

# Film production with groundnut extraction cake and its physico-mechanical properties with potential use for food packaging

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**Abstract**— The edible films have been produced from protein containing foods especially nuts by casting process and no available researches found on using the extracted proteins in dried extraction cake of groundnut seed. The aim of this research was to get an edible film from dried extraction cake of groundnut seed and to characterise their physico-mechanical, optical and barrier permeabilities with different concentration of alkali solution (NaOH). The films presented high values of  $L^*$  (average as 84.8) in terms of lightness. The tensile strength (MPa) and elongations at break (%) decreased with increase in alkali solution. The alkali solutions increased the water vapour permeabilities (WVP) but decreased oxygen permeabilities (OP) of the films. The protein fraction of extraction cake of groundnut seeds showed the potential to be processable into the edible films. Arginine (Arg) and cysteine (Cys) were the major amino acids in the films. The produced films were used to package olive oil for 60 days of storage at room temperature. The peroxide values of olive oil increased less than conditioned in produced films and good barrier plastic material (PP) during storage period. The films improved the olive oil chemical stability and it showed suitable film properties.

**Keywords**— Extraction cake; Film; Physico-mechanical properties; Amino acids; Chemical stability.

## PRACTICAL APPLICATION

The dried extraction cake from groundnut seed contained ingredients as 29.59 g 100 g<sup>-1</sup> protein, 27.41 g 100 g<sup>-1</sup> CH, 3.06 g 100 g<sup>-1</sup> moisture, 2.20 g 100 g<sup>-1</sup> ash, 33.71 g oil 100 g<sup>-1</sup> and 3.97 g 100 g<sup>-1</sup> fibre content and films that obtained from extraction cake of groundnut seed with an alkali solution of NaOH (0.25% w w<sup>-1</sup>) had higher tensile strength (MPa) and elongation at break (%) with low Young's modulus (MPa). The produced films had a higher percentage of arginine (14.89%), cysteine (10.41%) and aspartate (10.13%) with lower peroxide values.

## I. INTRODUCTION

Groundnuts (*Arachis hypogaea* L.) are one of the major cereal products grown in the world with huge amounts (47 million tons) that cultured every year and important agricultural food product in southern region (cities of Adana & Osmaniye, Turkey), especially where 81% of total agricultural crops (165.000 tons annually in Turkey) were conducted, [1]. It is characterised by mainly high protein (25-30%), oil content (46-55%), low content of CH (carbohydrates) and ash [2]. Groundnuts offer protein

source, which is specified by its functional attributes and better nutritional constituents.

Imitation milk from agricultural foods and their products have many benefits in terms of nutrition for humans due to high level of protein, fatty acids and minerals in terms of highly valuable ingredients for human nutrition [3,4]. Vegan milk (vegan food) can be obtained by immersing in water and grinding of nuts with distilled water to obtain a slurry form following after the filtration process [5,6] or alternatively, it can be processed by roasting and

milling groundnuts to get flour with full-fat or partially defatted products from nuts. After that water can be used with different ratios (1:6), mixed and filtered to obtain vegan milk [7]. The remaining portion (extraction cake of groundnut seed) is slurry form after vegan milk production and contained high valuable materials that can be used for further purposes that contained higher amount of total solids [7,12].

The edibility and coating attributes of films have an important property in preserving the food quality from many deterioration reactions. The film produces permeable structure against water vapour, gases, fats and volatiles of volatile substances [8]. The produced films and its coverings may act as a conveyor of food components (antioxidants, colour pigments and flavour compounds etc.) and the applications of this type of film improve the physico-mechanical attributes and preserve the structural uniformity of the food materials [9].

The protein containing foods were used mainly to obtain film materials, which are macromolecules forming a precisely structured and ordered by H-bonding structure. In case of that features, proteins show good setting material to many gases, as well as mechanical and structural properties. Nut containing foods are of interest as potential biopolymeric ingredients for films due to their high protein ingredient. Additionally, the glycerin, sorbitol or polyethylene glycol are being used as plasticizers to get edible films and protein films that crosslinked with glutaraldehyde that provide the highest strength and good elongation [10].

Some researches have improved films turned on with groundnut proteins. Many of these researches have been studied the physical and chemical attributes, as well as the improvement of structural properties of groundnut protein ingredients and its films [9-11]. Only a few researches have been allocated to the film producing capability of groundnut protein. It is reported that the physical properties and water vapour barrier abilities of film proteins are subordinate to the films that made of synthetics. The functional attributes of these proteins are mainly related with the uniformity of structure, thermal sensitivity and hydrophilic behaviours of these proteins [10].

