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Research Paper / Araştırma Makalesi

Use of Microwave Drying for Production of Protein-Oil Based Edible Films

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ABSTRACT

Soy protein isolate (SPI)-sunflower seed oil (SO) based edible films were produced from freeze-dried composite powder and for the first time, microwave drying (MD) was applied. The required drying time was shortened from 1-3 days at room condition to 3-6 min with microwave heating. Improved thermal stability, better water barrier property, increased solubility and protected natural yellow color were detected in edible films dried at 800W microwave power in comparison to 300W; however, at the same time, weakened film transparency and decreased mechanical properties were found. The overall findings of this study revealed that microwave drying, a new edible film drying method, could be safely used to produce edible films within minutes without losing film properties. Therefore, it could be easily concluded that this new drying for edible films might have a greate potential for the industrial production of biodegradable films.

Keywords: Microwave drying, Soy protein isolate, Sunflower oil, Time-efficient film production, Film properties

Protein-Yağ Bazlı Yenilebilir Filmlerin Üretiminde Mikrodalga Kurutmanın Kullanılması

ÖZ

Dondurularak kurutulmuş kompozit tozdan soya proteini izolatı (SPI)-ayçiçeği çekirdeği yağı (SO) bazlı yenilebilir filmler üretilmiş ve ilk kez mikrodalga ile kurutma (MD) yöntemi uygulanmıştır. Gerekli kuruma süresi oda koşullarında 1-3 gün iken mikrodalga ısıtma ile bu süre 3-6 dakikaya kadar düşürülmüştür. 300W ile karşılaştırıldığında 800W mikrodalga güç seviyesinde kurutulan örneklerde kuvvetlenmiş termal kararlılık, yüksek su bariyeri özelliği, artan çözünürlük ve zarar görmemiş doğal sarı renk tespit edilmiş, ancak bununla beraber film şeffaflığında ve mekanik özelliklerde azalma olduğu anlaşılmıştır. Bu çalışmanın genel bulguları, yeni bir yenilebilir film kurutma yöntemi olan mikrodalga kurutmanın, film özelliklerini kaybetmeden dakikalar içinde yenilebilir filmler üretmek için güvenli bir şekilde kullanılabileceğini ortaya koymuştur. Bu nedenle, yenilebilir filmlere yönelik bu yeni kurutma yönteminin biyobozunur filmlerin endüstriyel üretimi için büyük bir potansiyele sahip olabileceği sonucuna rahatlıkla varılabilir.

Anahtar Kelimeler: Mikrodalga kurutma, Soya proteini izolatı, Ayçiçek yağı, Zaman verimli film üretimi, Film özellikleri

INTRODUCTION

Edible packaging is a kind of food packaging suitable for healthier human consumption [1]. Films and coatings are the two classification of biodegradable packaging application. The main ingredients of the edible films and coatings are edible filmogenic biopolymers, such as hydrocolloids, lipids, or combinations of them [2]. As the edible materials are not dangerous for human health, the packaging molecule transmission into the food does not create any serious problem. Also they degrades faster than synthetic ones that means their usage considerably reduce the requirement of landfills [3]. For more than half a century, numerous scientific studies

has done in terms of development, characterization and improvement of the edible films [4]. However, their production is still on a laboratory scale and the desired industrial production success has not been achieved. One of the reasons for this situation is that the fabrication times of edible films and coatings are quite long [5]. Also, mechanical and barrier insufficiencies are the other challenging side of the biodegradable packaging. It is therefore essential to overcome these challenges as much as possible in order to scale up production on industrial area and to make edible films commercially successful. Nevertheless, there were very limited number of studies to lessen the film preparation time which can promoted the easier production and the higher capacity [6, 7]. Until this time, the most commonly used drying method to obtain films from soy proteins is air drying at ambient room conditions after the film solution is spread on the plate [8, 9]. Soy protein isolate (SPI) is one of the most widely preffered agriculture-derived biopolymers as a film-forming agent due to its good film forming ability, cost-effectiveness and availability [10]. Soy protein support to produce more flexible, smoother, and transparent films compared to films from other plant protein sources [11]. Sunflower seed oil (SO) was used as lipid supplement to enhance the water-barrier properties of SPI based film formulations because it is naturally a hydrophobic material. Microwave heating is a kind of a thermal treatment with its some of the positive sides such as fast and selective heating application, having successful power transference and being cost-effective [12]. However, surprisingly no scientific literature covers the usage of microwave drying in the preparation of soy protein isolate based films but very little for other types such as chitosan and whey protein isolate based [12, 7] by casting technique. In a previous study, improved mechanical properties were observed for 5 min microwave dried whey protein isolate-based edible films. Also similar trend of water vapor permeability for both the films produced by microwave heating and at room conditions were determined in the same study [7]. It is known that cast films contain high amount of water that should be evaporated to gain film form, that is needed considerably long drying times as 1-3 days. On the other hand, drying methods such as microwave do not have this evaporation stage and therefore they significantly save the time required for drying [3].

