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Development of Dry Walnut Shell Edible Film Plasticized with Glycerol and/or Sorbitol and Incorporated with Aloe Vera Gel and Lemon Essential Oil

Berika Girgin[1], Nurcan Tugrul[1]*

[1] Department of Chemical Engineering, Faculty of Chemical and Metallurgical Engineering, Yildiz Technical University, Davutpasa Campus, Davutpasa Street No. 127, Esenler, 34220 Istanbul, Turkey
* Corresponding author, e-mail: ntugrul@yildiz.edu.tr

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Abstract

Edible packaging films produced from biomaterials are environmentally friendly, promising alternatives against synthetic plastics films. The aim of this study was to produce a low-cost edible film from waste dry walnut shell by casting method. Effects of the plasticizer type and concentration, lemon essential oil (LEO) and aloe vera gel (AVG) addition on edible films properties were investigated. Produced edible films characterization analysis were realized by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Moisture content, water vapor transmission rate (WVTR), water solubility, swelling index, thicknesses and color parameters of the produced edible films were investigated. Moisture content of the films was decreased between 23.3–50.6% after LEO and AVG addition, except the moisture content of the film plasticized with 20% sorbitol was increased by 518%. WVTR of the films were increased between 8.7–72.3% after LEO and AVG addition due to the hydrophobic character of LEO. Glycerol plasticized edible films water solubility were decreased between 27.3–75.9%, sorbitol plasticized edible films water solubility were increased between 237.5–100.8% with LEO and AVG incorporation. The swelling index of C1 was reduced by 51.5%, C2 was reduced by 62.4%, C4 was reduced by 36.1%. The swelling index of the C3 was increased by 10.5%, C5 was increased by 21.5%. LEO and AVG addition increased to the film thickness maximum 79.2%. Total color changes (ΔE) of glycerol plasticized films were higher than sorbitol plasticized film. The edible film produced can be used in food packaging due to the appropriate physical and barrier properties.

Keywords

dry walnut shell, lemon essential oil, aloe vera gel, glycerol, sorbitol

1 Introduction

Being biodegradable, biocompatible, and renewable, edible packaging films produced from biomaterials are environmentally friendly and promising alternatives against synthetic plastics films. They increase the shelf life and the quality of food products by conserving them from chemical, physical, and biological decomposition. Biomaterial based edible films can be made of polysaccharides, lipids, proteins, and combination of these components [1–3]. Walnut is widely grown plant all over the world. According to FAO 2019 data, China is the largest walnut producer in the world [4]. And Turkey, with 5% of the world walnuts production, is ranked number 4 after USA and Iran [5, 6]. Dry walnut shell is the main waste material delivered from walnuts. Dry walnut shells comprise hemicellulose, cellulose and lignin and cellulose play essential role in bioplastic production [7, 8]. Since the antioxidant and antimicrobial properties of edible packaging materials combined with active compounds increase, they can be used for storage of food products and increasing shelf life. Dry walnut shell powder has good absorption properties and can also be used as a reinforcing material [9–11]. Synthetic additives usage in the food industry causes various diseases. For this reason, the need for the use of natural preservatives is increasing day by day. Essential oils are naturally occurring antibacterial, insecticidal, antiviral, and antifungal compounds which are incorporated into edible films to get minimum handled food products having long time shelf life. Cinnamon, lemon, tea tree, thyme or clove essential oils are added to edible films to ensure antimicrobial efficacy against pathogenic and spoilage microorganisms and improve barrier properties against moisture transfer because of

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the hydrophobic nature of essential oils [12–14]. Lemon essential oil (LEO) can be used as a natural food protective and flavoring agent because of antioxidant and antibacterial properties. However, the volatility, chemical instability and application costs limit its use. The loss of essential oil and utilized dose can be reduced by adding it into the formulation of edible coatings instead of adding it straight into the food [15, 16]. Studies on the production of edible films by using new compounds obtained from various plants are increasing day by day. Aloe vera gel (AVG) which includes 99% water and 1% solid substances like polysaccharides, vitamins, phenolic compounds, minerals, and organic acids, is acquired from the leaves of the aloe vera plant. Due to the active component acemannan presence, AVG has excellent anti-inflammatory, anticancer, antioxidant and antimicrobial properties. AVG protects food from UV light and prevents the destruction of its active ingredients such as lipids, vitamins, and proteins. It reduces firmness losses during storage, retards softening, and peel color changes, prevents loss of moisture, controls respiratory rate and maturation development, delays oxidative browning, and reduces microorganism proliferation in foods [17, 18]. The edible films quality must be optimized to produce efficient films for commercial usage. The plasticizer kind is the most important agent influencing the edible films characteristics. Plasticizers are generally small molecules that intersperse and intercalate among and between polymer chains, breaking hydrogen bonding and distributing the chains apart. Glycerol and sorbitol are often used as plasticizers owing to their good compatibility and water solubility, which makes the films stretchable and flexible [19–21].

