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Mechanical and Light Transmittance Properties of Locust Bean Gum Based Edible Films

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The behavior of locust bean gum (LBG) under heat was investigated by thermogravimetric (TG), differential thermogravimetric (DTG) and differential scanning calorimetric (DSC) methods. It was observed from the TG, DTG and DSC curves that LBG does not melt and is stable up to 300 °C, although exothermic degradation occurs at higher temperatures. The effect of the amount and molecular weight of polyethylene glycol (PEG) on the light transmittance and mechanical properties of these edible films was also examined. Haze increased and the luminous transmittance and total light transmittance values decreased with both the quantity and molecular weight of PEG. On the other hand, tensile strength and elongation decreased, but there was no regular relationship between the molecular weight of the PEG and the tensile strength of the films. It was concluded from the results of the mechanical and optical measurements that the most suitable plasticizer among the PEG plasticizers with different molecular weights is PEG 200 and that the maximum level for its use is 0.6 mL/0.7 g LBG in edible film formulations.

Key Words: Locust bean gum, Edible film, Plasticizer, Light transmittance, Mechanical properties.

Introduction

Locust bean gum (LBG) is obtained from the carob bean (*Ceratonia siliqua* L.), which is a perennial tree of the family Leguminasae that is widely cultivated in the semiarid regions in the south and east of the Mediterranean area[1]. LBG consists of a linear chain of β-D-mannopranosil units linked to 1,4 single, α-D-galactopranosil units linked to 1,6 of the main chain at side branches[2]. The most important property of this polysaccharide polymer is its high solution viscosity in a wide range of pH values and temperatures. Therefore it can be used in the food industry as a thickener or viscosity modifier, a free water binder, or as a suspending agent or stabilizer in cheeses, frozen confections, bakery products, pie fillings, meat, sauces and salad dressings. Its film forming property is used in the textile industry, making it ideal as a sizing and finishing agent, as well as in the pharmaceutical and cosmetics industries for the production of lotions and creams[3,4].

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The film formation and 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[4]. Edible films and coatings can improve the appearance of food, protect its properties during storage and handling, and extend its shelf life. Edible coatings may be applied to fresh foods to reduce moisture transfer, oxidation and respiration to prolong the shelf life of such foods[5]. Polysaccharide films have poor water vapor barrier properties because of their hydrophilic characteristics, but these hydrophilic polymers can form strong chain-to-chain interactions that provide a good barrier to O_2 and CO_2[6−9]. Aydinli et al. examined the effect of the amount and molecular weight of polyethylene glycol (PEG) on the water vapor permeability (WVP) properties of LBG based edible films[10]. They found that the WVP values of edible films increase with both the quantity and molecular weight of PEG up to PEG 600.

Hydrophobic materials such as beeswax, carnauba wax, paraffin wax and oil acids can be added to film solutions to add hydrophobic characteristics to hydrophilic films[11−15]. Plasticizers are the basic materials added to film forming polymers. They reduce intermolecular forces, increase the mobility of the biopolymer chains and improve the mechanical properties of the films.[4,8,10,16−24] The addition of a plasticizing agent is necessary in order to reduce brittleness and to increase flexibility through a reduction in film cohesion, although plasticizers can also increase film permeability[17−19]. Plasticizers must be compatible with the polymers and, if posssible, be readily soluble in the solvent. These additives alter the permeability properties to different extents. For example, whey protein films plasticized with sorbitol exhibit significantly lower water vapor permeabilities than those of similar films containing glycerol, PEG 200 or PEG 400[19]. Improving the barrier properties of film prevents it cracking during packing and transportation but adversely affects the barrier properties and increases the mass transfer through the films.

The aim of this study was to determine the mechanical (tensile strength and elongation) and optical (haze and luminous transmittance) properties of LBG based edible films containing PEG with different molecular weights as a plasticizer and to investigate the thermal properties of the LBG polymer, which has broad application areas in which thermal treatments are applied.

Materials and Methods

PEG with molecular weights of 200, 400 and 600 was purchased from the Sigma Chemical Company. Carob pods (*Ceratonia siliqua* L.) were supplied by Seryem A.Ş. Antalya/Turkey. Thermogravimetric (TG), differential thermograviemetric (DTG) and differential scanning calorimetric (DSC) thermal analyses were performed with V2.OB Dupont 9900 equipment. Haze and total light transmittance measurements were performed with Toyoseiki equipment and luminous transmittance was carried out with Gardner 4535 equipment. Tensile strength and elongation measurements were performed with Instron 4411 equipment.