The main objective of this work was to apply microwave heating on SPI-SO based composite films to decrease the long drying time so on to increase the potential of industrial production without losing the film characteristics. Two different energy power were studied to investigate the effect of the highest (800W) and the lowest (300W) adjustable power input according to used device on three different ratio of SO added SPI film properties. It is a fact that the different film preparation technique acceptability was determined with taking at least similar or better results than the usual one. Hence, physical, mechanical, thermal and barrier properties of the composite films were investigated. Also our previous innovative film forming solution preparation way was utilized in this study to decrease the total film production time literally by freeze dried powder usage [13, 6]. Accordingly, SPI-SO powder in composite form already produced by freeze drying method was simply mixed with glycerol and distilled water to obtain film solution. Thus, the film forming solution was prepared in a matter of seconds without any additional film production steps. In conclusion, this research was aimed to minimize the required duration for both film making and drying with acceptable film quality for the first time.

MATERIALS and METHODS

Materials and Chemicals

Soy protein isolate (min 90% protein content on dry basis) was provided by Gushen Biological Techn Group Company Limited (China). The seed oil of sunflower was purchased from a local market in Turkey. Glycerin (88% purity) and NaOH (98% purity) were obtained from Sigma-Aldrich (Aldrich, USA).

Film Manufacturing

Edible film production was basically carried out in two steps. In the first step, soy protein isolate (SPI) based composite powder was obtained by a newly developed freeze drying method [13, 6]. In the second step, film forming solutions were easily prepared from that previosly produced composite powder and finally microwave drying was applied for film formation. Detailed information was given as follows:

First step (Composite powder production): The film forming solutions containing 4% SPI and 0.05%, 0.10% and 0.15% sunflower oil (w/v) based on solution were prepared under constant stirring at 500 rpm by a stirrer for 2 min. Afterward the pH of the mixtures adjusted into10 by pH meter and homogenization was made at 20,000 rpm for 2 min. Denaturation of the solutions were achieved with a hot plate while stirring at 75°C for 20 min. The resulting solution was deaerated with an ultrasonic bath during 15 min. The freezers were used at -18°C (24 h) and -70°C (3 h) to freeze the film forming solutions. After that, Alpha 1-4 LD Plus freeze dryer (Christ Martin, Germany) at -55°C under vacuum condition (72 h) was utilized to frozen solutions. Dried layer was grinded by a simple coffee grinder during 1 min to obtain the powder form [13].

Second step (Film production by microwave heating): Freeze dried composite powder (0.25 g), glycerin (0.20 g) and distilled water (20 mL) were blended in a glass beaker under constant stirring on a hot plate at 80°C for two mins. This mixture was placed and dispersed onto a plastic dish (i.d: 9.6 cm). A programmable domestic microwave oven was used for drying which has adjustable power, time controllers and a turntable (Samsung, model MS23F300EEK, Malaysia, 2450 MHz). Actually, the turntable was a good property to achieve the desired device performance and to minimize the levels of reflected microwaves onto the magnetron. The oven was adjusted to two different power intensities, 300 W and 800 W, the lowest and the highest values of the device. Required drying times were determined with preliminary studies as 6 min for

300 W and 3 min for 800 W, respectively. In this study, 8 different film formulations were evaluated and 800-spi-c, 800-spi-1, 800-spi-2, 800-spi-3, 300-spi-c, 300-spi-1, 300-spi-2, 300-spi-3 notations were used throughout the paper. Numbers in the abbreviations were used to represent SO concentrations as 1: 0.05% SO (w/v), 2: 0.10% SO (w/v), 3: 0.15% SO (w/v) and c was referring control (no oil). The different microwave heating power intensities applied were expressed as 800 and 300 in the notations. All the produced edible films were stored in polystyrene bags under room conditions.

Characterization of Edible Film

Thickness and Density

The film thicknesses were measured using a digital type micrometer with a sensitivity of ±0.001 mm (Mahr GmbH., Göttingen, Poland). The film sample was gauged from at least 5 different regions and the mean value of them was taken. In order to determine the density, weight and volume ratio of the films were taken. The density test was carried out in triplicate.

Moisture Content

Pieces of the specimens (2×2 cm) were prepared for each film and weighted ($w_{initial}$). The pre-weighted film samples were dried in an laboratory oven at 105°C until they reach the constant-final weight (w_{final}). The moisture content can be explained as the percentage of water removed from the initial mass of the sample tested and can be calculated as follows (Eq. 1). The analysis were performed on samples in duplicate.

$$\text{Moisture Content (\%)} = ((w_{initial} - w_{final})/w_{initial}) \times 100 \quad (1)$$

Total Soluble Matter

Water solubility was tested by a gravimetric method [23]. The film specimens were prepared with the dimensions of 2×2 cm and they were dried in an air-circulating oven at 105°C for 24 h (initial dry weight). Dried pieces were placed in 30 mL water under constant agitation for 180 min. The insoluble remaining pieces of the samples were separated and dried again at 105°C for 24 h to constant weight (final dry weight). The analysis was repeated triplicate and total soluble matter (TSM) was calculated according to Eq. 2:

$$\text{TSM (\%)} = ((dw_{initial})-(dw_{final})/(dw_{initial})) \times 100 \quad (2)$$

where dw is dry weight.

Mechanical Properties

Texture analyzer (Stable Microsystems, TA-XT2i, Godalming, UK) was utilized for mechanical property examination of the samples in terms of film strength (tensile strength-TS) and its elastisity (elongation at break-EB). In preparing samples, the specimens were cut as rectangular shapes (7.5×2.5 cm). The specimens were held parallel with a grip separation of 5 cm. Two main parameters specified during the extension of the films mounted between the grips: force and distance. TS was calculated by taking the ratio of the max force value to film cross section area (film thickness × film width).