The main objective of this research was to produce an edible film that based on an extraction cake of groundnut and to describe its physical, chemical, optical, barrier and mechanical attributes with different concentrations of NaOH (0.25-1% w w<sup>-1</sup>).

## II. MATERIALS AND METHODS

### 2.1 Materials

Groundnut seeds (*Arachis hypogaea* L.) was supplied by local firm in Osmaniye, Turkey and the extraction cakes were get from groundnut during the imitation milk (vegan food) production. After that the extraction cakes were dried at atmospheric conditions (25 °C) to the final moisture contents and the dried portion were milled and sieved [12]. The oil extraction procedure was done with solvent of hexane for 6 h, and soluble carbohydrates were removed for 6 h by Soxhlet method with ethanol (70 %). After the extraction procedures, the extraction cakes were conventionally dried at 60 °C for 24 h [9]. Polypropylene film was obtained from Lidopack Company (Gaziantep, Turkey) with a thickness of 95 µm at a rate of oxygen transmission as 1.95 cm<sup>3</sup> m<sup>-2</sup> day<sup>-1</sup> Pa<sup>-1</sup>.

### 2.2 Producing films

The solution for film procedures was done according to the process that defined by Liu et al. [9,10,13] with some improvements of film producing process. The dried extraction cake was mixed with double distilled water (4 g 100 ml<sup>-1</sup>) and stirring process was done at 60 °C for 15 min. The solution of pH (6.59-6.87 at first) was calibrated (Orion Star-A211, Thermo Scientific, Singapore) to 9 to dissolve protein with the reagent grades of NaOH solutions (0.25-1% w w<sup>-1</sup>). Different ratios of glycerol (purity of 99.5%; ChemNovatic, Poland) were achieved as the plasticizer to protein (at a ratio of 1:2, 1:1 and 2:1 w w<sup>-1</sup>), and the obtained solutions were then stirred at 60 °C for 15 minutes. The solutions of film were cooled at room temperature, centrifuged (30 s) and degassing process was done under vacuumed conditions. The solutions that had the ratio of 1:1 and 2:1 in respect of glycerol to protein did not resulted the homogenous film structure. The best film forming solution was obtained with glycerol to protein ratio as 1:2 (w w<sup>-1</sup>) and after that the film casting procedure was used to obtain edible films and the solutions (10 ml) were transferred to the a horizontal silicone structure (diameter of 8.5 cm) and conventionally dried by forced air at 35 °C for 20 h (Memmert UF-55, Germany). The produced film thickness were determined by using a digital micrometer (Mitutoyo 293-340, Japan).

### 2.3 Chemical analysis

The chemical composition of extraction cake of groundnut seed was determined according to official methods of analysis [14]. The content of nitrogen was calculated by Kjeldahl method and converted to the percentage of protein by multiplying 5.46. The CH (carbohydrate) was calculated by the difference of the other ingredients, using the equation as below

CH % = 100% - (Protein, % + Oil, % + Ash, % + Moisture, %)

## 2.4 The edible film properties

### Moisture content

The moisture contents of films of dried extraction cake were determined according to the method that defined by Aguirre et al. [15] and the measurements were done in triplicate and moisture contents (%) were determined.

### CIELab (L\*,a\*,b\*) parameters

The colour measurement was done by using a Minolta colorimeter (CR-400, Japan). The L\*, a\* and b\* parameters were determined at different points (4 region) on each produced films. The L\*, a\* and b\* parameters ranged from L\*=0 referred as black point, to L\*=100 referred as white point, to -a\* referred as greenness, +a\* referred as redness, -b\* referred as blueness, +b\* referred as yellowness [9].

### Opacity

The film opacities were measured according to the process that described by Cao et al. [16]. Due to this method, the rectangular film pieces were placed into the cell of spectrophotometer and air was used as a reference. The formed film spectrum was measured in a UV-Vis spectrophotometer (Shimadzu 1800, Japan). The opacity was measured from the relationship between the film opacity of superposed on the black standart (Op<sub>B</sub>) and that of the film superposed on the white standart by using the ratio of black to white standards (Op<sub>w</sub>).

Opacity = (Op<sub>B</sub> / Op<sub>w</sub>) . 100

### Mechanical attributes

The tensile strenght (MPa) and the elongations at break (%) of the films were measured according to standard process of American Society for Testing and Materials [17]. The textrometer (Model of 3342, Instron Norwood M, USA) was used with the equipment (500 N) that operated at 0.5 mm per second. The edible films were separated into the lines at 1.5 cm wide and 0.5 cm (rectangular) length and placed between the grips of the analyzer. The tensile strength (MPa) and breaking elongation (%) were obtained from the stress vs curves of strain [9,18]. Young's modulus (MPa) was determined from the initial slope of linearity within force-deformation curve [10].