Preparation of LBG

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

TG and DSC analysis of LBG

For TG analysis under a nitrogen atmosphere a 14,677 mg sample of LBG was heated from 25 °C to 800 °C at a 20 °C/min heating rate and changes in the weight of the polymer were measured. DSC analysis was recorded as increase in temperature versus heat flow until 500 °C at a 10 °C/min heating rate under a nitrogen atmosphere.

Preparation of films

Film forming solutions were prepared by dissolving 0.7 g of LBG in 75 mL of water and were kept at 70 °C for 2 h using a water bath. The prepared film solutions were homogenized at 13,500 rpm for 2 min with an Ultra-Turrax T 25 homogenizer. Then different plasticizers were added to the film solution. For each film solution 0.3, 0.6 and 0.9 mL of PEG 200, PEG 400 and PEG 600 were added, respectively. Then each of these solutions was homogenized at 18,000 rpm for about 5 min. Due to the high viscosity of the resultant film solutions, removal of the dissolved air was not possible under the vacuum. Consequently, evaporation was carried out for degassing at 35 °C and under 2666 Pa pressure. During this evaporation, about 5 mL of water was removed. Solutions were then heated to 40 °C and spread on 20 x 20 cm glass plates by adjusting the hand operated plate coater of the Camag thin layer chromatography equipment. The spread films were dried at room temperature for 1 day [10].

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.

Haze and luminous transmittance of LBG based edible films

The haze and luminous transmittance of LBG based edible films were measured using ASTM D 1003-92[25]. All samples were cut from films 50 mm in diameter and then kept at 23 ±2 °C and in 50 ± 5% relative humidity for 48 h prior to testing. Thickness values for these films can be seen in Table 1. Four readings were carried out as shown in Table 2.

Total transmittance (T_t), diffuse transmittance (T_d) and percent haze values were calculated using the equations shown below.

$$T_t \text{ (Total transmittance) } = \frac{T_2}{T_1} \tag{1}$$

$$T_d \text{ (Diffuse transmittance) } = \frac{T_4 - T_3 \cdot \left(\frac{T_2}{T_1}\right)}{T_1} \tag{2}$$

$$\text{Haze \%} = \frac{T_d}{T_t} \times 100 \tag{3}$$

Table 1. Average thickness values of edible films containing PEG 200, PEG 400, and PEG 600 in varying concentrations as plasticizer.

Composition	Average film thickness (m)
PEG 200 (mL):LBG (g)	
PEG 200:LBG (0.3:0.7)	1.2×10^{-5}
PEG 200:LBG (0.6:0.7)	1.3×10^{-5}
PEG 200:LBG (0.9:0.7)	1.4×10^{-5}
PEG 200:LBG (1.2:0.7)	1.6×10^{-5}
PEG 400 (mL):LBG (g)	
PEG 400:LBG (0.3:0.7)	1.7×10^{-5}
PEG 400:LBG (0.6:0.7)	1.5×10^{-5}
PEG 400:LBG (0.9:0.7)	1.5×10^{-5}
PEG 400:LBG (1.2:0.7)	2.1×10^{-5}
PEG 600 (mL):LBG (g)	
PEG 600:LBG (0.3:0.7)	2.1×10^{-5}
PEG 600:LBG (0.6:0.7)	1.5×10^{-5}
PEG 600:LBG (0.9:0.7)	1.8×10^{-5}
PEG 600:LBG (1.2:0.7)	1.6×10^{-5}

Table 2. Readings of haze and luminous transmittance measurements of LBG based edible films.

Reading n designation	Specimen in position	Light trap in position	Reflectance standard in position	Quantity represented
T_1	no	no	yes	incident light
T_2	yes	no	yes	total light transmitted by specimen
T_3	no	yes	no	light scattered by instrument
T_4	yes	yes	no	light scattered by instrument and specimen

Tensile properties of LBG based edible films

Tensile strength and elongation of LBG based edible films were measured using ASTM D 882-91[26]. All samples were cut from films 15 mm in width and then kept at 23 ± 2 °C in 50 ± 5 % relative humidity for 48 h prior to testing. Thicknes values for these films are given in Table 1.