In previous studies, Mohan and Panneerselvam [9] produced an uncontaminated polymer nanocomposite film for packaging and medical applications from walnut shell powder. However, the produced film was not used in edible film production. Harini et al. [10] developed an active packaging material by mixing pomegranate peel extract with walnut shell cellulose reinforced cashew nutshell starch films. Walnut shell cellulose was used as raw material. Harini and Chandra Mohan [11] aimed to convert microcrystalline cellulose found in different agricultural industrial wastes such as walnut shell, corn cob and sugarcane pulp into nanocrystalline cellulose fiber. In literature, walnut shell has been used in addition to the raw material to enrich the edible film and improve its properties. In this study, different from the literature, walnut shell was used as a polysaccharide raw material, not as an enriching additive. The waste shell of dry walnut, which is a widely consumed in Turkey, was plasticized with glycerol and/or sorbitol and was used in the production of alternative low-cost edible film by adding LEO and AVG. The purpose of this work is to develop efficient biodegradable films that are not-only safe for food packaging but-also for edible use by casting method using dry walnut shell [22]. The effect of glycerol, sorbitol, LEO and AVG addition on the moisture content, water vapor transmission rate, water solubility, swelling index, film thicknesses, color parameters and morphological structure of the dry walnut shell based edible film were studied. It was observed that the edible film produced was more successful in preserving the quality of the food when the natural antioxidants AVG and LEO were used together. The efficacy of plasticizers was compared by using glycerol and sorbitol separately or together. The consequences of this study will make possible, waste shell of dry walnut to be recycled to produce a natural edible film.

2 Materials and methods

2.1 Materials

The dry walnut shells used in this study were provided free of charge from local markets in Zonguldak, Turkey in June 2021. Aloe vera leaves were purchased from local markets in Istanbul, Turkey, in June 2021. Glycerol was purchased from Merck (Germany), sodium alginate from AFG Bioscience (USA), D-sorbitol from Carlo Erba (France), LEO from Arifoğlu (Turkey).

2.2 Preparation of dry walnut shell powder and aloe vera gel

The dry walnut shells were crushed and screened to smaller than 180 μm particle size. The resulting peel powder was stored in low-density polyethylene bags at room temperature (22 + 0.5 °C).

Fresh aloe vera leaves were washed with cold tap water then by pure water to remove any surface impurities. After this, aloe vera leaves were peeled with a knife to remove the outer green colored skin layer. The resulted AVG was blended, then was mixed with the Bandelin Sonopuls HD 2070 (20 kHz) model ultrasonic probe (Bandelin electronic GmbH & Co. KG, Berlin, Germany) for 20 min to form a uniform solution. Finally, it was filtered to remove impurities arising from cell walls. The gel matrix was pasteurized at 70 °C for 45 min. After pasteurization, the gel was cooled to a room temperature (22 + 0.5 °C). The prepared gel extract was stored at refrigerator [18, 23, 24].

2.3 Preparation of dry walnut shell edible film

Ground dry walnut shell (5 g) and sodium alginate (0.50 g) were dissolved in 100 ml distilled water using different ratios of glycerol and/or sorbitol according to the compositions listed in Table 1, to determine its plasticizing effect. While creating the edible film prescription, the literature was examined, and it was determined that generally the film was formed using the ratios of 0.25:0.75 and 0.75:0.25. However, since high yields were obtained in the ratios of 0.35:0.65 and 0.65:0.35 in the preliminary experiments made with walnut shells, it was decided to work at these ratios. The mixtures (C1, C2, C3, C4, C5) were stirred in a magnetic stirrer at 500 rpm for 60 min., at 60 °C [25, 26]. In order to obtain more homogeneous film solutions, they were first mixed with the Bandelin Sonopuls HD 2070 (20 kHz) model ultrasonic probe (Bandelin electronic GmbH & Co. KG, Berlin, Germany) for 10 min. Next, they were placed in an ultrasonic water bath (Isolab, Wertheim, Germany) for 10 min, at 50 °C, until the mixtures were completely solubilized. Biodegradable edible films were prepared by using solution-casting method. The film solutions were cast in Petri dishes with a diameter of 10 cm followed by drying at 50 °C in an oven for 24 h. Finally, the films were peeled off and conditioned in a desiccator, at 50% RH and room temperature (22 + 0.5 °C) until analyzed, after cooling [17, 27–29].

2.4 Preparation of composite edible film developed by mixing dry walnut shell, aloe vera gel and lemon essential oil

To form the dry walnut shell/aloe vera gel/lemon essential oil composite film, ground dry walnut shell (5 g) and sodium alginate (0.50 g) were dissolved in 100 ml distilled water by adding glycerol and/or sorbitol in the ratios indicated in Table 1. Then, LEO (1 ml) and AVG (1 ml) were added to the resulting mixtures (CL1, CL2, CL3, CL4, CL5). The film solutions were obtained following the procedure in Section 2.3.

Table 1 Formulation of edible films

Composition	Glycerol (g)	Sorbitol (g)	LEO (ml)	AVG (ml)
C1	1.00	-		
C2	-	1.00		
C3	0.50	0.50		
C4	0.35	0.65		
C5	0.65	0.35		
CL1	1.00	-	1.00	1.00
CL2	-	1.00	1.00	1.00
CL3	0.50	0.50	1.00	1.00
CL4	0.35	0.65	1.00	1.00
CL5	0.65	0.35	1.00	1.00

2.5 Characterization of films

2.5.1 Fourier transform infrared spectroscopy (FT-IR)

The chemical structure of the films was analyzed by FT-IR using a PerkinElmer Spectrum One FT-IR spectrometer (Waltham, MA, USA) equipped with a universal attenuation total reflectance sampling accessory with a spectral range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. The films were cut to 10 × 10 mm and placed onto the ATR platform.

2.5.2 Scanning electron microscopy (SEM)

The morphological properties of the films were examined with scanning electron microscope (SEM, Zeiss EVO LS10), having accelerating voltage of 7 kV and magnification of 10.000×. The film samples were cut into 1 cm × 1 cm pieces, they were fixed on copper stubs and were coated with gold.