### Amino Acid Analysis

The film samples of extraction cake of groundnut were placed into the tubes and after that HCl acid solutions (6 N, 1 ml) were poured to the glass container (tube) for hydrolysis (110 °C, 24 hour). After that the distilled water added to the hydrolyzed samples, the mixture was filtered and after then filtrated phase (1 ml) was poured to the glass container and then it was evaporated by an ainer machine. The solution of HCl acid (5 ml, 0.02 N) were introduced to the glass

container in order to dissolve the amino acids. The obtained sample (50 µm) were injected into the amino acid analyzer, which has an ion exchange column (2.6×150 mm, Hitachi, L-8900, Japan) to determine amino acids. The standarts of amino acid that used in this analysis were supplied from Merck Company (Germany) [7].

### Barrier abilities of films

The water vapour permeability and oxygen permeabilites (g. m.m<sup>-2</sup>.day<sup>-1</sup>.Pa) were measured using H<sub>2</sub>O and O<sub>2</sub> diffusion sisyems according to the standart methods of ASTM [17]. The oxygen and water vapour permeability tests were done under with RH (100% for water vapour, 50% for oxygen) at different temperatures (30-50 °C) with three replications. 1 atm for pressurre (101.325 Pa) was assumed for oxygen permeability.

### Oxidative control with olive oil sample

The oxidative control of films were rearranged due to procedures that made by Riveros et al. [9] so the films of groundnut cake (0.5% and 1.0% NaOH treated) were cut in 9.5x9.5 cm pieces, sealed to produce packages of (4.75x9.5 cm) with each one containing 9 ml olive oil. The packaged oil samples were stored at a temperature of 20 C at storing period (60 days) for peroxide measurements (meq O<sub>2</sub>/kg).. Olive oil control samples were also stored in high barrier plastic materials that made of PP of 95 µm thickness (the rate of oxygen transmission as 1.95 cm<sup>3</sup> m<sup>-2</sup> day<sup>-1</sup> Pa<sup>-1</sup>) as a comperative treatment (made by synthetic material) and in petri dishes (9x14 mm). Peroxide value was accepted as lipid oxidation indicator that was expressed as miliequivalent of active oxygen per kg of olive oil.

### Statistical analysis

Statistical analysis system for Windows (v. 9) was used for the statistical analysis, variance analysis by one way (ANOVA) and Duncan's test for multiple comparison were used to determine the differences (P < 0.05). The all measurements were done in triplicate.

## III. RESULTS AND DISCUSSIONS

The used portion of extraction cake of groundnut seed (L\*:81.58, a\*:-1.04, b\*:9.27) contained 29.59 g 100 g<sup>-1</sup> protein, 27.41 g 100 g<sup>-1</sup> CH, 3.06 g 100 g<sup>-1</sup> moisture, 2.20 g 100 g<sup>-1</sup> ash, 33.71 g oil 100 g<sup>-1</sup> and 3.97 g 100 g<sup>-1</sup> fibre content. The obtained films from dried extraction cake of groundnut seeds were transparent, light yellow and the thickness varied from 0.134 mm to 0.149 mm (Figure 1). The protein contents of films that obtained from dried extraction cake varied from 48.28 (%) to 50.75 (%) (Table 1).

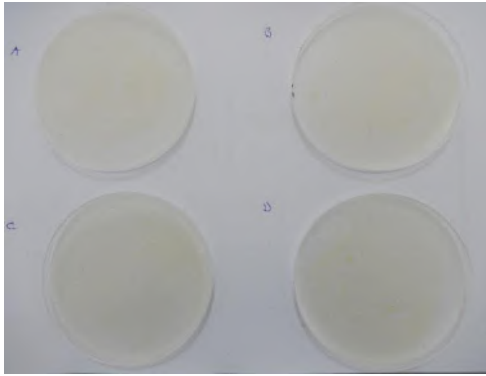


Fig.1: The produced films from dried extraction cakes of ground nut seeds with different concentrations of NaOH (A:1%, B:0.75%, C:0.50%, D:0.25%)

