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Research Article

Effect of Ethylene Glycol and Glycerol Concentrations on Properties of Rye-Based Films

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Abstract

Rye flour based edible films were produced by using glycerol and ethylene glycol as plasticizers at concentrations ranging between 40 to 100% (w/w of rye flour). The structural, mechanical, physical, and chemical properties of the films were investigated. The results showed that increasing the plasticizer concentration resulted in a greater the thickness, water vapor permeability, and water solubility of the films. While water vapor permeability and solubility were not affected by the plasticizer type, the thickness of glyserol-containing films was significantly higher. Good mechanical properties were obtained for the composites, where the greatest tensile strength of 7.47 MPa was measured in the film containing 40% ethylene glycol (w/w rye flour) and the highest elongation of 69.3% was observed in the film containing 100% glycerol (w/w rye flour). The increase in added plasticizer had an adverse effect on antioxidant activity and the total phenolic content of the films, due to probable dilution effect in the composites.

Keywords: Edible film, rye flour, glycerol, ethylene glycol, plasticizer.

Etilen Glikol ve Gliserol Konsantrasyonlarının Çavdar Esaslı Filmlerin Özelliklerine Etkisi

Öz

Çavdar unu bazlı yenilebilir filmler, %40 ila %100 (a/a çavdar unu) arasında değişen konsantrasyonlarda plastikleştirici olarak gliserol ve etilen glikol kullanılarak üretilmiştir. Filmlerin yapısal, mekanik, fiziksel ve kimyasal özellikleri incelenmiştir. Sonuçlar, plastikleştirici konsantrasyonunun arttırılmasının filmlerin kalınlığını, su buharı geçirgenliğini ve suda çözünürlüğünü arttırdığını göstermiştir. Filmlerin su buharı geçirgenliği ve çözünürlüğü plastikleştirici türünden etkilenmezken, gliserol içeren filmlerin kalınlığı önemli ölçüde daha yüksek çıkmıştır. Kompozitler için iyi mekanik özellikler elde edilmiş olup, en yüksek çekme mukavemeti 7,47 MPa ile %40 etilen glikol (a/a çavdar unu) içeren filmde ölçülmüş ve en yüksek uzama %69,3 ile %100 gliserol (a/a çavdar unu) içeren filmde gözlemlenmiştir. Eklenen plastikleştiricideki artış, kompozitlerdeki olası seyreltme etkisinden dolayı, filmlerin antioksidan aktivite ve toplam fenolik içeriği üzerinde olumsuz etkisi olmuştur.

Anahtar Kelimeler: Yenilebilir film, çavdar unu, gliserol, etilen glikol, plastikleştirici.

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1. Introduction

To minimize oil-based plastic consumption in packaging, a significant effort has been directed towards formulation and production of environmentally friendly edible films for food applications. These materials are mostly proteins, polysaccharides, and lipids in nature and by predetermined modifications, they may acquire properties desired by consumers. Well-designed alterations or specific formulations are developed to obtain packaging materials with functional properties (Rong & Xie, 2021). In the selection of materials to be used, the edible packaging composition is determined depending on the type of product to be protected and the typical storage conditions the target food might endure (Fakhouri & Mei, 2012). Therefore, composition formulation is made by firstly determining what the edible film will be used for.

Many studies focus on edible films made with flour as a raw material. Flour is preferred because it has better properties than starch-based films produced from the same source of carbohydrate polymers (Gutierrez, 2021). In addition, the lack of any separation, purification procedure for acquiring of the raw material provides a cheap, readily available alternative to starch-, gum-, or protein-based composites. Another important component considered in compozite formulations is the plasticizer, which have a great influence on mechanical properties of films. Studies have shown that concentration and type of plasticizer affected film' tensile strain and elongation (Maniglia et al., 2019; Toth & Halasz, 2019). Beside mechanical properties, the hydrophilic nature of a plasticizer inflences the solubility, water vapor permeability (WVP), degradability of films, as well as the release of biocative compounds in its structure.