Color and Film Transparency

Transparency property of the manufactured samples was determined by employing previosly described method [14]. According to this method, the film absorbance was tested at 550 nm wavelength with a UV-Visible spectrophotometer (Shimadzu, Japan). Calibration was made by measuring the transparency of an empty cell at 550 nm and it was used as reference for the test. Afterwards, the specimens were cut into rectangular pieces which is a suitable shape to place inside the spectrophotometer test cell. The absorbance readings from the device were recorded. The *L** (lightness), *a** (redness) and *b** (yellowness) values of the film samples were determined by a Hunter Lab colorimeter with CIE Lab scale (Reston, VA, USA). The average value of 5 readings was reported for each color property. A standart plate with known values of the lightness and chromaticity parameters were used as reference. Substraction of the standard reference values from the sample readings was given the actual color results of the film specimens. Following equations were used for optical property determination:

$$\Delta E = \sqrt{(L^* - L_s)^2 + (a^* - a_s)^2 + (b^* - b_s)^2} \quad (3)$$

where ΔE was total color, WI was whiteness index, *L*, a*, b** were the standard plate parameters (*L**: 93.41; *a**: -1.12; b*: 1.07) while L_s, a_s, b_s were the parameters of the samples.

$$WI = 100 - \sqrt{(100 - L_s)^2 + (a_s)^2 + (b_s)^2} \quad (4)$$

Differential Scanning Calorimetry

Thermal properties were investigated by a Differential Scanning Calorimetry (DSC 4000, Perkin Elmer, USA). Nitrogen was the used purge gas which had a flow capacity of 20 mL/min. DSC pan temperature range was between 20°C to 250°C and its rate was set as 10°C/min [15]. DSC calibration was achieved with indium and an the reference was an empty aluminium pan. The film samples (4-6 mg) were cut into tiny pieces and put inside the device's pan. The temperature of glass transition (T_g) and melting point (T_m) were investigated. At least duplicate measurements were made from each sample to achieve reliable data.

Water Barrier Properties

Water permeability of the film sample were determined by a gravimetric method [16]. Initially, small glass cups with a diameter of 30 mm were filled with silicagel in order to obtain 0% RH and the specimens were sealed on these cups with the help of thin elastic bands. Afterwards, they placed in a prepared chamber containing saturated NaCl solution to create 75% RH at 24°C. The below formula was used to calculate barrier property of the film samples:

$$WVP = (S \times d) / (A \times \Delta P) \quad (5)$$

where WVP (g mm m^{-2} h^{-1} kPa^{-1}) is the water vapor permeability, S is linear portion (g/h), A (m^2) is the film area, ΔP (kPa) is the difference of partial pressure, and d (mm) is the film thickness.

Fourier Transform Infrared Spectroscopy

FTIR spectral images of the composite film samples were obtained on a Perkin Elmer Spectrum, model 100, at room temperature (Beaconsfield, UK) [17]. The measurements were carry out in a wavenumber region of 4000–650 cm^{-1}. Triplicate samplings were done for each specimen.

Morphological Properties

Microstructures of film surfaces and cross-sections were studied with a Zeiss Gemini S300 scanning electron microscope (Oberkochen, Germany). Before testing all film samples were sputter-coated with gold. They were then examined at 10.0 kW and at different magnifications of 1000× and 2500×.

Statistical Analysis

SPSS software version 23.0 (Chicago, USA) were utilized to analyze the data. All experiments conducted with at least triplicate trials and the mean values were used. Data evaluation was made by one-way analysis of variance (ANOVA), and then Tukey's multiple range test was employed to determine significant differences ($p<0.05$) among measurement results of the films.

RESULTS and DISCUSSION

Film Thickness and Density Measurements

Thickness and density values can be affected by some key properties of the films such as permeability, transparency or mechanical. Table 1 shows the thickness values which were changed between 0.18 and 0.20 mm but any statistical difference was detected ($p>0.05$). Kevij et al. stated similar thickness observations at the range of 183 and 194 μm for whey protein isolate based films activated with curcumin [14]. Table 1 presents close density values for SPI films dried at both 800W and 300W microwave heating levels, but 300-spi-1 and 300-spi-3 were found to have the lowest values (0.025 g/cm^3). These detected values were lower than those found for salep glucomannan based films (1.12–1.27 g/cm^3) [23] and whey protein films plasticized at different glycerol concentrations (1.26-1.38 g/cm^3) [18]. It was reported that different density values of the films might be attributed to their own composition, homogeneity and interaction of the components of the polymeric film structure [19]. This probably means that higher molecular chain interaction occurs for some of the 300W microwave power applied SPI films.