The results of chemical constituents of the extraction cake were similar to defatted peanut flour in terms of carbohydrate level (23.90-25.14 g 100 g<sup>-1</sup>) but contained lower amount of protein (53.22 -55.88 g 100 g<sup>-1</sup>) that obtained by Riveros et al. [9] and Wu et al. [18] respectively. The oil contents were higher than the results that determined by Riveros et al. [9] (4.06 g 100 g<sup>-1</sup> oil) and Wu et al. [19] (1.50 g 100 g<sup>-1</sup>). The differences in

composition of extraction cake comparing to defatted and groundnut flour can be explained by milk extraction process. The vegan milk from groundnut seed contains 15.92 g/100 g total solids, containing 5.74 g/100 g, 4.24 g/100 g, 5.58 g/100 g fat, carbohydrate and protein respectively [7]. According to the results, the dried extraction cake of groundnut seed presented higher protein and lower carbohydrate content comparing with other raw materials such as achira flour that reported by Andrade-Mahecha et al. [19] (4.5 g 100 g<sup>-1</sup> for protein, 71.7 g 100 g<sup>-1</sup> for carbohydrate) and banana flour that reported by Pelissari et al. [21] (3.2 100 g<sup>-1</sup> for protein, 83.2 g 100 g<sup>-1</sup> for carbohydrate). The films of extraction cake of groundnut seeds contained around 48.2-50.7% protein and these values are comparable to that results of defatted peanut flour films that researched by Riveros et al. [9] (53.06%). It is reported that groundnut seeds contain higher amount of amino acids especially arginine (Arg) and glutamic acid (Glx), which are major amino acids in groundnut flour. The films that obtained from defatted peanut flour contained higher amount of aspartic acid (Asx), threonine (Thr), serine (Ser), histidine (His) and cysteine (Cys) respectively [9] (Riveros et al. 2018) so it is reported that the amino acid compositions are important for the production of biodegradable films [22].

Table1. The film properties of dried extraction cake of ground nut seeds that obtained different ratios of NaOH

Properties	Alkali concentrations of NaOH (%)			
	0.25%	0.50%	0.75%	1.0%
Moisture (%)	23.85 <sup>b</sup>	24.04 <sup>b</sup>	24.24 <sup>b</sup>	24.97 <sup>a</sup>
Protein (%)	48.28 <sup>a</sup>	48.97 <sup>a</sup>	49.16 <sup>a</sup>	50.75 <sup>a</sup>
Opacity (nm mm <sup>-1</sup> )	1.98 <sup>b</sup>	2.04 <sup>a</sup>	2.07 <sup>a</sup>	2.11 <sup>a</sup>
Thickness (mm)	0.134 <sup>a</sup>	0.137 <sup>a</sup>	0.141 <sup>a</sup>	0.149 <sup>a</sup>
L*	88.77 <sup>a</sup>	86.45 <sup>a</sup>	83.22 <sup>b</sup>	81.13 <sup>b</sup>
a*	-1.89 <sup>c</sup>	-1.82 <sup>c</sup>	-2.14 <sup>b</sup>	-2.47 <sup>a</sup>
b*	7.30 <sup>c</sup>	8.34 <sup>b</sup>	8.55 <sup>b</sup>	9.66 <sup>a</sup>

Different small letters for films in row show significantly difference ( $P < 0.05$ )

**Film properties**

The moisture content of films that obtained from dried extraction cake of groundnut were ranged from 23.85% to 24.97% and these values were higher than the results that obtained by Riveros et al. [9] (21.10%) and the results that obtained by Borneo et al. [23] (16.50%). It is reported that the moisture characteristics are related with the polarity and the plasticizer of the polymer [9]. The glycerol was used in the production of films from groundnut extraction cake. It is assumed that the glycerol proportion (ratio of 1:2 w w<sup>-1</sup>)

in the production of film with a certain thickness allowed the formation a film with good barrier properties.

The measured L\* values varied from 81.13 to 88.77 for the films of extraction cake with different ratios of NaOH (0.25-1%) (Table 1). The increase in alkali concentration (NaOH) decreased the L\* values and these L\* values were close to Riveros et al. [9] (L\*:86.83) that obtained from defatted groundnut flour. It is reported that films treated with formaldehyde had the highest colour (L\*:76.32) compared to the glutaraldehyde-treated films (L\*:59.19) for groundnut protein films that researched by

Liu et al. [10]. The  $a^*$  values varied from -1.89 to -2.47, indicative of red-green chromaticity and increasing alkali concentrations (NaOH) lowered  $a^*$  values, which were lower than Riveros et al. [9] ( $a^*:-0.98$ ). The observed  $b^*$  values, yellow-blue chromaticity varied from 7.30 to 9.66 and these values were higher than defatted groundnut flour films ( $b^*:5.89$ ) [9]. It is reported that the film redness increased from CIE  $a^*$  around 5 times for the control samples to more than 13 times for films that treated with glutaraldehyde, and the  $b^*$  (yellowness) increased from 30 to 35 times respectively. According to the results of research that made by Liu et al. [10], formaldehyde-treated films exhibited high L values among the films that treated with different chemicals as formaldehyde, glutaraldehyde, anhydrides of acetic and succinic acids. Although it is reported that the reason of colorization from yellow to brown associated with the interaction of protein-aldehyde explaining by various intermediate substances or final products of the maillard reactions [10], the films of extraction cake of groundnut had higher  $L^*$  values than glutaraldehyde-treated films for peanut protein films.