In this study, the effect of different concentrations of glycerol and ethylene glycol plasticizers on structural, mechanical, and physicochemical properties of rye flour-based edible films was investigated. A comparison between films containing a commonly used plasticizer- glycerol- and rarely reported - ethylene glycol- was established

2. Material and Method

2.1. Materials

Rye flour was purchased from Demircibaşı (Turkey). Glycerol (Himedia®), ethylene glycol (Emplura®), 1,1-Diphenyl-2-pycrylhydrazyl free radical (DPPH) (TCI, Japan) were used as received.

2.2 Preparation of films

Solution casting method was used in film preparation. Rye flour (5% w/v) and plasticizers (40-100% (w/w flour)) were mixed in distilled water. After half an hour cooking at 90°C, 20 g of the blends were poured into 90 mm x 8 mm plastic petri dishes and dried in an oven at 40°C for 24 hours. The formed films were peeled from the petri dishes after 1h- conditioning at 25°C and 50% relative humidity. The obtained films were placed in plastic bags and stored at refrigeration temperature prior analyses.

2.3 Characterization of films

2.3.1. Film thickness

Film thickness was measured at 5 random positions on the film samples with a digital micrometer (Asimeto 307-06-A) (Daudt, 2017).

2.3.2. Opacity

Film strips were placed in a UV- Vis spectrophotometer (UV-2600 Shimadzu) test cell employing empty cuvette as reference (Liu & Lin, 2021). Film opacity was determined by Eq. (1):

$$Opacity = \frac{A_{600}}{x} \quad (1)$$

where x is the film thickness (mm) and A_{600} is the absorbance at 600 nm.

2.3.3. Water vapor permeability (WVP)

WVP studies were carried in a closed chamber at 25ºC and 50% relative humidity. 30 mL of distilled water was poured in glass bottles and the films were placed on I-CHEM lids with a surface area of 1.767 cm^2. The prepared test vessels were placed in the closed chamber and the weight change in the test bottles was measured against time. Weighing was done using a precision balance with an accuracy of ± 0.0001 g. Water vapor permeability (WVP) was calculated using (Eq. 2).

$$WVP = \frac{\Delta m \times x}{A \times \Delta t \times \Delta P} \quad (2)$$

where $\Delta m/\Delta t$ is the moisture loss per unit time (ng s^{-1}); A is the film area exposed to moisture transfer (1.767×10^{-4} m^2); x the film thickness (m); and ΔP the water vapor pressure difference between the two sides of the film (Pa). At least three replicates per film were measured.

2.3.4. Solubility

The film solubility was determined according to Nouraddini (2018) and was expressed as the percentage of dry matter of the film solubilized after 24 h immersion in water (Nouraddini & Esmaiili, 2018). Film samples were cut into 1 × 1 cm pieces and weighed. Then, the film pieces were immersed in 40 ml of distilled water, and the system was shaken for 24 h at room temperature. After removing excess water by filter paper, samples were dried in an oven at 70 °C. The water solubility of the films was calculated according to Eq. (3):

$$Solubility\ (\%) = \frac{(w_0 - w_t)}{w_0} \times 100 \quad (3)$$

where, wo and wt are the initial and final weights of the dried samples, respectively.

2.3.5. Mechanical properties

A texture analyzer (Instron 5944MTS) was used to analyze tensile strength (TS, MPa) and elongation at break (EB, %) of the films according to the ISO 527-2-5a standard method. The cut film samples were placed between the two jaws of the device and pulled at a pulling speed of 5 mm/min. Strength values at break and elongation values were calculated with the help of a computer program connected to the test device. Each sample film was tested at least 5 times (Cai & Zhao, 2022).

2.3.6. Thermogravimetric analysis (TGA)

TGA of the samples was performed by a thermogravimetric analyzer (Perkin-Elmer STA 6000). Each film sample (5-6 mg) was sealed in a ceramic plate and heated from 40 °C to 600 °C at a heating rate of 50 °C/min in a nitrogen atmosphere (20 mL/min) (Du & Chen, 2021)

2.3.7. Fourier transform infrared spectroscopy (FTIR)

The samples were scanned at a wavenumber range of 650−4000 cm−1 with 4 cm−1 resolution in transmission mode, via a FTIR spectroscopy apparatus (Thermo Nicolet, İS10 FTIR) (Zahra & Yazdi, 2020).