Table 1. Physical and mechanical properties of film samples

Film type	Thickness (mm)	Density (g/cm^3)	Moisture content (%)	Solubility (%)	TS (MPa)	E (%)
800-spi-c	0.18±0.009^{a}	0.033±0.002^{a}	35.16±1.76^{a}	48.81±2.44^{a}	3.35±0.17^{a}	10.68±0.58^{a}
800-spi-1	0.19±0.009^{a}	0.033±0.001^{a}	31.97±1.59^{a}	48.25±2.41^{a}	4.73±0.24^{b}	9.50±0.48^{a}
800-spi-2	0.19±0.008^{a}	0.032±0.002^{a}	34.55±1.73^{a}	45.77±2.29^{a}	6.65±0.33^{c}	11.64±0.58^{a}
800-spi-3	0.20±0.008^{a}	0.036±0.003^{ab}	35.58±1.78^{ac}	46.82±2.34^{a}	3.46±0.19^{a}	10.06±0.50^{a}
300-spi-c	0.19±0.009^{a}	0.034±0.002^{a}	26.73±1.34^{b}	38.80±1.94^{b}	3.15±0.17^{a}	9.22±0.47^{a}
300-spi-1	0.18±0.010^{a}	0.025±0.002^{c}	31.85±1.60^{a}	38.95±2.02^{b}	4.80±0.25^{b}	32.06±1.60^{b}
300-spi-2	0.19±0.008^{a}	0.039±0.002^{b}	35.26±1.76^{a}	45.45±2.19 ^{a}	4.02±0.23^{ab}	28.86±1.44^{c}
300-spi-3	0.18±0.009^{a}	0.025±0.003^{c}	40.19±2.01^{c}	48.24±2.45^{a}	4.91±0.24^{b}	29.62±1.48^{bc}

800-spi-c: 800W power intensity, soy protein isolate; 800-spi-1: 800W power intensity, soy protein isolate-0.05% sunflower oil; 800-spi-2: 800W power intensity, soy protein isolate-0.10% sunflower oil; 800-spi-3: 800W power intensity, soy protein isolate-0.15% sunflower oil; 300-spi-c: 300W power intensity, soy protein isolate; 300-spi-1: 300W power intensity, soy protein isolate-0.05% sunflower oil; 300-spi-2: 300W power intensity, soy protein isolate-0.10% sunflower oil; 300-spi-3: 300W power intensity, soy protein isolate-0.15% sunflower oil. Values were given as mean ± standard deviations. Different superscript letters in the same column indicates statistical differences (Tukey's test, $p<0.05$).

Moisture Content

In order to examine the plasticizing effect of water, the moisture contents of the samples were examined and are given in Table 1. The values belong for the samples conditioned at 50±2% RH. The moisture content values ranged from 26.73% and 40.19%. Films dried at 800W microwave power were found to be statistically the same ($p>0.05$), but an increasing trend was observed at 300W. Normally, the addition of oil to the film structure would be expected to reduce hydrophilicity and decrese moisture content [22]. Nevertheless, having different and higher drying time when compared with 800W, may have caused some chemical structure changes in the 300W power applied films. This reinforcing moisture absorption effect on SPI-SO matrix for 300W dried film samples can be explained by relatively irregular lipid distribution due to slower evaporation than 800W's. In our previous study, moisture content were ranged from 32.75% to 37.85% for the same but not microwave dried SPI-SO film samples [6]. It is understood that microwave drying did not affect the moisture uptake characterization of the edible films.

Solubility in Water

One of the important physical properties of edible film is solubility. Depending on the intended use, higher or

lower solubility values can be desired for films. Water solubility values were ranged between 45.77% and 48.81% for 800W microwave power applied SPI films; but that was 38.80% for 300-spi-c, and 38.95% for 300-spi-1. In this study, the films with the lowest solubility values also showed the lowest moisture contents. This behavior may be related to better water resistance. It was understood that oil addition did not have any effect on the solubility of 800W power applied films ($p>0.05$), while it caused an increase for the 300W applied ones ($p<0.05$). In a study, Paglione et al. [31] reported that the addition of oregano essential oil to soy protein films slightly improved the solubility ability of the film samples. The researchers claimed that the presence of oil created a less cohesive film structure, thus revealing more solubilized hydrophilic groups. Galus and Kadzinska [32] found the solubility of whey protein film 42.4%, which can be considered close to our soy protein-based film results. They tested the effect of two different oils (walnut and almond oils) on WPI-based films. According to their results, the addition of almond oil increased the solubility significantly, but no statistical change was observed with the addition of walnut oil. The authors were supposed that oil and protein chemical interactions can result in a smooth structure of emulsion films and this situation possibly increased the solubility. Water solubility is related to the hydrophilicity and hydrophobicity of the films [33]. These two properties are directly proportional to each other. It can be said that the higher the solubility of the film in water, the higher the hydrophilic character of the film. When coated foods come into contact with water, the high solubility may cause the coating to break down. For this reason, water insolubility is generally preferred for more durable packaging films.

Mechanical Properties

Examining the mechanical properties of films is very important to have an idea of their resistance to the different types of physical stresses they can be deal with during their use [23]. In this study, strength and flexibility of the film samples were determined by “Tensile Strength (TS)” and “Elongation (E%)” parameters (Figure 1 and Table 1). The parameters are indicator of the film strength and elasticity, respectively. The TS of 300W microwave power applied films was higher in general manner than 800W’s and SO addition promoted stronger film structure. When 3.35 MPa strength was observed for 800-spi-c, the value increased up to 6.65 MPa with 0.10% SO addition (800-spi-2), however decreased with further incraese of oil concentration (800-spi-3) (Table 1). Improvement in film strength may attributed to the formation of a rigid continuous network between functional groups of soy protein (such as carboxyl and hydroxyl groups) and oil through interfacial strong hydrogen interactions. The rise in mechanical properties reach with such interactions. The highest level of SO utilization in 800W microwave dried film (800-spi-3) caused agglomeration and/or non-uniform dispersion and that resulted in higher film fragility. The flexibility values were given in Figure 1 and Table 1. According to the results obtained, the Elongation(%) values were found to be statistically the same for the films with 800W heating ($p<0.05$), but a significant increasing trend was observed for the 300W films ($p>0.05$). It was found that applying a power density of 300W and adding SO to the film matrix simultaneously improves the mechanical resistance. This is indicative of the good interaction between soy protein and oil which was resulted in an efficient transfer of applied stress across the film. In addition, it was understood that the application of slower (6 min) and lower microwave power intensity (300W) provided an equal distribution of stress and reduced stress concentrations [24]. In the previous study, the tensile strength of SPI-SO based films with the same content but dried at ambient temperature was reported to be in the range of 0.17-0.33 MPa, while the elongation values were reported as 55.29-92.08% [6]. According to the results, microwave drying process application provides less elastic but stronger film structure.