The opacity values of dried extraction cake of groundnut seed varied from  $1.98 \text{ nm mm}^{-1}$  to  $2.11 \text{ nm mm}^{-1}$  and these values were lower than the result of defatted groundnut flour films that obtained by Riveros et al. [9] ( $2.35 \text{ nm mm}^{-1}$ ). There were a few research for opacity values in

literatures, some of them reported that the opacities varied from 1.1 to  $2.2 \text{ nm mm}^{-1}$  for the films of amaranth proteins that obtained under high modified pressure and varied from 1.2 to 3.0 for amaranth protein films [24,25]. However, although the films produced in this research showed low values of opacity, and as such could be considered as practically transparent.

The tensile strengths of the produced films were varied from 4.72 to 5.16 (MPa) and increasing the alkali concentrations used in film production from extraction cake lowered the tensile strength (Table 2). The elongation at break (%) values varied from 32.9 to 51.4 and films produced at low concentration of NaOH (0.25%) had the higher tensile strength (TS) with breaking elongation but lower Young's modulus (MPa). There were significant decreases in tensile strength (MPa), elongation at break (%) but increase in Young's modulus when the NaOH concentration changed from 0.25% to 0.50% as seen in Table 2. It is reported that an increase in NaOH (%) decreased the tensile strength (TS) and breaking elongation (%) for thermoplastic films of peanut proteins from meal that conducted by Reddy et al. [18] and the films that obtained at low concentration of NaOH (0.25%) had the higher tensile strength and breaking elongation but lower Young's modulus (MPa) respectively.

Table 2. The barrier properties of films of dried extraction cake of ground nut seeds that obtained different ratios of NaOH

Properties	Alkali concentrations of NaOH (%)			
	0.25%	0.50%	0.75%	1.0%
Tensile strength (MPa)	5.16 <sup>a</sup>	4.89 <sup>b</sup>	4.74 <sup>b</sup>	4.72 <sup>b</sup>
Elongation at break (%)	51.4 <sup>a</sup>	37.7 <sup>b</sup>	33.8 <sup>b</sup>	32.9 <sup>b</sup>
Young's modulus (MPa)	81 <sup>b</sup>	137 <sup>a</sup>	134 <sup>a</sup>	122 <sup>a</sup>
WVP ( $\times 10^{-6} \text{ g. m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$ )	59.43 <sup>b</sup>	59.00 <sup>b</sup>	60.42 <sup>b</sup>	63.35 <sup>a</sup>
OP ( $\times 10^{-6} \text{ g. m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$ )	19.57 <sup>a</sup>	18.33 <sup>b</sup>	16.83 <sup>c</sup>	16.17 <sup>c</sup>

Different small letters for films in row show significantly difference ( $P < 0.05$ )

However, additional increase in NaOH (%) from 0.75% to 1%, had not significant effects in terms of tensile strength (MPa) and Young's modulus (MPa). There was a general decreasing trend in tensile strength and elongation at break for the films of dried extraction cake of groundnuts (Figure 2). The extracted proteins from extraction cake of groundnut

seed were hydrolyzed to a greater amount compared with the extracted proteins due to the lower concentration of NaOH. Increase in NaOH concentration (from 0.5 to 1.0%) caused the decrease in breaking elongation (%) and tensile strength (MPa) of the films therefore lower concentration of NaOH ( $\leq 0.25\%$ ) can be used for optimizing the film