An appropriate load range was selected and the rate of grip separation was set to give a 100 mm/min strain rate based on the initial 10 cm distance between the grips.

Results and Discussion

The TG and DTG thermograms of LBG polymer carried out under a nitrogen atmosphere are given in Figure 1. The polymer decomposed with a sharp loss in weight near 300 °C and the rate of this decomposition reached 34.27% weight loss/min at 330 °C. Up to 400 °C the sample lost 80% of its weight and when it was heated to 800 °C with 20 °C/min heating rate, a loss of 87.39% of its weight was observed.

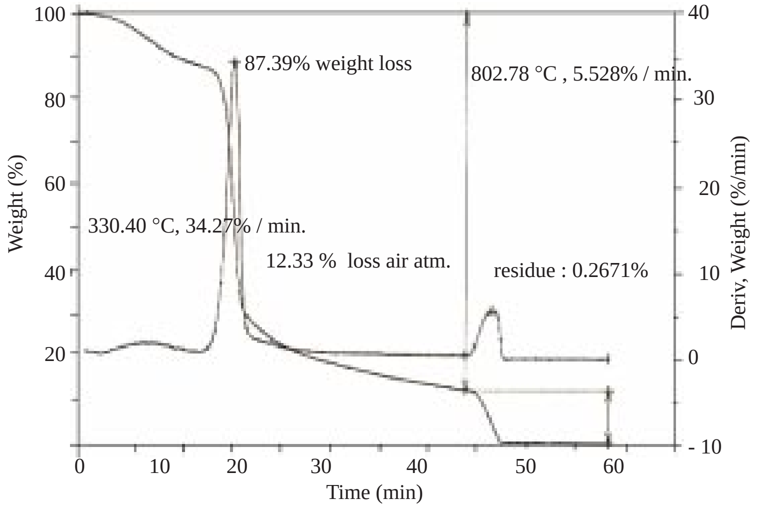

Figure 1. Thermogram of LBG recorded by dynamic thermogravimetric (TG, DTG) methods.

Under an air atmosphere there was rapid decomposition with a 5.53% weight loss/min being detected. A 12.33% weight loss was observed under O_2 atmosphere. The linearity of the thermogram at 803 °C means that oxidation under O_2 atmosphere was complete. The residue was 0.2071%. The 10% loss in weight observed in the early stages of heating up to 175 °C was due to the water content of the polymer.

To determine whether the thermal decomposition was exothermic or endothermic DSC levels were recorded (Figure 2). The endothermic activity at 151.20 °C probably resulted from the evaporation of the water. This activity corresponds to the initial loss in weight observed in the thermogram of the same polymer up to 175 °C. This endothermic transformation could not be thought of as the melting of the polymer. If it were, this would be an increase in the energy of the system and not a loss in weight due to the phase transition in the TG curve. However, as shown in Figure 2, a loss in weight occurred at this temperature range proving the reduction in the water content of the polymer.

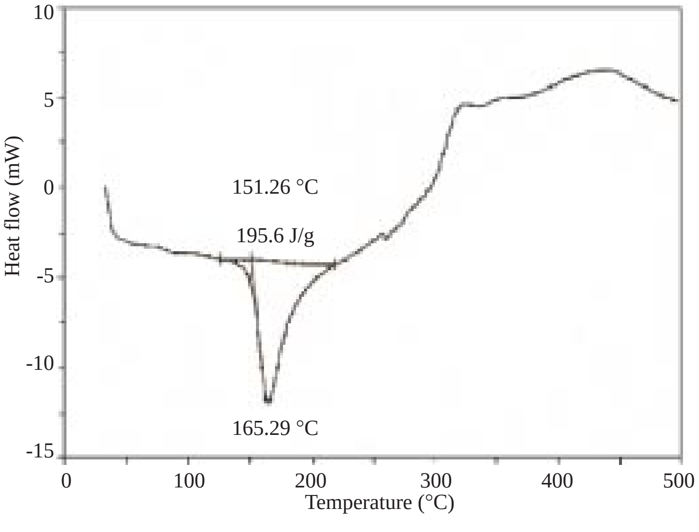

Figure 2. Thermogram of LBG recorded by differential thermal calorimetry (DSC).

