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# Microwave drying effects on properties of whey protein isolate edible films

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**Abstract**

Whey protein isolate (WPI) edible films were dried using microwave drying or at room conditions. The drying time of the films required 5 min in microwave oven and 18 h at room conditions. Water vapor permeability (WVP), mechanical properties, gloss and haze of WPI based edible films were determined. Water vapor transmission rate (WVTR) increased with increasing temperature, but the results showed that WVP did not show a similar trend. Microwave drying and drying at room conditions gave similar results for the WVP. Application of microwave increased the elongation and tensile strength values. © 2000 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Edible films and coatings may have potential applications in the food industry (Şümnü & Bayındırlı, 1995). Edible films and coating are generally formed from a solution or dispersion of the film-forming agent, followed by any of the several means to separate the film-forming agent from the fluid carrier, or by solidification of the film-forming material from a melt (Kester & Fennema, 1986). Films and coatings may be differentiated on the basis of an application method. A film can be preformed and applied to a food at any time, much like a synthetic package, whereas a coating must be applied in liquid form to a food directly (Sherwin, 1998). The specificity of the edible films needs further studies to improve the mechanical and barrier properties (Kester & Fennema, 1986).

Whey protein, a by product of cheese manufacture, is produced in large quantities and has excellent functional properties and could potentially be used for edible films. Barrier and mechanical properties of whey protein isolate based films have been studied by some researchers, but generally they have been studied at 25°C and 100–0% relative humidity (RH) gradient (McHugh & Krochta, 1994a; Chen, 1995; Fairley, Monahan, German & Krochta, 1996; Krochta & De Mulder-Johnston, 1997). WPI films can be made from 8% to 12% whey protein solutions (McHugh & Krochta, 1994b). It was found that below 8%, WPI intact films were not formed, presumably due to lack of intermolecular interactions upon film dehydration (McHugh, Aujard & Krochta, 1994). On the other hand, after 11% of WPI, whey protein solutions become gel during heating. Plasticizers, such as glycerol and sorbitol, are used generally for WPI-based edible films to enhance the film flexibility and extensibility (McHugh & Krochta, 1994b; McHugh, Avena-Bustillos & Krochta, 1993; Banerjee & Chen, 1995; Mate, Frankel & Krochta 1996).

Most types of edible films are prepared by air drying (ca. 24 h) after spreading film solution over the plate, a fairly rapid film formation is generally required for industrial reasons. As microwave drying is one of the fastest drying methods, it was thought that microwave drying could be applied to dry films.

One of the most useful functions of edible films is their ability to act as water, gas (mainly, oxygen and carbon dioxide) and oil barriers. Water vapor permeability is one of the most important and widely studied property of edible films. Mechanical properties are as important to edible films as barrier properties are. Adequate mechanical strength ensures the integrity of a film and its freedom from minor defects, such as a pin hole, which ruin the barrier property (Chen, 1995). Tensile strength expresses the maximum stress developed in a film during a tensile test and offers a measure of integrity and heavy duty use potential for films and percentage elongation at break is a quantitative

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representation of a film's ability to stretch (Gennadios, Weller & Testin, 1993).

The aim of this study is to apply microwave drying during preparation of edible films to shorten film drying time. The most important factor for applicability of different preparation techniques is obtaining similar or better properties than usual drying methods. Therefore, WVP, tensile strength, elongation, gloss and haze of the films were determined. Since the aim of this study is not studying drying characteristics of WPI films dried with microwave or air drying, the drying characteristics were not investigated. Further studies are needed for improving the microwave application and analyzing drying characteristics.

## 2. Materials and methods

### 2.1. Materials

WPI (BiPro, 98.1% protein) used to make films was supplied by Davisco International, Le Seur, MN. All chemicals used were reagent grade and the water was doubly distilled.

### 2.2. Film formation

Aqueous solutions of 8% and 10% (w/w) WPI were prepared and heated with stirring to 90 ± 2°C for 15 min (total heating time is 30 min) over a hot plate. Solutions were cooled to room temperature and vacuum was then applied to remove dissolved air. Glycerine (G) was added as an equal weight of WPI originally dissolved to provide 50% WPI/50% G films, total solids basis. Solutions containing 2.6 g total solids were pipetted per glass plate (15 cm × 15 cm) to minimize thickness variations between treatments. Ten plates were cast per formula. The solutions were spread evenly with a glass rod (Avena-Bustillos & Krochta, 1994) allowed to dry at room conditions (20 ± 2°C and 40 ± 5% RH) overnight and dried films were peeled from casting surface. Then dried films were left at 23 ± 2°C and 45 ± 5% RH for conditioning for one day.