producing process from extraction cake of groundnut seeds. It is revealed that pH affected peanut films properties by physicochemically, there was no effect on tensile strength but breaking elongation (%) increased with increase in pH [26]. With respect to the groundnut films properties, the tensile strength and breaking elongation (%) values were comparable to that some relevant studies related with the films that produced from peanut containing materials such as defatted flour and meals. The obtained results of films of extraction cake of groundnut seed were lower than the tensile strength (6.7 MPa) and elongation at break (118 %) but higher than Young's modulus (51 MPa) of wheat gluten films that obtained by Chen et al. [27] respectively. It is reported that the tensile strength and elongation at break (%) of peanut protein films that cross-linked with citric acid were 4.6 (MPa) and 66 (%) with 102 (MPa) modulus respectively. Increase in protein concentrations affected significantly, tensile strength ranged from 2.7 to 5.1 (MPa) with an increase in elongations at break varied from 14 to 77 (%) [13]. This phenomena can be explained an increase in protein contents caused the interactions among proteins yielding higher tensile strength. The results of modulus (MPa) were similar to that obtained by Reddy et al. [13] (84-115 MPa) but higher than the results that obtained by Liu et al. [10] (1.79 MPa). The flours of some agricultural products such as defatted peanut, peanut meal and peanut protein, extraction

cake of groundnut seed films exhibit good mechanical properties in respect of tensile strength, breaking elongation and Young's modulus compared with the biodegradable films.

It is reported that there was a close relationship among glycerol concentration and mechanical properties of groundnut protein films in respects of tensile strength (MPa) and elongations at break (%). Increase in glycerol content negatively affected the tensile strength and Young's modulus respectively [13](Reddy et al. 2012). The higher tensile strength obtained without any glycerol content (12.3 MPa) but the produced films become very brittle structure in case of lower elongation break (%). Additionally using high amount of glycerol at a ratio in terms of protein (0.67-1.67 g/g) yielded higher tensile strength that ranged from 4.1 to 5.14 MPa for peanut protein films that conducted by Jangchud&Chinnan [26]. It is reported that 3 (%) addition of glycerol content decreased the film strength by 3.5 times within by 4 times for Young's modulus and concentration of glycerol with 5-7.5 (%) gaved similar mechanical attributes in respect of tensile strength (MPa) and breaking elongation (%) in that research. Although a concentratin of 5 to 7.5 (%) of glycerol is assumed as thresold values for optimizing film producing conditions from peanut proteins, a ratio of protein to plasticizer of 1:2 (w w<sup>-1</sup>) provided similar mechanical properties in this research.

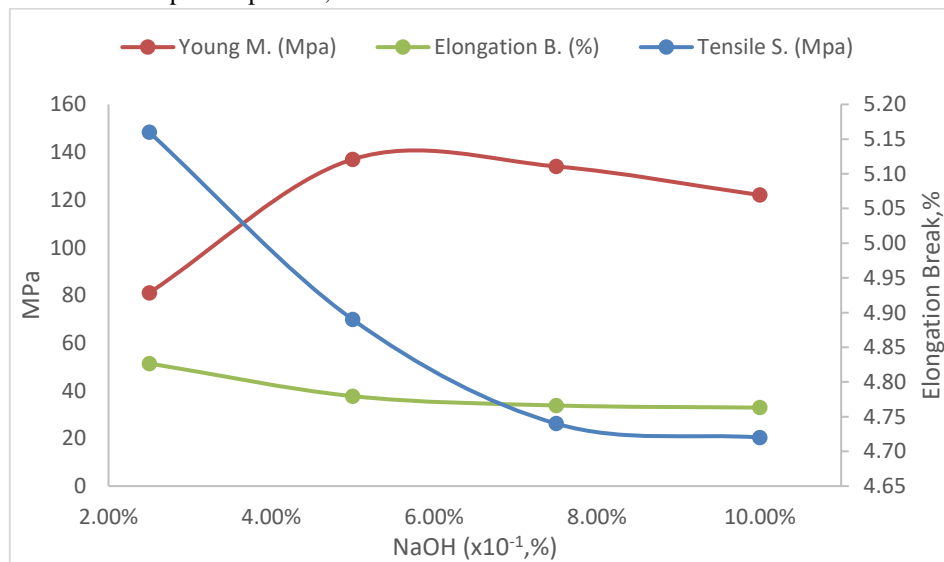


Fig.2: Young modulus (MPa), elongation break (%) and tensile strength (MPa) of films from dried extraction cakes of ground nut seeds with different concentrations of NaOH

The water vapour permeabilities of films of dried extraction cakes varied from 59.43 to 63.35 10<sup>-6</sup> g.m<sup>-1</sup> day<sup>-1</sup>.Pa (Table 2). The lower values of water vapour permeabilities show the excellent barrier ability for the

extraction cake of groundnut films. These results were higher than the defatted peanut flour films that obtained by Riveros et al. [9] (167.9 10<sup>-11</sup> g m<sup>-1</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>) and the mixtures of peanut protein isolate-gum that obtained by Li et al. [28]