2.5.3 Water vapor transmission rate (WVTR)

Water vapor transmission rate of the film samples was calculated, with minor modifications, in accordance with the method described by Shafie et al. [30] and ASTM E96/96M-22a [31]. The film samples were dried in a hot air oven at 105 ± 2 °C for 24 h until they reach a constant weight. Then the glass test tubes were filled with 5 g of silica gel, the mouth of the tubes (diameter of 13 mm) was closed with the film sample dried in the oven and surrounded with paraffin (for the tube to be completely closed). The prepared samples were weighed every 24 h (at the same time every day) for 5 days. All the experiments were carried out in triplicate. The WVTR was calculated according to Eq. (1):

$$\mathrm{WVTR} = \Delta W / (\Delta t \times A) \tag{1}$$

$\Delta W/\Delta t$ = the amount of water transferred (g) per unit time (s), and A = the exposed area (m^2).

2.5.4 Moisture content

The moisture content of the edible films was calculated in accordance with the method of ASTM International (2022) [32]. Edible films were cut to 3 × 3 cm and dried at 105 ± 2 °C for 24 h using a hot air oven. Before (M_0) and after (M_1) drying, the weight loss of the edible films was measured as water content until constant

weight was reached. All the experiments were carried out in triplicate:

$$\text{Moisture } (\%) = \frac{(M_0 - M_1)}{M_0} \times 100 \quad (2)$$

M_0 = initial weight, M_1 = dry weight of the film [33, 34].

2.5.5 Water solubility

Water solubility was calculated in accordance with the method expressed by Dash et al. [33] and Sushmita et al. [35], with some changes. The film samples were dried in a hot air oven at 105 ± 2 °C for 24 h. Dried films were cut to 2 × 2 cm and then they were weighed. 10 ml of distilled water was added to the weighed samples and mixed at 100 rpm at room temperature (22 + 0.5 °C) for 6 h. The unsolvable part of the film samples was filtered, dried at 105 ± 2 °C for 24 h. and weighed. All the experiments were carried out in triplicate. Water solubility calculated using Eq. (3):

$$\text{Water solubility } (\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (3)$$

W_1 = dry weight and W_2 = dry weight of the insoluble fraction of the film.

2.5.6 Swelling index

The edible films swelling index was calculated following the method expressed by Susmitha et al. [35] and Pacheco et al. [36], with some changes. Edible films were cut to 2 cm × 2 cm, dried at 105 ± 2 °C for 24 h and weighed initially (W_0). The dried films were submerged in 15 mL distilled water for 2 min at room temperature (22 + 0.5 °C). The swelled samples were dried with filter paper and weighed (W_1). All the experiments were carried out in triplicate. The absorbed water amount was calculated using Eq. (4):

$$\text{Swelling index } (\%) = \frac{W_1 - W_0}{W_0} \times 100\,, \quad (4)$$

where swelling index % was the percentage of swelling index and W_0 and W_1 the weights of dried and the wet samples.

2.5.7 Film thickness

Mitutoyo micrometer (Tokyo, Japan) was used to measure edible films thicknesses (with 0.01 mm. sensitivity). The measurements were taken from five different point and the average value was recorded [37].

2.5.8 Color

The lightness or darkness are presented with L^* values in Hunter color system. Also, the positive a^* values represent redness, and the negative ones represent greenness as the positive b^* values represent yellowness, and the negative ones represents blueness. Color of films (40 mm × 40 mm) were measured by using a handheld colorimeter (PCE-CSM 1; PCE Instruments UK Ltd., Southampton Hampshire, United Kingdom). All the experiments were carried out in triplicate. Total color changes (ΔE) were calculated in Eq. (5):

$$\Delta E = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2} \quad (5)$$

where L_0, a_0 and b_0 are the color values of the control films and L, a and b are the color values of the produced films [24].

2.5.9 Statistical analysis

Statistical analysis by the analysis of variance (ANOVA) was done by SPSS® 16. All tests were carried out in three independent runs, and the obtained parameters were averaged and expressed as the mean standard error (±) where each value is considered as a significant at $p < 0.05$.

3 Results and Discussion

3.1 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the dry walnut shell based edible films (control films) and dry walnut shell based AVG and LEO added edible films (composite films) were determined using FTIR and shown in Fig. 1 and Fig. 2, respectively. The broad peaks at around 3390–3418 cm^{-1} indicate the alcoholic or phenolic –OH groups present in dry walnut shell (Figs. 1, 2); hydroxyl groups of polysaccharides, phenols and carboxylic acids present in aloe vera, and the stretching vibrations of the C–H group present in LEO (Fig. 2) [17, 38–40]. The peaks at around 2923–2933 cm^{-1} are assigned to C–H stretching vibrations of the aliphatic molecules in dry walnut shell, in aloe vera and in LEO. The bands at around 1741–1745 cm^{-1} corresponds to elongation of C=O bond attributed to aldehydes or saturated acid in dry walnut shell, and acetyl in aloe vera (Figs. 1, 2) [41–43]. The bands at around 1615–1622 cm^{-1} are due to stretching vibration bond C=C of the olefin structure in dry walnut shell (Figs. 1, 2), while the bands at around 1614–1621 cm^{-1} confirm the presence of the carbonyl-containing substances in aloe vera (Fig. 2) [9, 17]. The bands at around