Color and Film Transparency

Consumer acceptance and visual appeal are affected by film color and its UV light blocking ability. Table 2 shows the opacity and color properties in terms of *L*, a*, b**, DE and WI. It was found that higher microwave power intensity application to SPI based films tended to increase film opacity. Stronger power application reduces drying time however rapid water migration can cause uneven particle dispersion in film structure. Heterogeneity and/or accumulation of oil particles promoted poor transparency, resulting in reduced UV light transmission [20]. Previously higher *L** value observations were found for SPI and rapeseed oil based films that produced with air drying by Galus [21]. Hence, our poor lightness observations of the samples indicate that these microwave-dried films tend to be dark. This behavior could be due to the increment of film surface roughness because of typical characteristic fast drying rate of microwave technique. Also, negative *a** value observations are indicative of a greenish color trend for them. The original yellow color of SPI was better protected by 800W power applied films that proved with significantly higher *b** values ($p<0.05$). The situation may be due to the reduced heat exposure time of those films, because the higher the microwave power density, the shorter the drying application time. As a result 3 min-800W drying procedure application helps to better color prevention than that of 6 min-300W. There were no significant differences in the total color ($\Delta\mathbf{E}$) and visual appearances of film samples ($p>0.05$) (Figure 2).

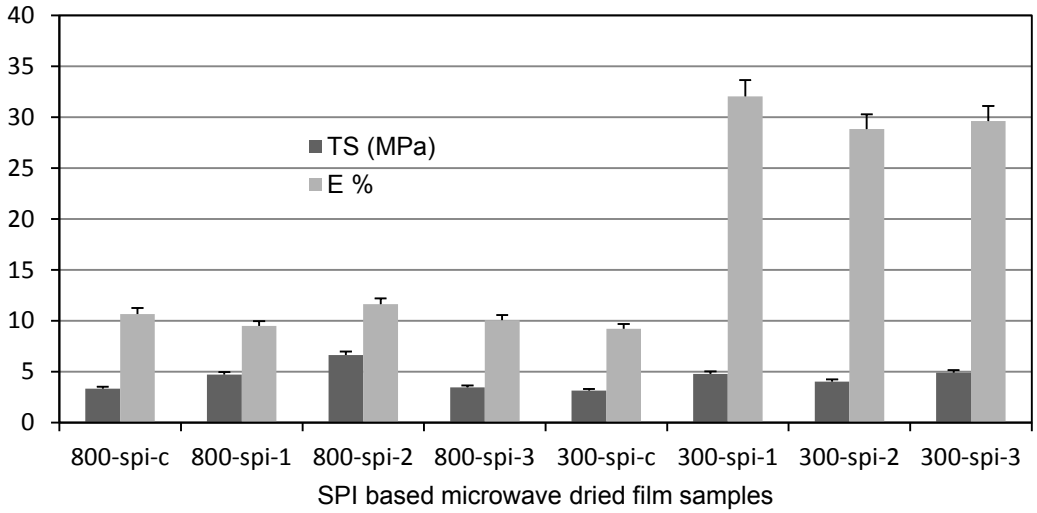


Figure 1. Effect of 800 and 300W power intensities on mechanical properties of SO incorporated SPI films

Table 2. Optical properties of SPI-SO composite films dried at different microwave power intensities.

Film type	Opacity (abs/mm)	*L**	*a**	*b**	ΔE	WI
800-spi-c	0.46±0.023^{a}	26.99±1.35^{ac}	-0.85±0.04^{a}	1.92±0.09^{a}	66.42±3.32^{a}	26.95±1.35^{ac}
800-spi-1	0.49±0.025^{a}	24.36±1.34^{ab}	-0.59±0.03^{b}	1.07±0.05^{b}	69.05±3.45 ^{a}	24.35±1.22^{ac}
800-spi-2	0.54±0.027^{b}	24.28±1.34^{ab}	-0.40±0.02^{c}	0.42±0.02^{c}	69.13±3.15^{a}	24.27±1.20^{ac}
800-spi-3	0.57±0.028^{b}	22.29±1.12^{ab}	-0.57±0.03^{b}	1.19±0.06^{d}	71.12±3.55^{a}	22.27±1.10^{b}
300-spi-c	0.38±0.019^{ac}	29.03±1.45^{c}	-1.20±0.06^{d}	-0.64±0.03^{e}	64.40±3.20^{a}	29.01±1.45^{c}
300-spi-1	0.39±0.020^{ac}	24.70±1.33^{a}	-0.53±0.03^{b}	-0.16±0.01^{f}	68.72±3.43^{a}	24.69±1.23^{ac}
300-spi-2	0.42±0.022^{a}	25.52±1.34^{ac}	-0.40±0.02^{c}	-0.46±0.02^{g}	67.91±3.39^{a}	25.51±1.27^{ac}
300-spi-3	0.48±0.024^{a}	25.57±1.34^{ac}	-0.75±0.04^{a}	-0.68±0.03^{e}	67.86±3.37^{a}	25.56±1.28^{ac}