In the case of microwave drying, the emulsions spread over glass plates were dried in a microwave oven (Arçelik, ARMD 580, with power output 700 W, operated at 2450 MHz) for 5 min. The boiling and bubbling were not observed during drying. The dried films were peeled-off and the same conditioning used for the microwave dried films was applied.

### 2.3. Film thickness

Thickness of films was measured with a micrometer (R&B cloth thickness tester, James H. Heal, Halifax, England) having a sensitivity of 0.001 mm. Films were cut into 3.2 cm diameter circles and thickness of each film was measured at six random positions around the film following WVP tests. Mean values were used for the calculations (SD ± 0.02).

### 2.4. Water vapor permeability

Water vapor transmission of films was measured using procedures described by some researchers (Kamper & Fennema 1984; Aydt, Weller & Testin 1991; Park & Chinnan, 1995; Sherwin, 1998). Circular glass test cups with a diameter of 3 cm and a depth of 3 cm were used. After placing 10 ml of distilled $H_2O$ in each cup, they were covered with the edible films. Films were cut circularly with a diameter slightly larger than the diameter of the cup and then they were sealed using melted paraffin. The cups were weighed with their contents and placed in a desiccator containing saturated $Mg(NO_3)_2$ solution at the bottom. The relative humidity value of saturated $Mg(NO_3)_2$ solution at each temperature range studied was found as 0.5916, 0.5438 and 0.514 at 4°C, 20°C and 30°C, respectively (Labuza, 1984). The desiccators were kept in the incubator (Nüve ES 500) at 4°C, 20°C or 30°C. Cups were weighed up to 30–40 h. Three replicates of each film were tested. Height of air gap between film and desiccant in cups was measured initially and finally and relative humidities and WVP values were calculated using WVP Correction Method.

### 2.5. The water vapor permeability calculations

The relative humidity inside the cup was provided as 100% by placing the water into the cup. The relative humidity outside the cup was around 50% by placing saturated $Mg(NO_3)_2$ solution into the desiccator. Weight loss graphs were plotted with respect to time, slopes of them (correlation coefficients of them were larger than 0.997) obtained linear least-square method used to calculate water vapor transmission rate (WVTR) in the following Equation (Chinnan & Park, 1995):

$$\mathrm{WVTR} = \frac{\text{Slope}}{\text{Film area}} = \frac{\mathrm{g}}{\mathrm{h\ m^2}}, \quad (1)$$

where Slope = weight loss vs. time. Film area is the cup test mouth area.

Two WVP values were determined by using the methods (defined as classical methods throughout the study) described by Chinnan and Park (1995) and Ayranci and Çetin (1995), and corrected method suggested by Gennadios, Weller and Gooding (1994a). Eq. (2) was used to find WVP in the classical method used as neglecting gap resistance inside the cup between the solution and film layer,

$$WVP = \frac{WVTR}{p_2 - p_1} L, \quad (2)$$

where WVP is the water vapor permeability, $p_1$ the apparent pressure (kPa) inside the cup, $p_2$ the water vapor partial pressure (kPa) at the film outer surface in the system. $L$ the average film thickness (mm). The $p_1$ and $p_2$ values were calculated from the product of vapor pressure of pure water and the relative humidity of the medium at the defined temperatures and given in Table 1. In the classical methods, vapor pressure of water inside ($p_1$) the cup were assumed as pure water vapor pressure: 0.817, 2.346 and 4.246 kPa, at 4°C, 20°C and 30°C, respectively.

The corrected WVP values were calculated as based on the reported methods by Gennadios et al. (1994a). First of all true pressure ($p_1'$) of the film underside was calculated.

$$p_1' = p_T - (p_T - p_0) \exp\left(\frac{WVTR(RT)\Delta z}{p_T D(MW)}\right), \quad (3)$$

where $p_T$ is the total atmospheric pressure (1 atm), $p_0$ the partial pressure (atm) of water vapor in air at the surface of the solution (or desiccant) in the cup, $p_1$ the partial pressure (atm) of water vapor at the underside of the film. $\Delta z$ the mean stagnant air gap height (mm). $R$ the gas constant ($82.1 \times 10^{-6}$ m$^3$ atm/g mol K), $T$ the absolute temperature (K), $D$ the diffusivity of water vapor in air (cm$^2$/s) found in the literature at each temperature, MW the molar weight of water (18 g/g mol). From Eq. (3), calculated $p_1'$ values (Table 1) were employed in Eq. (2) to calculate the corrected WVP.

