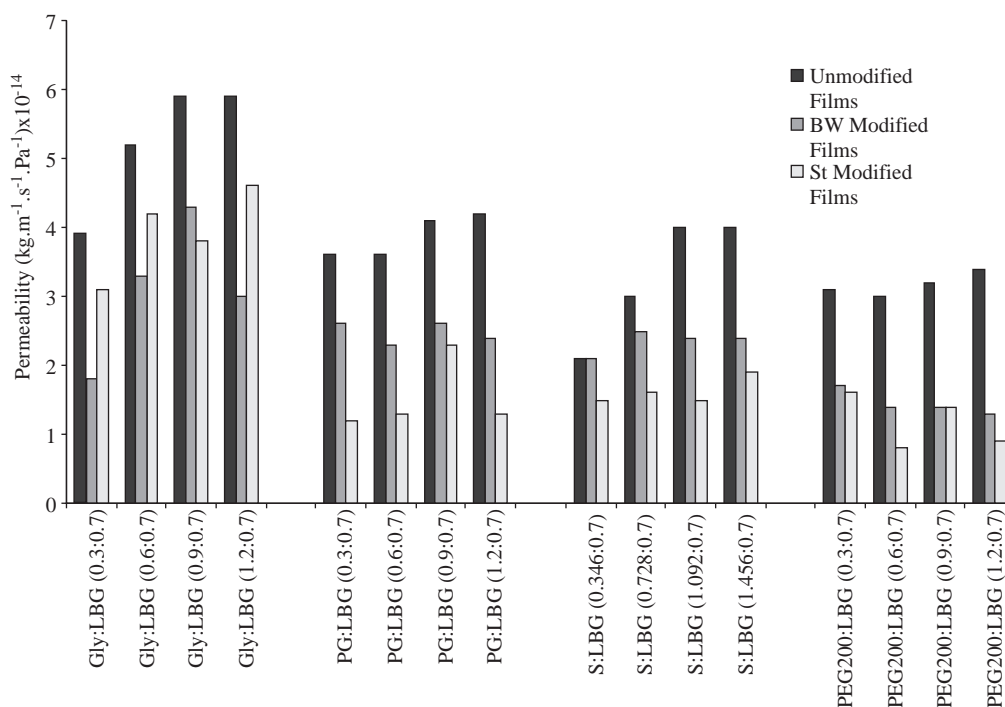| Composition	Average film thickness (m)
Gly(mL):BW(g):LBG(g)	
Gly:BW:LBG (0.3:0.1:0.7)	1.5×10^{-5}
Gly:BW:LBG (0.6:0.1:0.7)	2.2×10^{-5}
Gly:BW:LBG (0.9:0.1:0.7)	2.8×10^{-5}
Gly:BW:LBG (1.2:0.1:0.7)	2.2×10^{-5}
PG(mL):BW(g):LBG(g)	
PG:BW:LBG (0.3:0.1:0.7)	2.2×10^{-5}
PG:BW:LBG (0.6:0.1:0.7)	2.2×10^{-5}
PG:BW:LBG (0.9:0.1:0.7)	2.2×10^{-5}
PG:BW:LBG (1.2:0.1:0.7)	2.2×10^{-5}
S(g):BW(g):LBG(g)	
S:BW:LBG (0.346:0.1:0.7)	2.2×10^{-5}
S:BW:LBG (0.728:0.1:0.7)	2.2×10^{-5}
S:BW:LBG (1.092:0.1:0.7)	2.2×10^{-5}
S:BW:LBG (1.456:0.1:0.7)	2.2×10^{-5}
PEG 200(mL): BW(g):LBG(g)	
PEG200:BW:LBG (0.3:0.1:0.7)	2.2×10^{-5}
PEG200:BW:LBG (0.6:0.1:0.7)	2.2×10^{-5}
PEG200:BW:LBG (0.9:0.1:0.7)	2.2×10^{-5}
PEG200:BW:LBG (1.2:0.1:0.7)	2.2×10^{-5}

Figure. Water vapour permeability values of 3 different kinds of LBG–based edible films.

In some cases, the WVP values of PG–plasticised films were lower than those of films containing S and this can be attributed to the lower film thickness of these emulsion films. As mentioned before, the same thickness effect was also observed for films containing PEG 200.

Table 4. Comparison of WVP values of LBG-based edible films with other edible and non-edible films.