800-spi-c: 800W power intensity, soy protein isolate; 800-spi-1: 800W power intensity, soy protein isolate-0.05% sunflower oil; 800-spi-2: 800W power intensity, soy protein isolate-0.10% sunflower oil; 800-spi-3: 800W power intensity, soy protein isolate-0.15% sunflower oil; 300-spi-c: 300W power intensity, soy protein isolate; 300-spi-1: 300W power intensity, soy protein isolate-0.05% sunflower oil; 300-spi-2: 300W power intensity, soy protein isolate-0.10% sunflower oil; 300-spi-3: 300W power intensity, soy protein isolate-0.15% sunflower oil. Values were given as mean ± standard deviations. Different superscript letters in the same column indicates statistical differences (Tukey's test, $p<0.05$).

800-spi-c 800-spi-3 300-spi-c 300-spi-3

Figure 2. Visual appearance of some of the SPI based microwave dried edible films.

Thermal Properties

The temperatures of glass transition (T_g) and melting point (T_m) of the produced SPI films were examined using a Differential Scanning Calorimetry unit. T_g is the phases where the material structure changes from amorphous to viscose rubbery, and Tm is another stage of the transition from solid to liquid state. The obtained values of T_g and T_m are listed in Table 3. The results showed that both of the temperatures (T_g and T_m) are statistically increased for 800W MD film samples ($p<0.05$). However, no significant differences were observed for 300W MD specimens ($p>0.05$). A rise in thermal properties for oil incorporated 800W MD samples can be related with strengthened biopolymer structure, to cause decreased molecular movements which leading to stricted intermolecular free space [25]. According to Table 3, all film samples have a T_g profile that between 136.40 and 203.68°C. Different T_g values for SPI films reported in the literature [6,15]. Because many factors such as the type and amount of plasticizer, the purity of the protein isolate, and the mixing method can affect the transition temperature. In a study, it was determined that high-temperature transitions decrease with increasing plasticizer content. Because glass transition temperature of used glycerol was about -93°C [34]. The examples demonstrate that the ideal T_g value for SPI films can vary depending on the specific application, and researchers use different approaches to determine this value.

Table 3. Thermal properties of SPI based films with respect to their SO content and power intensity that dried.

Film type	T_g (°C)	T_m (°C)	WVP (g.mm/m^2.h.kPa)
800-spi-c	141.44±7.07^a	155.08±7.75^a	0.012±0.001^a
800-spi-1	136.94±6.85^a	156.57±7.83^a	0.013±0.001^a
800-spi-2	178.10±8.91^b	210.10±10.51^b	0.014±0.002^a
800-spi-3	203.68±10.18^c	208.33±10.41^b	0.013±0.002^a
300-spi-c	143.34±7.17 ^{a}	166.11±8.30^a	0.026±0.001^b
300-spi-1	136.40±6.82^a	152.42±7.62^a	0.026±0.003^b
300-spi-2	141.48±7.07^a	158.06±7.90^a	0.027±0.002^b
300-spi-3	137.72±6.88^a	157.39±7.87^a	0.026±0.001^b

800-spi-c: 800W power intensity, soy protein isolate; 800-spi-1: 800W power intensity, soy protein isolate-0.05% sunflower oil; 800-spi-2: 800W power intensity, soy protein isolate-0.10% sunflower oil; 800-spi-3: 800W power intensity, soy protein isolate-0.15% sunflower oil; 300-spi-c: 300W power intensity, soy protein isolate; 300-spi-1: 300W power intensity, soy protein isolate-0.05% sunflower oil; 300-spi-2: 300W power intensity, soy protein isolate-0.10% sunflower oil; 300-spi-3: 300W power intensity, soy protein isolate-0.15% sunflower oil. Values were given as mean ± standard deviations. Different superscript letters in the same column indicates statistical differences (Tukey's test, $p<0.05$).

Water Vapor Permeability

Water vapor permeability (WVP) of microwave heated SPI film is shown on Table 3. Permeability values of the films increased at about 2 times with the application of 300W microwave power compared to 800W; however, it did not change with SO addition. Actually, diffusion is the responsible mechanism that occurs in permeation of vapor through the film sample. In this mechanism, water vapor dissolves in the film matrix from high to low concentration [26]. The film characteristic can be determined by the degree of permeability. Cohesiveness promotes better barrier structure in films due to its lower porosity. When protein is heated, chain length and the structural cohesivity of matrix increases due to covalent disulphide bonds formed among polypeptide chains [27]. Table 3 shows that higher microwave power application (800 W) gives more satisfactory barrier results than 300 W film samples, probably because increased the structural cohesivity of the matrix, decreasing the free volume to the vapor diffusion. In our previous study, fairly higher water permeability values were observed for the same but not-microwave-dried SPI-SO film samples. In that study, WVP of the control SPI was 1.69 g mm m^{-2} h^{-1} kPa^{-1} and while composite formulations (SPI-SO) ranged from 1.17-1.53 to 1.26 g mm m^{-2} h^{-1} kPa^{-1} [6]. This success in reducing water vapor permeability by microwave drying can be attributed to the better preservation of the lipid-protein interconnection network, which leads to a decrease in the water absorption of the film and therefore an increase in hydrophobicity. It was understood that microwave drying enhanced the water barrier properties of SPI films, thus increasing their functionality.