### 2.6. Tensile strength, percent elongation, elastic modulus, gloss and haze

Mechanical properties were determined using four films cast from each solution. Eight strips, 15 cm × 2 cm, were cut from each type and after conditioning at 23 ± 2°C and 45 ± 5% RH for at least 48 h prior to tests, samples were tested for tensile strength and percent elongation according to ASTM Standard Method D 882 (ASTM, 1993). A TIRATEST 2602 (TIRA Maschinenbau GmbH Raunstein, Germany) was used to measure tensile strength, percent elongation and elastic modulus of the sample. Initial grip separation and crosshead speed were set at 100 and 500 mm/min, respectively. The mean of thickness of these films was 0.075 mm. Haze of samples was measured by using EEL-Spherical Hazemeter BS 2782 London, England (ASTM, 1970a). Gloss was reported in percentage at 45° from a line normal to the surface ASTM, 1970b (micro-TRI-gloss, BYK-Gardner, Silver Spring, MD). The gloss and haze values reported were based on four samples and four measurements per sample. These tests were applied at room conditions (23 × 2°C and 45 ± 5% RH). It is necessary to test the mechanical properties of the films at controlled temperature and relative humidity in order to achieve good reproducibility. Since all kinds

Table 1
WVTR, WVP and corrected RH (%) values, measured at different temperatures, of 8% and 10% WPI:G film dried using a microwave or room conditions (± SD)[a]

| Drying Methods | Temperature (°C) | Thickness (mm) | WVTR (g/h m$^2$) | RH inside Cup (%) | WVP (g mm/ kPa h m$^2$) | |
|---|---|---|---|---|---|---|
| | | | | | Classical | Corrected |
| Microwave[b] | 4 | 0.12 | 4.38 (±0.1) | 84 (±0.3) | 1.64 (±0.10) | 2.68 (±0.12) |
| | 20 | 0.11 | 20.38 (±0.1) | 75 (±0.8) | 1.90 (±0.10) | 4.32 (±0.13) |
| | 30 | 0.12 | 40.53 (±0.1) | 73 (±0.5) | 2.36 (±0.07) | 5.40 (±0.11) |
| Room conditions[b] | 4 | 0.11 | 4.85 (±0.1) | 82 (±0.9) | 1.59 (±0.08) | 2.81 (±0.14) |
| | 20 | 0.10 | 20.31 (±0.1) | 75 (±0.7) | 2.09 (±0.11) | 4.70 (±0.12) |
| | 30 | 0.12 | 40.51 (±0.1) | 73 (±1.0) | 2.45 (±0.10) | 5.66 (±0.13) |
| Microwave[c] | 4 | 0.10 | 3.11 (±0.1) | 88 (±0.9) | 0.97 (±0.05) | 1.32 (±0.12) |
| | 20 | 0.12 | 9.87 (±0.2) | 86 (±0.7) | 1.10 (±0.07) | 1.51 (±0.14) |
| | 30 | 0.13 | 30.01 (±0.1) | 77 (±1.1) | 1.92 (±0.10) | 3.62 (±0.17) |
| Room conditions[c] | 4 | 0.11 | 3.06 (±0.3) | 89 (±0.9) | 1.09 (±0.06) | 1.49 (±0.11) |
| | 20 | 0.13 | 9.23 (±0.2) | 87 (±0.8) | 1.10 (±0.07) | 1.53 (±0.13) |
| | 30 | 0.13 | 30.66 (±0.1) | 76 (±0.8) | 2.03 (±0.10) | 3.69 (±0.20) |

[a] Thickness are mean values (SD ± 0.02). Relative humidity at the inner surface of the film and corrected WVP values were calculated as described by Gennadios et al. (1994). RH outside cups was 50%.
[b] 8% WPI films.
[c] 10% WPI films.

of films were measured at the same room condition, it was possible to compare the tensile strength and percent elongation of the films.

### 2.7. Statistical analysis

Sigma Plot V. 3.0 (Jandel Scientific Graphing Software) was used for all statistical analysis. Analysis of variance (ANOVA) procedures were used to analyze data. Duncan's Multiple Range Test ($p < 0.05$) was used to detect differences in film property mean values.