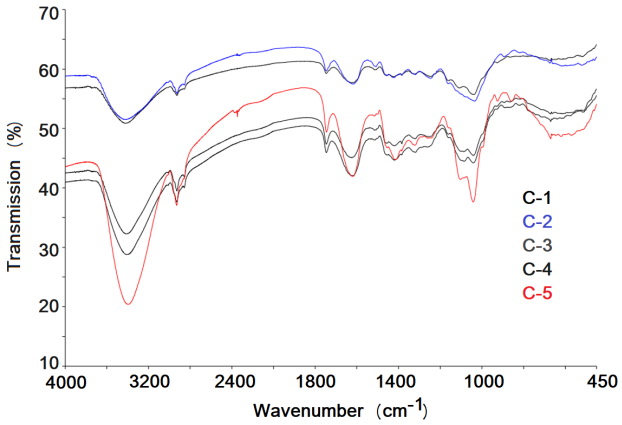


Fig. 1 FTIR Spectrum of control films

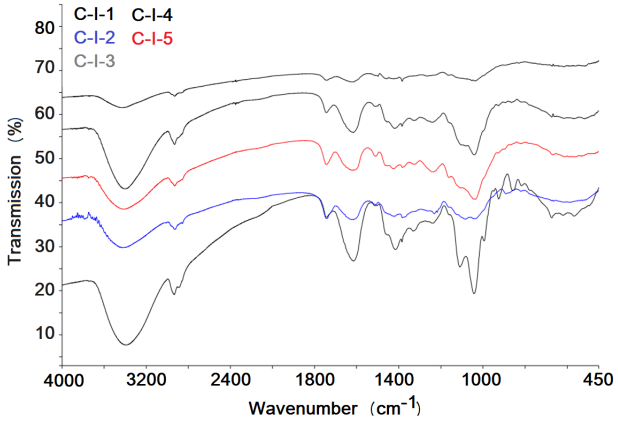


Fig. 2 FTIR Spectrum of composite films

1381–1423 cm^{-1} indicate symmetric stretching of CH_3 and COO– in aloe vera, and C–O–C stretching of LEO. The spectrum of lemon essentials oil shows characteristic bands at around 1614–1743 cm^{-1} corresponding to C=C (Fig. 2). The band located at 1109 cm^{-1} correspond to C–O stretching of terpenoid components at LEO. The bands at around 1035–1042 cm^{-1} are assigned to vibration binding of C–O, which indicates the presence of ester group in dry walnut shell (Figs. 1, 2), and the stretching vibration peak of C–H on benzene ring of LEO (Fig. 2). The bands in the region between 1083 and 614 cm^{-1} are assigned to C–O–C and stretching vibrations related to polysaccharides and sugars present in aloe vera (Fig. 2) [40–43]. When the FTIR spectra of edible composite films were examined, it was observed that no new peak formation occurred. This showed that there is no chemical interaction between them and that each one maintained its own structure.

3.2 Scanning electron microscopy (SEM)

The surface morphology of the AVG and LEO incorporated dry walnut shell-based edible film, produced using optimized parameters, was analyzed by SEM. Previous studies have indicated that walnut shell has multilayer structure in linear bundles and loud lignin concentration caused the adhesive nature [10]. Walnut shells containing different sizes and shapes of cellulose fiber, have amorphous nature and heterogeneous morphology [36]. The standard sodium alginate film has a rough surface with sharp and long spikes [44, 45]. The surface of the dry walnut shell based edible film produced with the addition of sodium alginate and glycerol was roughness, while sodium alginate and sorbitol added film surface was less divided and has straight aspect (Fig. 3: C1, C2). The sorbitol incorporation to the films contributed to the complete gelatinization of the films and induced a compact and uniform surface. When glycerol was added, gelation did not occur, and a rough surface was formed. Due to its high solubility and hydrophilic properties, AVG is completely dissolved in the film-forming solution and does not affect the surface microstructure of the films [46]. The addition of LEO to the films increases the surface roughness due to the advancing of oil droplets towards the film surface and the volatility of LEO. The evaporation of water in addition to the volatilization of essential oil causes an irregular film surface formation [14]. It was observed that, the surface of LEO and AVG incorporated film was rougher than that of the control film (Fig. 3: C-L-1, C-L-2).

3.3 Water vapor transmission rate (WVTR)

WVTR indicates the moisture transfer permeability of edible films, between atmosphere and food. The water vapor permeability of films is a significant factor for product shelf-life because water may transfer from the internal or external environment through the film, causing the corruption of