Fourier Transform Infrared Spectroscopy

Analysis of functional groups on the surface of microwave dried films based on soy protein isolate by FTIR spectrophotometer is shown in Figure 3. The broad peak at 3270 cm^{-1} was assigned to the stretching vibration of O-H groups [28]. The other peak located approximately 2930 cm^{-1} was responsible for C-H aliphatic absorption. The presence of the peak between 1700 and 1600 cm^{-1} corresponded to the amide (I) vibration that related to the secondary structure of protein due to C-O stretching vibration and C-N stretching vibration [28]. The broad peak approximately 1640 cm^{-1} in the spectrum of protein films is attributed to the existence of water. Amide (III) bands (1235 cm^{-1}) represented N-H in plane bending [29]. The peaks between 1107.9 and 1108.5 cm^{-1} correspond to C-O-C stretching frequencies.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) images suggest the relationships of some of the film properties such as mechanical resistance and optical properties with the film structure. Figure 4A and Figure 4B show SEM micrographs of the surface and transversal (cross section) for all film types such as control, sunflower oil incorporated and microwave dried film samples. In general manner, all samples showed smooth and continuos surface without large pores. However in detail, incorporation of SO resulted in slight increment of cavity, pore and air bubble amount on the surface microstructure of blend films. This can be attributed to the short duration of degassing operation [14]. Also increasing of oil amount cause aggregation on the surface due to its natural hydrophobic structure. This situation was in parallel with the optical results (Table 2). Control films had lower opacity values, while SO added samples had higher values. The transversal section images of the films with different oil concentrations did not present any obvious drastic differences in structure. Some hole and crack observations were detected for all types which can be related to decreased hydrogen bonding and the repulsion between the hydrophobic long carbon chains and hydrophilic groups [30]. These observations suggested that microwave heating was a successful edible film drying application and there was an acceptable good interaction between SPI and SO.