## 3. Results and discussion

### 3.1. Water vapor permeability

The relative humidity gradient is an important parameter in calculation of WVP (McHugh et al., 1993), generally in the literature 100–0%RH (inside–outside the cup) was applied (McHugh et al., 1994; Mate et al., 1996).The relative humidity gradient was selected as 100–50% since most of the foods have high water activity (>0.95) and environmental RH is generally 50%. WVTR values obtained from the slopes of the lines (regression coefficients of the lines were >0.993 at $p < 0.05$), obtained from weight loss of cups covered with 8% and 10% WPI films prepared with either microwave drying or room conditions, were represented in Fig. 1. The increasing WVTR values with increasing temperature were observed. It was generally accepted that WVTR increased with an increase in temperature (Kamper & Fennema, 1984; Gontard, Guilbert & Cuq, 1993) as it was observed in this study.

Classical and corrected WVP of the 8% and 10% WPI:G films, dried at room conditions or in microwave oven, are tabulated in Table 1. It was observed that there was no significant difference between WVP values of films dried by using these drying methods ($p < 0.05$). Classical WVP methods gave lower WVP values than calculated values using corrected methods, as it was expected, because classical methods ignore air resistance between film and solution inside the cup (Gennadios et al., 1994a). It was found that microwave drying or drying at room conditions gave similar results in WVP, so it was possible to use a microwave for drying of WPI films (Table 1). Mean WVP of 8% WPI films were higher than of 10% films, but it was found that there was no significant difference in WVP values ($p < 0.05$). McHugh et al. (1994) reported that there was no significant difference in WVP at 8% and 10% WPI:G concentrations. They used 37.5% sorbitol as plasticizer and 0–100% RH (out/in) and found that WVP values of the WPI films (8% and 10%) were the same (2.71g mm/kPa h $m^2$) and they also reported that glycerol addition instead of sorbitol increased WVP. The result of this study was in a good correlation with their result.

The WVP values of 8% and 10% WPI:G films, dried either in a microwave oven or at room conditions, with respect to temperature were given in Fig. 2. Increasing WVP with the increasing temperature were observed. The different observations were given in the literature with the case of temperature dependency of WVP of hydrophilic films, while decrease in WVP with increase in temperature was observed for wheat gluten and soy protein isolate (Gennadios, Branderburg, Park, Weller & Testin, 1994b), increase in WVP with increase in temperature was observed for methyl cellulose and hydroxypropyl methyl cellulose films (Chinnan & Park, 1995).

### 3.2. Tensile strength, elastic modulus, percent elongation, gloss and haze

Guilbert (1986) suggested that rapid drying can cause some undesirable mechanical problems such as

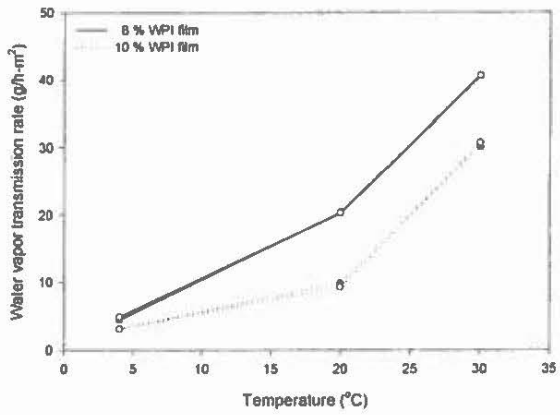


Fig. 1. Effect of temperature on WVTR values of 8% and 10% WPI:G film dried using microwave (•) or room condition (○).

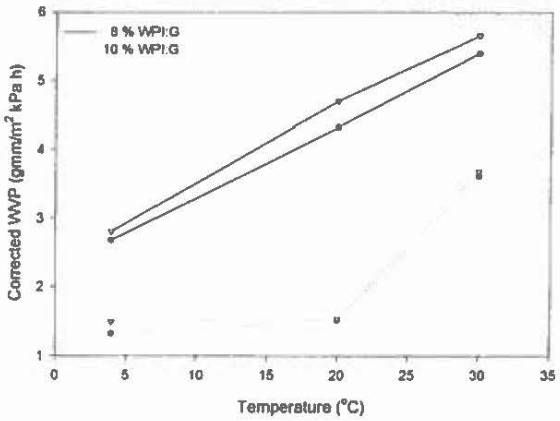


Fig. 2. Effect of temperature on WVP values of 8% and 10% WPI:G film dried using microwave (•) or room condition (▽).