( $139.8 \cdot 10^{-11} \text{ g m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ), but lower than the results of peanut protein films that obtained by Liu et al. [10] ( $9.14 \cdot 10^{-6} \text{ g} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ) respectively. It is reported that the water vapour permeabilities of peanut films that cross-linked with citric acid is  $44.5 \text{ (g h}^{-1} \cdot \text{m}^{-2})$  that researched by Reddy et al. [9] and an increase in citric acid concentration increases tensile strength and modulus (MPa) but decreases breaking elongation (%) and water vapour permeabilities [9]. The results of dried extraction cake films were similar to that obtained by Reddy et al. [9] in terms of tensile strength and elongations at break (%) respectively. The oxygen permeabilities of dried extraction cake of films varied from  $19.57 \cdot 10^{-6}$  to  $16.17 \cdot 10^{-6} \text{ g} \cdot \text{m}^{-1} \cdot \text{day}^{-1} \cdot \text{Pa}^{-1}$  and these permeabilities were similar to that obtained by Liu et al. [10] ( $1.68 \cdot 10^{-5} \text{ g m}^{-1} \cdot \text{day}^{-1} \cdot \text{Pa}^{-1}$ ). It reported that heating process at a certain time ( $70 \text{ }^\circ\text{C}$ , 30 min) yields stronger films permeabilities with respect to water vapour and oxygen. It is reported that this phenomena can be explained by cross-linking of the protein yielding in a tighter and more complex protein structure [10].

Arginine (Arg) and cysteine (Cys) were the major amino acids in the films of extraction cake of groundnuts (Table 3). The films of groundnut cakes had a higher percentage of arginine (14.89%), cysteine (10.41%), aspartate (10.13%), glutamate (9.09%) and leucine (6.28%) in average respectively. Davis and Dean [22] reported that glutamate (Glu) and arginine (Arg) were the main amino acids in groundnut seed and Riveros et al. [9] reported that defatted groundnut seed and its films contained higher glutamic acid and arginine amino acids. Another researcher, Gayol et al. [29] reported that groundnut oil cake and the concentrated form contained aspartate, glutamate and cystein+valine+methionine

respectively. Biodegradable films that produced from other raw materials contained higher amount of glutamate (9.11%) and aspartate (5.91%) as the major amino acids in defatted flours of soybean, glutamate (12.48%) and arginine (6.73%) in the flour of cottonseed respectively [30].

Gamli and Atasoy [7] reported that groundnut milk that produced from groundnut seed by extraction of water contained different amounts of amino acids. These researchers reported that the major essential amino acids that found in groundnut milk were as threonine, isoleucine, leucine, valine and major non-essential amino acids as proline, alanine, aspartate and cystein respectively. The amino acids known as essential amino acids are necessary for the protein synthesis and the required portion should be maintained from daily diet. It is reported that the proline, alanine and aspartate were major amino acids that found in groundnut milk (9.54%, 8.16% and 7.91%) and the films that obtained from groundnut extraction cake contained arginine, cysteine and aspartate (by the average of 14.89%, 10.41% and 10.13%) respectively. The obtained results showed that alkali concentrations had no effects on amino acid concentration significantly (Table 3) and that results are similar with the results of Riveros et al. [9], Gamli and Atasoy [7] and Gayol et al. [29] in terms of containing such amino acids respectively.

The changes in peroxide values for groundnut extraction cake films, control sample and PP material at room temperature ( $20 \text{ }^\circ\text{C}$ ) were illustrated in Figure 3. The peroxide values increased with storage period in olive oil samples. Olive oil that stored in petries (control sample) had a higher peroxide values and resulted significant differences during after the storing day of 30, compared to olive oil that stored in groundnut cake films and PP pouches.