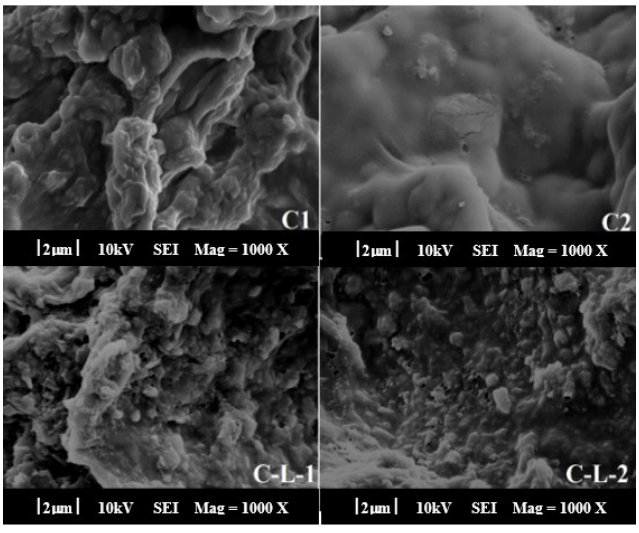


Fig. 3 SEM of optimum control films and composite films

product quality and shortening the shelf-life [19]. The presence of lipid compounds in the film structure increases the water barrier properties by increasing tortuosity. The water permeation occurs through the hydrophilic part of the films [47–49]. The presence of hydrophobic compounds such as LEO, can decrease WVTR by reducing the permeation of the films. And the increase of the WVTR of the films is due to AVG addition [15, 50]. The water vapor transmission rate of control film C1 increased by 8.7%, C2 increased by 51.1%, C3 increased by 72.3%, C4 increased by 59.9% and C5 increased by 44.6% after the LEO and AV addition. The lowest WVTR value was obtained from CL2 and CL4 films.

3.4 Moisture content

The moisture content value indicates the total null volume filled by water molecules in the microstructure of the edible film [33]. The shelf life of the films is related to their moisture content directly. After the LEO and AVG addition to the edible film, moisture contents of C1 decreased from 17.9 to 13.7%, C3 decreased from 12.8 to 6.3%, C4 decreased from 10.9 to 6.2%, C5 decreased from 15.5 to 8.1%. Only the moisture content of the edible film plasticized without glycerol (CL2) increased, from 0.6 to 2.9%, at the same time, it has minimum moisture content value (Table 2). Essential oils increase the water barrier properties of edible films and reduce water absorption capacity, because of their hydrophobic nature. AVG addition to the edible films increased to the moisture content because of their hygroscopic properties. Dry walnut shell, LEO and AVG interaction reduce with the addition of AVG, and consequently free hydroxyl groups can absorb more water [46]. C2 and CL2 edible films were produced using sorbitol as plasticizer. Using sorbitol as a plasticizer reduces the moisture retention of the C2 film, while aloe vera and lemon essential oil increase this. Because sorbitol has lower hydrophilicity and is easily soluble in water. Glycerol plasticized edible films has high hydrophilicity than sorbitol plasticized films because of the high moisture content of glycerol. High moisture content films are more stretchable and flexible and can be used in different food areas [51–53].

3.5 Water solubility

Water solubility is a considerable property related to hydrophilicity, for biodegradable edible films. Solubility can influence the water resistance of the edible film, especially in a humid environment [19, 52]. Edible films must be insoluble in water to protect product stability and water resistance, for use in food packaging. However, high water solubility can be useful for the application of edible coating [54]. The addition of LEO and AVG, with glycerol as a plasticizer, decreased the solubility of film in water. On the contrary, the addition of LEO and AVG, with sorbitol as a plasticizer, increased to the solubility of film because, glycerol plasticized edible films has high hydrophilicity than sorbitol plasticized films because of the high moisture content of glycerol [19, 35]. Water solubility of the edible films produced with LEO and AVG addition, are shown in Table 2. It was seen that CL3 has the highest and CL1 has the lowest water solubility. The edible film with low water solubility exhibits high water resistant which is an essential parameter for food packaging.

3.6 Swelling index

Swelling index demonstrate the conservation of quality during packaging and storage of food products [55]. The swelling index refers to the hydrophilic ability of material in the case of sufficient water [56]. Swelling index of the films plasticized with different concentrations of glycerol and sorbitol and produced with LEO and AVG

Table 2 Characterization of edible films

Film	Moisture (%)	WVTR (g cm^2/s)	Solubility (%)	Swelling (%)	Thickness (mm)
C_1	17.9 ± 0.15	$9.7.10^{-8}$ ± 0.11	16.0 ± 0.12	168.36 ± 3.44	0.24 ± 0.09
CL_1	13.7 ± 0.05	$10.5.10^{-8}$ ± 0.09	3.4 ± 0.07	81.68 ± 2.09	0.43 ± 0.04
C_2	0.6 ± 0.06	$6.8.10^{-8}$ ± 0.05	3.7 ± 0.05	285.69 ± 3.70	0.47 ± 0.07
CL_2	2.9 ± 0.05	$10.2.10^{-8}$ ± 0.07	8.9 ± 0.10	107.31 ± 3.62	0.47 ± 0.03
C_3	12.8 ± 0.06	$7.4.10^{-8}$ ± 0.10	16.6 ± 0.07	114.55 ± 1.48	0.40 ± 0.04
CL_3	6.3 ± 0.09	$12.7.10^{-8}$ ± 0.05	16.8 ± 0.09	126.57 ± 3.39	0.44 ± 0.02
C_4	10.9 ± 0.05	$6.4.10^{-8}$ ± 0.09	4.3 ± 0.06	241.46 ± 1.19	0.19 ± 0.01
CL_4	6.2 ± 0.05	$10.2.10^{-8}$ ± 0.05	5.6 ± 0.17	154.37 ± 6.70	0.29 ± 0.00
C_5	15.5 ± 0.11	$8.2.10^{-8}$ ± 0.14	68 ± 0.05	106.14 ± 6.64	0.38 ± 0.01
CL_5	8.1 ± 0.12	$11.8.10^{-8}$ ± 0.05	4.9 ± 0.10	128.93 ± 1.21	0.48 ± 0.02