Table 2
Some physical properties of films prepared with 8% and 10% WPI dried using a microwave or room conditions (±SD)*

| Drying methods | Haze | Gloss | Tensile strength (MPa) | Modulus of elasticity (MPa) | Elongation (%) |
|---|---|---|---|---|---|
| Microwave[A] | 2.1 (±0.2)[b] | 95 (±2)[b] | 2.23 (±0.2)[a,b] | 27.08 (±9.5)[a] | 36.1(±5.3)[a] |
| Room conditions[A] | 2.9 (±0.1)[c] | 89 (±1)[a] | 1.94 (±0.2)[a] | 20.87 (±8.3)[a] | 26.1(±2.4)[a] |
| Microwave[B] | 1.8 (±0.1)[a] | 96 (±2)[b] | 2.43 (±0.1)[b] | 20.17 (±7.0)[a] | 35.9 (±4.3)[a] |
| Room conditions[B] | 3.2 (±0.2)[b] | 87 (±2)[a] | 2.28 (±0.3)[a,b] | 18.91 (±5.3)[a] | 26.5 (±3.1)[a] |

* Numbers with different following letters differ at $P = 0.05$ level.
[A] 8% WPI.
[B] 10% WPI.

brittleness. However there have been some studies conducted at higher temperatures rather than at ambient conditions (ca. 23°C). For examples, Kamper and Fennema (1984) dried fatty acid and hydroxypropyl methylcellulose bilayer films at 90°C for 15 min, and Gennadios and Weller (1991) dried soymilk protein films at 100°C for 1 h. It was planned to dry films by a microwave, a rapid dryer, and to control the possible increase in brittleness due to rapid drying by knowing mechanical properties.

The tensile strength, percent elongation and elastic modulus results were given in Table 2. The 8% and 10% WPI:G-based films gave similar results, but microwave dried films had higher tensile strength and elongation values than dried films at room conditions. If the results of this study (Table 2) were compared with the results given in literature, the elongation values have been found in the similar range (4.10% and 30.8% for WPI:G 5.7:1 and WPI:G 2.3:1, respectively (McHugh & Krochta, 1994b)), but the tensile strength values of this study were lower than of the literature (9.20 and 13.9 MPa for WPI:G 3:1 (Fairley et al., 1996) and WPI:G 2.3:1 (McHugh & Krochta, 1994b), respectively. Modulus of elasticity is the ratio of stress to strain over the linear range and measures the intrinsic stiffness of the film (Chen, 1995). Although the most frequently reported tensile properties of edible films are tensile strength and elongation, nowadays modulus of elasticity has been given by some reporters (Chen, 1995; Fairley et al., 1996). Modulus of elasticity values of WPI films dried using microwave or room conditions are given in Table 2. It was observed that there was no significant difference between modulus of elasticity of the films dried using both drying methods. Fairley et al. (1996) reported that in all types of edible films, a small increase in glycerol level results in a large drop in tensile strength and an increase in elongation. Their tensile stress, elongation and modulus of elasticity (Young's modulus) were 9.2 MPa, 13.7% and 401 MPa, respectively. Since they used WPI:G composition 3:1, the lower tensile strength and higher elongation values observed in this study than their report could be due to the high glycerol amount in the solution.

On the other hand, it was known that specular gloss is used mainly as a measure of the shiny appearance of films and surfaces, and the measurement of haze provides some information on the homogeneity of the surface and internal defects which can contribute to the diffusion or deviation of light. So, the main aim of measuring haze and gloss values was to control the possible invisible physical degradation of microwave drying on films, actually there was not any visible degradation.

The gloss and haze of the WPI:G films dried using microwave or room conditions, given in Table 2, were comparable with the synthetic films, such as gloss (measured at 45°) and haze values of the synthetic polypropylene films (Süper film-Biaxially oriented polypropylene film) are 90% and <1.5%, respectively. The gloss and haze values of microwave dried films are better also than those dried at room temperature. So, microwave drying could be applied for drying of WPI based edible films.

## 4. Conclusion

Application of microwave drying to WPI:G based edible films did not affect the water vapor permeability characteristics. The effect of microwave drying on the mechanical properties should be studied in more detail, but it was possible to indicate that microwave drying could be applied for drying of WPI films. It was important to indicate that gloss and haze properties of WPI:G based edible films dried by both methods have been found as good as the synthetic films.

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