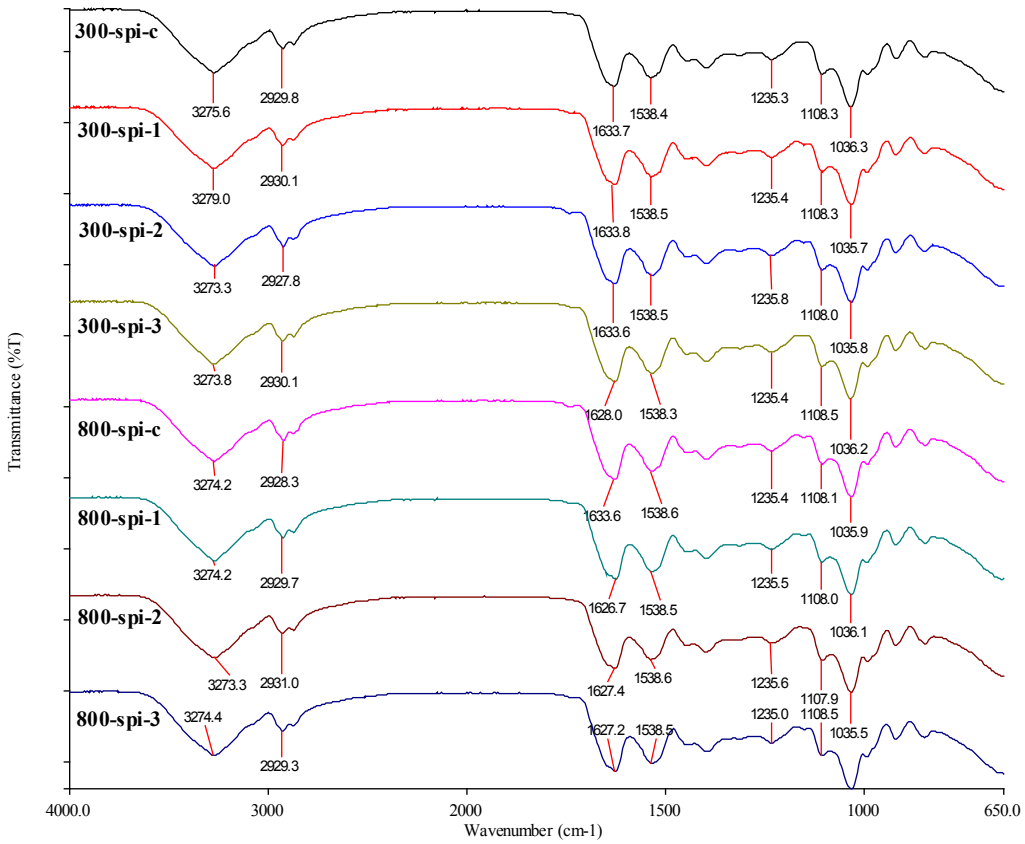
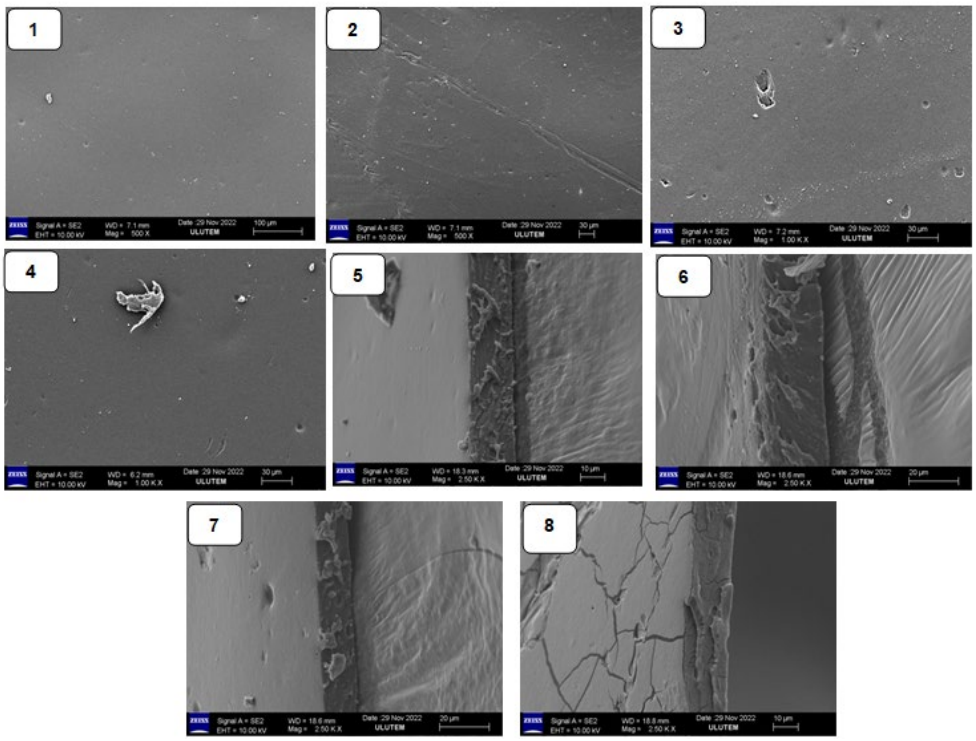
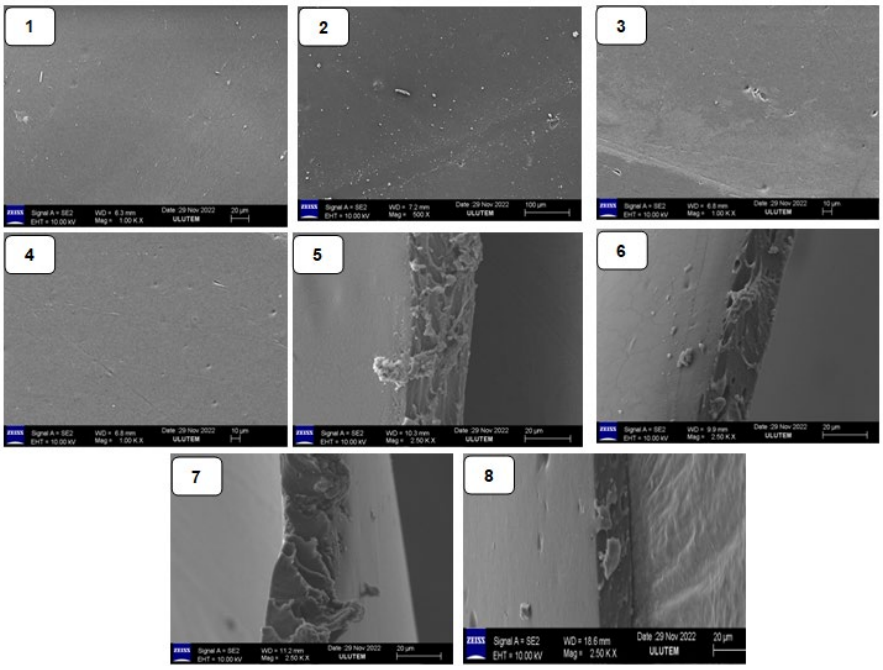


Figure 3. FTIR spectra of microwave dried SPI based film samples.



A

Figure 4A. SEM images of the surface (1000 × magnification) and the cross section (2500 × magnification) of the SPI based microwave dried film samples. Scale bar corresponds to 20 µm. (A1-surface, A5-cross section) 300-spi-c, (A2-surface, A6-cross section) 300-spi-1, (A3-surface, A7-cross section) 300-spi-2, (A4-surface, A8-cross section) 300-spi-3.



B

Figure 4B. SEM images of the surface (1000 × magnification) and the cross section (2500 × magnification) of the SPI based microwave dried film samples. Scale bar corresponds to 20 µm. (B1-surface, B5-cross section) 800-spi-c, (B2-surface, B6-cross section) 800-spi-1, (B3-surface, B7-cross section) 800-spi-2, (B4-surface, B8-cross section) 800-spi-3.

CONCLUSION

In this study, the new SPI-SO composite powder was used during the preparation of the biocomposite film forming solution, followed by the microwave drying method, which allows the edible films to dry in just a few minutes. Incredably fast drying was achieved with microwave drying process, as well as easy manupulation and power transfer efficiency. The results showed that both power levels (800 and 300W) were applicable, but thermal stability and barrier properties increased with 800W level, while better mechanical and optical properties were detected in films drying at 300W. Compared to control films, SO usage significantly increased the elongation profile and make the films more opaque. The SEM images revealed that SO were successfully introduced into the SPI matrix without aggregation, although some pores were exist on the surface. In conclusion, this research provides a time-effective edible film production route for future industrial applications in terms of both the film forming solution preparation and film drying step using a combination of composite powder and microwave drying method.

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