Values are mean of three replicates ± SD

addition are shown in Table 2. The swelling index of C1 was reduced by 51.5%, C2 was reduced by 62.4% and C4 was reduced by 36.1%. Conversely, the swelling index of the C3 was increased by 10.5% and C5 was increased by 21.5%. It has been assumed that the swelling index is related to the extent of crosslinking and normally the swelling index decreased as the degree of crosslinking increased. Addition of the active compound AVG to the film increased to the degree of swelling. LEO containing films has higher swelling index than the control group. This is ascribed to intense intermolecular interactions between the polymer matrix and phenolic compounds of LEO, which decrease the integration of film matrix resulting breaking apart of such films [55–57]. Because of this, swelling index of C3 and C5 has been increased after AVG and LEO addition. The control films C2 and C4 has higher swelling index because they have higher sorbitol %. The films with lower glycerol % contain greater number of free hydrophilic groups within the edible-film network, such as carboxyl and hydroxyl groups, which can interact with water molecules and allow swelling of the samples. LEO and AVG added composite film CL4 have the highest and CL1 has the lowest swelling index.

3.7 Film thickness

The thickness of edible films plays an important role in physical properties, such as barrier properties. Different chemical components in LEO increase the distance between the particles in the matrix, resulting in an increase in the film thickness [58]. The thickness of the film is affected by glycerol, sorbitol, AVG and LEO content [48, 50]. It is preferred that the film thickness is less than 0.3 mm so that the packaged food can be eaten together with the edible film. Produced edible film thickness are shown in Table 2. The results indicated that the LEO and AVG addition increased the film thickness. The control film C4 and the composite film CL4 has the lowest thickness [59].

3.8 Moisture content, water solubility, swelling index and film thickness of references studies

The thickness, swelling (%), solubility (%) and moisture (%) values of edible film prepared from different sources are given in Table 3 and produced edible films images were given in Fig. 4. Produced edible control film C4 (0.2 mm) thickness value is lower than, corn starch-gelatin based edible films incorporated with mango and

Table 3 Film properties of references studies

Films	Thickness (mm)	Swelling (%)	Solubility (%)	Moisture (%)	Ref.
CSG	0.22 ± 0.00^{e}	24.6 ± 3.44^{f}	64.1 ± 3.68^{a}	13.7 ± 0.44^{d}	[35]
5% MP	0.24 ± 0.00^{de}	63.7 ± 2.09^{cde}	35.4 ± 3.80^{bc}	17.2 ± 1.12^{cd}	
10% MP	0.25 ± 0.01^{cd}	73.5 ± 3.70^{c}	49.8 ± 1.75^{ab}	19.8 ± 0.51^{abc}	
15% MP	0.25 ± 0.00^{cd}	73.7 ± 3.62^{c}	49.9 ± 8.39^{ab}	22.8 ± 1.78^{a}	
5% MPP	0.27 ± 0.02^{bc}	74.24 ± 1.48^{bc}	30.5 ± 3.37^{c}	18.3 ± 1.4^{bc}	
10% MPP	0.28 ± 0.00^{ab}	54.8 ± 3.39^{e}	41.8 ± 4.45^{bc}	17.1 ± 0.67^{c}	
15% MPP	0.30 ± 0.00^{a}	66.4 ± 1.19^{cd}	26.8 ± 9.44^{c}	21.3 ± 1.10^{ab}	
5% PP	0.25 ± 0.00^{cd}	88.9 ± 6.70^{a}	45.2 ± 7.55^{b}	16.4 ± 2.71^{cd}	
10% PP	0.22 ± 0.00^{e}	84.9 ± 6.64^{ab}	52.3 ± 11.23^{ab}	14.1 ± 0.61^{d}	
15% PP	0.27 ± 0.00^{bc}	58.8 ± 1.21^{de}	50.5 ± 0.88^{ab}	16.9 ± 1.80^{cd}	
0% CEO	0.07 ± 2.45^{f}		52.8 ± 1.01^{a}		[37]
0.5% CEO	0.08 ± 3.41^{e}		42.6 ± 0.88^{b}		
1.0% CEO	0.10 ± 3.43^{d}		24.3 ± 0.66^{d}		
1.5% CEO	0.11 ± 3.14^{c}		18.7 ± 0.94^{e}		
2.0% CEO	0.12 ± 3.77^{b}		26.1 ± 0.96^{d}		
2.5% CEO	0.13 ± 3.87^{a}		29.1 ± 1.21^{c}		
Control	0.07 ± 0.007^{a}	52.8 ± 4.14^{a}	59.3 ± 1.55^{a}	24.4 ± 0.72^{ab}	[48]
CH-L	0.09 ± 0.003^{b}	15.9 ± 0.82^{d}	28.9 ± 1.63^{de}	22.3 ± 1.65^{bc}	
CH-T	0.10 ± 0.004^{bc}	20.0 ± 2.21^{bc}	42.9 ± 1.03^{b}	25.3 ± 1.73^{a}	
CH-C	0.09 ± 0.007^{bc}	15.4 ± 2.42^{d}	39.2 ± 3.17^{bc}	23.6 ± 1.95^{ab}	
CH-LT	0.09 ± 0.003^{bc}	17.1 ± 0.63^{cd}	34.9 ± 3.05^{cd}	22.5 ± 1.38^{bc}	
CH-LC	0.09 ± 0.006^{b}	11.3 ± 0.51^{e}	25.3 ± 2.14^{e}	20.1 ± 1.95^{d}	
CH-TC	0.10 ± 0.002^{c}	23.5 ± 1.35^{b}	43.7 ± 4.03^{b}	21.9 ± 1.84^{cd}	

Table 3 Film properties of references studies (Continued)