Exothermic decomposition observed above 300 °C was an oxidative decomposition corresponding to an excess loss in the weight of the polymer. It was determined from thermal analysis that LBG polymer is resistant to heat up to 300 °C and that above that temperature it decomposes exothermically.

As can be seen from the results of the TG and DTG analyses LBG polymer does not decompose up to 300 ^{u}C. This suggests that up to 300 °C, LBG polymer can be used safely in foods including bakery products. It can also be seen from the thermogram that it is difficult to remove the water from this polymer.

Investigation of the effects of plasticizer amount and molecular weight on the light transmittance properties of LBG based edible films

If these edible films are to be used as surface coatings in food applications, they must be transparent. The effects of the amount and molecular weight of the plasticizer, PEG, on the transmittance properties of edible films were therefore investigated.

Polymer film solutions were prepared according to the formulations given in Table 1. Haze, luminous transmittance and total (light) transmittance values of these films were determined by hazemeter at 23 ± 2 °C and in 50 ± 5% relative humidity. Data for these measurements are given in Figure 3 from which it can be seen that as the amount and molecular weight of PEG are raised, an increase in the haze values of edible films is observed. It can be also seen from these figures that the change in haze values is inversely proportional to the change in luminous transmittance values (Figures 3, 4).

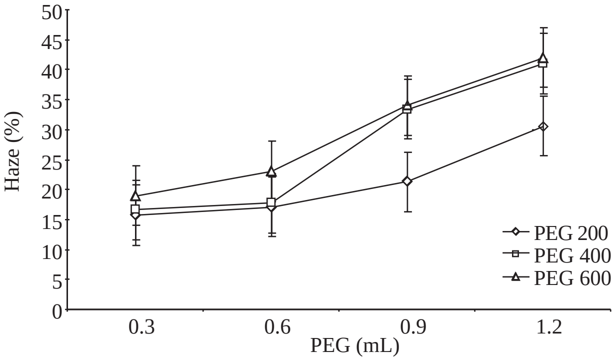

Figure 3. The effect of molecular weight and concentration of PEG on the haze of edible films.

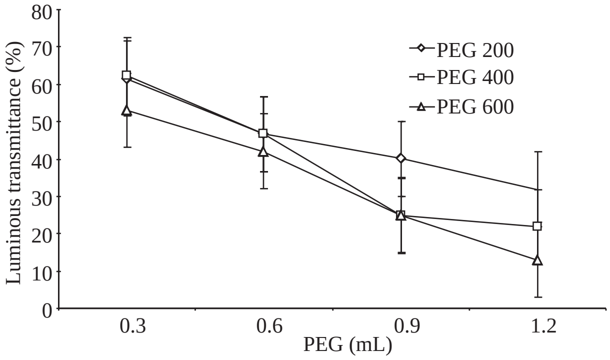

Figure 4. The effect of molecular weight and concentration of PEG on the luminous transmittance of edible films.

As haze is the cloudy or turbid appearance of an otherwise transparent specimen caused by light scattered from within the specimen or from its surface, an increase in the concentration of the plasticizer in the edible film leads to an increase in light scattering.

Due to the hydrophilic nature of the LBG polymer, the use of high molecular weight PEG plasticizers causes more heterogeneous and more opaque edible films than those caused by low molecular weight plasticizers.

Figure 5 shows that the most suitable plasticizer is PEG 200, and total light transmittance decreased in the order PEG 200, PEG 400 and PEG 600. The reason for this decrease is thought to be incompatibility between the film forming polymer and the plasticizer with high molecular weight. The lowest haze values among the edible films were observed for those containing PEG 200. As the increase in the molecular weight causes an increase in the hydrophobic nature of the PEG plasticizers, the haze values of edible films increase in the order PEG 200, PEG 400 and PEG 600. The edible films containing 0.3 and 0.6 mL of PEG had significantly lower haze values than those containing 0.9 and 1.2 mL of PEG. This was due to the appearance of incompatibility between the LBG polymer and PEG plasticizers as the amount and the molecular weight of the plasticizer increased. This incompatibility causes a phase separation, which leads to a heterogeneous film surface.