Composition	Average film thickness (m)	Conditions	Permeability $kg.m^{-1}.s^{-1}.Pa^{-1}$	Reference
PG:St:LBG (0.3:0.1:0.7)	1.2×10^{-5}	25 ± 1 °C 84.34 % RH	$(1.2 \pm 0.4) \times 10^{-14}$	
PG:BW:LBG (0.3:0.1:0.7)	2.2×10^{-5}	25 ± 1 °C 84.34 % RH	$(2.6 \pm 0.2) \times 10^{-14}$	
PEG200:St:LBG (0.3:0.1:0.7)	2.1×10^{-5}	25 ± 1 °C 84.34 % RH	$(1.6 \pm 0.1) \times 10^{-14}$	
PEG200:BW:LBG (0.3:0.1:0.7)	2.2×10^{-5}	25 ± 1 °C 84.34 % RH	$(1.7 \pm 0.2) \times 10^{-14}$	
PEG200:LBG (0.3:0.7)	1.6×10^{-5}	25 ± 1 °C 84.34 % RH	$(3.1 \pm 0.1) \times 10^{-14}$	16
PEG 400:LBG (0.3:0.7)	2.0×10^{-5}	25 ± 1 °C 84.34 % RH	$(1.7 \pm 0.1) \times 10^{-14}$	16
PEG 600:LBG (0.3:0.7)	2.0×10^{-5}	25 ± 1 °C 84.34 % RH	$(1.8 \pm 0.3) \times 10^{-14}$	16
PEG 1000:LBG (0.3:0.7)	2.3×10^{-5}	25 ± 1 °C 84.34 % RH	$(1.9 \pm 0.9) \times 10^{-14}$	16
Zein:Gly (4.9:1)	$(1.2-3.3) \times 10^{-4}$	21 °C 85 % RH	$(8.9-13) \times 10^{-14}$	29
WG:Gly (3.1:1)	$(3.8-4.2) \times 10^{-4}$	21 °C 85 % RH	$(5.9-6.3) \times 10^{-14}$	29
WPI:Gly (1.7:1)	1.2×10^{-4}	25 °C 79 % RH	8.1×10^{-13}	30
WPI:S (1.7:1)	1.3×10^{-4}	25 °C 65 % RH	7.2×10^{-13}	30
WPI:BW:S (3.5:1.8:1)	1.6×10^{-4}	23 °C 94 % RH	2.4×10^{-13}	31
CC:Gly (2:1)	1.1×10^{-4}	25 °C 72 % RH	2.2×10^{-12}	32
HPMC:PEG 200 (9:1)	3.6×10^{-5}	25 °C 85 % RH	6.3×10^{-14}	29
HPMC(22000):PEG 400 (3:1.8)	1.4×10^{-5}	25 °C 52 % RH	1.6×10^{-14}	29
HPMC:SA (0.8:1)	1.9×10^{-5}	27 °C 85 % RH	0.3×10^{-15}	31
LDPE	-	38 °C 90 % RH	0.9×10^{-15}	31
HDPE	2.5×10^{-5}	38 °C 90 % RH	0.2×10^{-15}	31
SARAN	-	38 °C 95 % RH	0.1×10^{-15}	31

WG: Wheat gluten, WPI: Whey protein isolate, CC: Calcium caseinate, HPMC: Hydroxypropyl methyl cellulose, LDPE: Light density polyethylene, HDPE: High density polyethylene

BW was the second modifier used in the preparation of edible films by the emulsion technique. In the Figure, the WVP values of emulsion films containing 0.1 g of BW are given. The highest permeability value among the films containing Gly was 0.9 mL Gly/0.1 g BW/0.7 g LBG and this was due to the high thickness of this film. Gly–plasticised films containing BW had the lowest permeability values among the

other Gly–plasticised films. BW is more hydrophilic than St, and is therefore more compatible with Gly. As a result, the hydrogen bonding between various components of the film structure provides better resistance to water vapour transmission. During the experiments it was also observed that as all the Gly–plasticised films, (except those containing 0.3 mL Gly/0.1 g St/0.7 g LBG and 0.3 mL Gly/0.1 g BW/0.7 g LBG), are quite tacky, they cannot be used as suitable edible films.

Due to their increased hydrophobic nature emulsion films containing 0.1 g BW and PG showed lower WVP values. Similar to Gly–plasticised films, only 0.3 mL PG/0.1 g St/0.7 g LBG and 0.3 mL PG/0.1 g BW/0.7 g LBG films are suitable as edible films. When the amount of PG was increased, the adhesion of the resultant films to the glass plates was quite strong, and it was very difficult to remove them. This situation was observed especially in the case of unmodified PG–plasticised films and, therefore, the addition of a modifier to prevent adhesion was necessary. Due to blooming on the surface during drying, edible films containing S modified with BW showed similar permeability values. If we compare the 3 kinds of edible films containing S we see that films modified with St had the lowest permeability values, while, 0.356 g S/0.1 g St/0.7 g LBG and 0.356 g S/0.1 g BW/0.7 g LBG were the best combinations for making reasonable edible films. The WVP values of PEG 200–plasticised edible films modified with BW decrease slowly with increasing amounts of plasticiser and these films had the lowest WVP values for other films containing PEG 200.

As seen in Table 4, LBG–based edible films have WVP values comparable to some protein– and polysaccharide–based edible films. We therefore hope that LBG–based edible films will be used for food applications in the future. We suggest that these edible films be used as coatings for food products which have high lipid content levels such as cheese, sausages or deep–fried products.

Conclusion

Edible films with potential applications in the field of food packaging can be prepared from LBG. To obtain more stable and structurally entire edible films, LBG-based edible film formulations may contain PEG 200 as a plasticiser and they must be modified with St or BW to reduce their WVP values to the levels of other protein- and polysaccharide–based edible films.

List of Abbreviations

BW:	Beeswax
Gly:	Glycerol
LBG:	Locust bean gum
PEG 200:	Poly(ethylene) glycol 200
PG:	Propylene glycol
S:	Sorbitol
St:	Stearopten
WVP:	Water vapour permeability
WVTR:	Water vapour transmission rate

Acknowledgement

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