Films	Thickness (mm)	Swelling (%)	Solubility (%)	Moisture (%)	Ref.
SRC-Control	0.05 ± 0.001^{a}		42.8 ± 1.6^{a}	8.8 ± 0.6^{ab}	
SRC-20G	0.06 ± 0.001^{bc}		44.4 ± 1.3^{ab}	9.8 ± 0.3^{bc}	
SRC-25G	0.07 ± 0.002^{d}		45.9 ± 1.7^{b}	10.2 ± 1.4^{cd}	
SRC-30G	0.07 ± 0.001^{e}		49.5 ± 1.9^{c}	14.5 ± 1.0^{e}	[51]
SRC-20S	0.06 ± 0.002^{b}		42.6 ± 1.4^{a}	7.7 ± 0.2^{a}	
SRC-25S	0.06 ± 0.001^{bc}		44.9 ± 1.2^{ab}	9.6 ± 0.6^{bc}	
SRC-30S	0.07 ± 0.002^{d}		46.3 ± 0.6^{b}	11.0 ± 0.5^{d}	
G 0.3%-E 0%	0.08 ± 8^{E}	503.1 ± 20.44^{A}	53.1 ± 6.01^{A}	8.2 ± 0.48^{A}	
G 0.3%-E 0.5%	0.10 ± 1^{D}	247.7 ± 11.53^{C}	41.6 ± 2.55^{B}	7.3 ± 0.08^{BC}	
G 0.3%-E 1%	0.14 ± 14^{AB}	178.0 ± 10.87^{EF}	25.9 ± 1.32^{C}	6.8 ± 0.08^{BC}	
G 0.6%-E 0%	0.09 ± 8^{E}	467.2 ± 24.58^{B}	51.4 ± 2.02^{A}	7.5 ± 0.30^{AB}	
G 0.6%-E 0.5%	0.12 ± 7^{BC}	223.9 ± 8.53^{CD}	39.3 ± 0.40^{B}	7.1 ± 0.60^{BC}	[53]
G 0.6%-E 1%	0.14 ± 7^{A}	162.1 ± 2.09^{F}	25.5 ± 1.05^{C}	6.7 ± 0.59^{BC}	
G 0.9%-E 0%	0.11 ± 10^{CD}	460.3 ± 4.87^{B}	50.6 ± 2.53^{A}	7.2 ± 0.05^{BC}	
G 0.9%-E 0.5%	0.12 ± 1^{C}	203.7 ± 6.45^{DE}	37.9 ± 0.12^{B}	6.8 ± 0.26^{BC}	
G 0.9%-E 1%	0.12 ± 5^{BC}	153.9 ± 4.21^{F}	24.6 ± 0.94^{C}	6.6 ± 0.04^{C}	
C_1	0.24 ± 0.09	168.4 ± 3.44	16.4 ± 0.12	17.9 ± 0.15	
CL_1	0.43 ± 0.04	81.7 ± 2.09	3.9 ± 0.07	13.7 ± 0.05	
C_2	0.47 ± 0.07	285.7 ± 3.70	3.7 ± 0.05	0.6 ± 0.06	
CL_2	0.47 ± 0.03	107.3 ± 3.62	8.9 ± 0.10	2.9 ± 0.05	
C_3	0.40 ± 0.04	114.6 ± 1.48	16.6 ± 0.07	12.8 ± 0.06	Our work
CL_3	0.44 ± 0.02	126.6 ± 3.39	16.8 ± 0.09	6.3 ± 0.09	
C_4	0.19 ± 0.01	241.5 ± 1.19	4.3 ± 0.06	10.9 ± 0.05	
CL_4	0.29 ± 0.00	154.4 ± 6.70	5.6 ± 0.17	6.2 ± 0.05	
C_5	0.38 ± 0.01	106.1 ± 6.64	6.7 ± 0.05	15.5 ± 0.11	
CL_5	0.48 ± 0.02	128.9 ± 1.21	4.9 ± 0.10	8.1 ± 0.12	

Different letters in the same column indicate significant differences among film samples ($p < 0.05$).