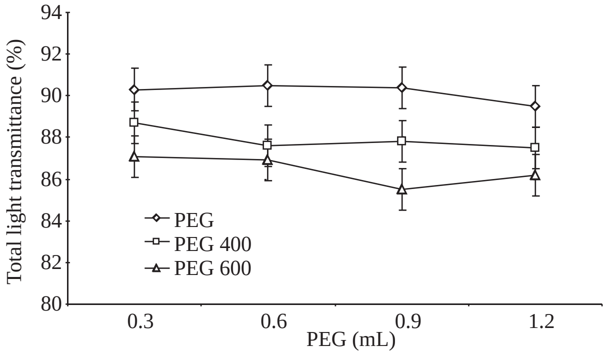

Figure 5. The effect of molecular weight and concentration of PEG on the total light transmittance of edible films.

Investigation of the effects of plasticizer amount and molecular weight on the mechanical properties of LBG based edible films

Figures 6 and 7 show that as the amount of plasticizer was raised in the film formulations composed of LBG and PEG 200, PEG 400 and PEG 600, both the tensile strength and elongation values of the films decreased. Figure 6 shows that there is no discernable effect between the molecular weight of the plasticizer and tensile strength. However, it may be that phase separation caused by the incompatibility between the polymer and the plasticizer is responsible for the lower tensile strength values of the edible films containing 0.9 and 1.2 mL of plasticizer.

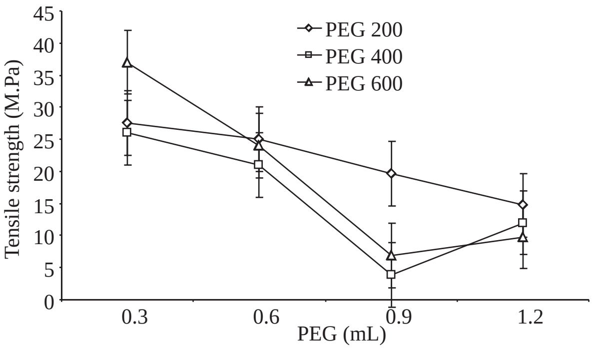

Figure 6. The effect of molecular weight and concentration of PEG on the tensile strength of edible films.

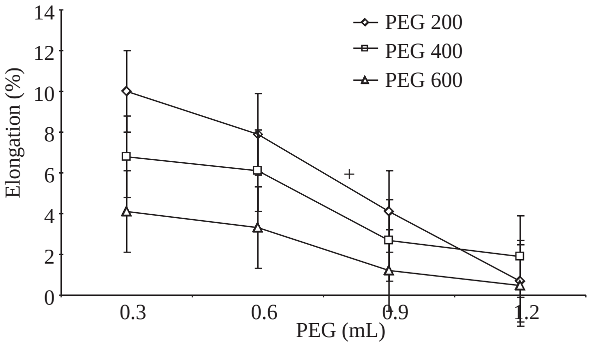

Figure 7. The effect of molecular weight and concentration of PEG on the elongation of edible films.

In a similar study in which MC and HPC based edible films were investigated (Park et al., 1993)^{27}, it was determined that the effect of the type and amount of plasticizer used on the tensile strength and elongation of edible films was such that, when the concentration of the plasticizer was raised, tensile strength was found to decrease but elongation was found to increase. On the other hand, in our LBG based edible films, as the amount of plasticizer increased, the elongation of the films also decreased. It is thought that the observed decrease in the elongation values of edible films resulted from the phase separation between the LBG and plasticizer in film formulations. It is obvious that for the films containing 0.9 mL and 1.2 mL of plasticizer such a phase separation weakens the interactions between different linear polymer chains, and so elongation decreases.

Conclusion

The TG, DTG and DSC thermograms showed that LBG polymer, which has broad industrial applications, is resistant to heat up to 300 °C and that an exothermic degradation with an excess decrease in weight occurs above that temperature. Therefore LBG polymer can be used safely in foods, including bakery products, up to 300 °C. From the results of the analyses of the mechanical and optical properties of LBG based edible films it can be concluded that the most suitable plasticizer among the PEG plasticizers with different molecular weights is PEG 200 and that the maximum level for its use is 0.6 mL/0.7 g LBG in edible film formulations.

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