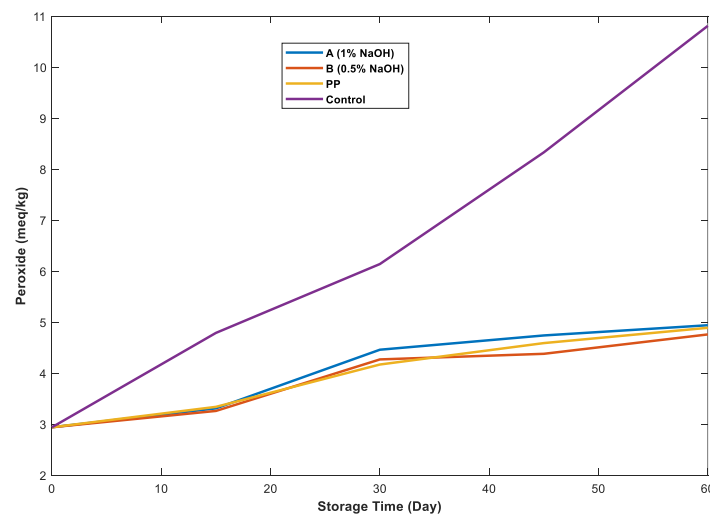


Fig.3: Peroxide value (PV) in olive oil conditioned in petridishes (C), olive oil conditioned in A (0.5% NaOH treated), olive oil conditioned in B (1% NaOH treated) film and olive oil packaged in plastic pouches (PP) at room temperature ( $20 \text{ }^\circ\text{C}$ )

Table 3. The amino acid composition (g/100 g protein) of dried cake of ground nut seeds that obtained different ratios of NaOH

Amino Acids	Alkali concentrations of NaOH (%)			
	0.25%	0.50%	0.75%	1.0%
Glutamate	8.85±0.22	9.04±0.28	9.24±0.27	9.27±0.29
Serine	4.28±0.08	4.97±0.08	4.16±0.09	5.75±0.09
Glycine	5.98±0.11	5.04±0.10	5.07±0.09	4.91±0.10
Threonine*	3.13±0.05	3.43±0.05	3.74±0.06	3.94±0.05
Arginine*	14.77±0.16	14.45±0.15	15.22±0.16	15.13±0.10
Alanine	3.89±0.14	3.82±0.11	3.74±0.13	3.97±0.10
Tyrosine	4.30±0.09	4.34±0.08	4.55±0.11	4.66±0.10
Leucine	5.74±0.14	6.19±0.14	6.49±0.17	6.74±0.18
Lysine	3.44±0.07	3.57±0.08	3.71±0.09	3.89±0.07
Cystein	10.14±0.19	10.01±0.17	10.74±0.19	10.89±0.21
Histidine*	4.87±0.07	4.43±0.08	4.67±0.10	4.99±0.11
Proline	3.14±0.06	3.44±0.08	3.71±0.08	3.82±0.09
Valine*	5.21±0.11	5.44±0.10	5.48±0.14	5.71±0.11
Isoleucine*	4.16±0.08	4.21±0.07	4.56±0.09	5.07±0.08
Aspartate	9.74±0.10	10.02±0.11	10.14±0.12	10.47±0.13

\*Essential amino acid; Result expressed as mean +standard deviation (n:3)

Among the packaging procedures, groundnut cake film that treated with 0.5% NaOH and PP film presented lower peroxide values and there were no significant differences among the films after the storage time of 30 days. The results of chemical reactions during storage evidence were similar manner to PP that the groundnut cake film retards to the oxidation reactions in olive oil.

The peroxide values obtained in this research were comparable values with the results that researched by Riveros et al. [9] and De Moraes Crizel et al. [31] for sunflower oil that stored in EVOH film and at room temperature respectively. The authors revealed that EVOH pouches showed the lowest peroxide values and exhibited significant differences during storage than defatted groundnut flour films after day 45. The peroxide values of olive oil that stored with the films of extraction cake of groundnut changed from 2.94 to 4.87 meq O<sub>2</sub>/kg during storage time of 60 days and these values were lower than that the results of sunflower oil made by Riveros et al [9] and De Moraes Crizel et al. [31]. The measured peroxide values (meq O<sub>2</sub>/kg) obtained at the end of 60 days of storage were lower than 10 meq O<sub>2</sub>/kg except control sample of olive oil in petri dishes. The results of this research revealed that films of extraction cake of groundnut both showed a preserving effect against lipid oxidation and prolonged olive oil shelf life.

#### IV. CONCLUSIONS

The results of in this research implied that dried extraction cake of groundnut seed can be used for the production of edible films that exhibit good physico-mechanical attributes and good barrier abilities in terms of water vapour and oxygen. The low concentration of alkali (0.25%, NaOH) approved higher tensile strength (MPa) and elongation at break (%). The increased barrier abilities are all desirable improvements in the production of films from protein containing foods and physico-mechanical attributes of edible films can be improved by inducing cross-linking structure of the protein. The films contained arginine (Arg), cysteine (Cys) and aspartate (Asx) as main amino acids. The films of extraction cake of groundnut improved the chemical stability of olive oil by preventing lipid oxidation during storage so the produced films could present an effective method to preserve some food materials with similar physicochemical properties of olive oil. As a result, due to higher protein content, extraction cake of groundnut can be used as an ingredient of edible films for producing packaging materials and other uses in food industries.

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