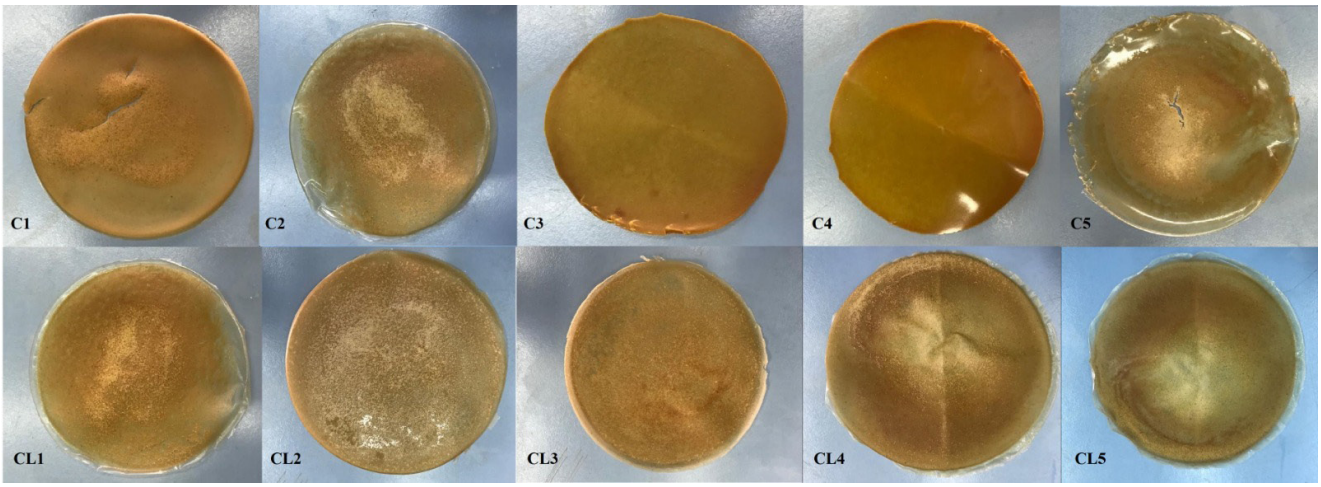


Fig. 4 Edible control and composite films photos

pineapple [35], but its higher than the other films studied. Optimum solubility (3.9%) and swelling (81.7%) in the films studied, was obtained from CL1 composite edible film. The second optimum solubility value (18.7%) was obtained from, cinnamon essential oil incorporated cassava starch-based edible film [37]. Lemon and cinnamon essential oil added chitosan film demonstrate lower swelling degree (11.3%) than the produced edible films [52].

Produced edible control film moisture content (17.9%) is higher than, semi-refined kappa-carrageenan based edible films plasticized with glycerol or sorbitol (14.5%) [48] and, edible films from Persian gum under different concentrations of glycerol and emulsified oil droplets (8.2%) [54]. But its lower than the other films studied.

3.9 Color

The color of the edible film is a significant factor in term of the product appearance, and the consumer receiving [19, 60]. The color parameter of the films plasticized with different concentrations of glycerol and sorbitol and produced with LEO addition are shown in Table 4. However, the addition of LEO and AVG caused color change in the produced films. The color parameters (L^*, a^*, b^* and total color difference (ΔE)), are given in Table 4. After the incorporation of LEO and AVG to the films, there was a reduction in lightness (L^*) values of CL1, CL2, CL3 and CL5 and an increase in lightness (L^*) values of CL4. The a^* value of CL4 was decreased, while the a^* value of CL1, CL2, CL3 and CL5 increased by tending to the red. The b^* value of CL1, CL2, CL4 and CL5 was increased by tending to the yellow, and there was a reduction in yellowness (b^*) values of CL3. The highest ΔE value 18.42 was obtained from the CL3 composite film.

Table 4 Color parameters of edible films

Film	L^*	a^*	b^*	ΔE
C1	50.05 ± 0.42	14.37 ± 0.01	27.50 ± 1.01	
CL1	44.21 ± 0.45	18.59 ± 0.03	28.82 ± 0.33	7.32 ± 0.40
C2	58.58 ± 0.27	13.16 ± 0.05	28.26 ± 0.21	
CL2	57.82 ± 0.37	14.27 ± 0.20	30.64 ± 0.07	2.73 ± 0.47
C3	60.92 ± 0.53	13.56 ± 0.49	28.13 ± 0.14	
CL3	43.04 ± 0.48	17.51 ± 0.72	26.10 ± 0.56	18.42 ± 0.44
C4	54.70 ± 0.20	14.42 ± 0.11	28.65 ± 0.74	
CL4	55.79 ± 0.32	13.86 ± 0.08	29.27 ± 0.85	1.372 ± 0.22
C5	57.87 ± 0.06	14.72 ± 0.12	29.64 ± 0.68	
CL5	52.36 ± 0.21	14.80 ± 0.23	31.07 ± 0.47	5.70 ± 0.33

Values are mean of three replicates ± SD

4 Conclusions

This study showed that a new edible film can be produced successfully from dried walnut shell plasticized with glycerol and/or sorbitol with the addition of LEO and AVG. FTIR spectra of produced edible films confirmed the successful incorporation of glycerol, sorbitol, LEO and AVG. The surface morphology analysis of the edible composite film showed that sorbitol is more suitable plasticizer for dry walnut shell-sodium alginate edible film. AVG is completely dissolved in the film-forming solution, conversely LEO increases the surface roughness. The presence of hydrophobic compounds such as LEO, can decrease WVTR by reducing the permeation of the films. And the increase of the WVTR of the films is due to AVG addition. Minimum WVTR values was obtained from sorbitol plasticized control film CL4 ($6.4.10^{-8}$ g cm^2/s). Dry walnut shell, LEO and AVG interaction reduce with the addition of AVG, and consequently free hydroxyl groups can absorb more water. Glycerol plasticized edible films has high hydrophilicity than sorbitol plasticized films because of the high moisture content of glycerol. Control (C1) and composite (CL1) edible films added glycerol as a plasticizer, have the highest moisture content (17.9% and 13.7% respectively). The addition of LEO and AVG, with sorbitol as a plasticizer, increased to the solubility of film. LEO and AVG incorporation, with glycerol as a plasticizer, decreased the solubility of film in water and CL1 has the lowest water solubility (3.9%). AVG and LEO addition to the film increase the degree of swelling. The films with lower glycerol % allow swelling of the samples. The composite edible film CL1 plasticized with glycerol has the lowest swelling index. LEO and AVG addition increased to the film thickness and caused color change in the produced films. The control film C4 (0.2 mm) and the composite film CL4 (0.3 mm) have the lowest thickness values. Minimum color change was occurred to the C4 edible film ΔE = 1.372. The use of waste dry walnut shell in edible film production is the biggest difference of this work from the past works. In the continuation of this work, the edible film produced will be used as food packaging material.

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