2.3.8. DPPH radical scavenging capacity

The antioxidant activity of the film was estimated using DPPH (1,1-diphenyl-2-picrylhydrazyl) according to the method described by Adilah & Hanani (2016). Briefly, 0.1 gram of composite film was added to 5 mL of methanol and mixed. The mixture was kept in the dark for 1 hour. Then, 0.1 mL sample was taken and mixed with 3.9 mL of DPPH methanol solution (0.56 mmol/L) and incubated in the dark at ambient temperature for 30 min. The absorbance of solutions was measured at 517 nm against methanol (blank). Finally, the antioxidant activity was expressed as the percentage of DPPH free radical scavenging activity and calculated by Eqn. (4):

$$\%Radical\ scavenging\ activity = \frac{(Abs_{DPPH} - Abs_{\ sample})}{Abs_{\ DPPH}} \times 100 \qquad (4)$$

where Abs_{DPPH} was the absorbance of the methanolic solution of DPPH and Abs_{sample} was the absorbance of the sample extracts measured at 517nm.

2.3.9. Total phenolic content

0.1 grams of film and 5 mL of distilled water were placed in centrifuge tubes, vortexed for 1 minute and kept for one hour in a dark environment. In test tubes, 0.1 mL aliquots of the extracts, 0.5 mL of 10% Folin Ciocalteau reagent and 1.5 mL 20% sodium carbonate solution were combined and stirred. Sample absorbances were measured at 750 nm, after 2 h of rest (Barros % Boas, 2021). The results were expressed in mg gallic acid equivalent (GAE) g^{-1} of sample.

3. Results and Discussion

3.1 Water Vapor Permeability, Thickness, Solubility and Opacity of Films

After production of the rye flour films, their physical properties were investigated. Table 1 shows the values of water vapor permeability, thickness, and solubility of 5% rye flour (w/w) films containing varying amounts of different plasticizers.

In general, the increase in the amount of plasticizer increased the film thickness. This might be related to the swelling ability of plasticizers as they absorb moisture. The higher the plasticizer content the greater the swelling and, consequently, the thicker the film. The thicknesses of the films made with glycerol varied between 145 and 232 µm. These values were close to the ones reported in the literature (Dick & Pagno, 2015). The thicknesses of films prepared with ethylene glycol were half of the glycerol-containing films, ranging between 77 and 84 µm (Marron, 2019).

The water vapor permeability of glycerol-containing films was slightly higher than ethylene glycol-containing films (Blacido & Sobral, 2011). Overall, the increase in the amount of plasticizer caused an increase in water vapor permeability.

Table 1. Water vapor permeability, thickness, and solubility of films

Film composition*	**WVP** (ng.Pa^{-1} s^{-1} m^{-1})	**Thickness** (µm)	**Solubility** (%)
R5G%40	1.08±0.02	145.3±25	58.60±2.85
R5G%60	1.13±0.02	159±16	63.27±0.77
R5G%80	1.25±0.00	185±29	67.16±3.68
R5G%100	1.44±0.01	232±17	68.07±1.96
R5EG%40	1.02±0.04	78±4	56.36±6.90
R5EG%60	1.00±0.01	76.67±8	56.83±1.45
R5EG%80	1.01±0.02	77±20	61.41±3.70
R5EG%100	1.02±0.14	84±6.8	61.05±3.45

*R: rye flour; G: glycerol; EG: ethylene glycol

If a distinct, outer packaging is to be made, films with high solubility are preferred; so that their consumption with food ispossible. However, if the film is preferred as a stand-alone packaging, in order to protect the edible film only on the food surface and extend its shelf life, it is more appropriate to prefer films that do not dissolve quickly in water (Erdoğan, 2020). Due to high hydrophilic characteristics of both plasticizers, in 24 h approximately half of the films were dissolved. The solubility studies showed that as the amount of plasticizer increased, films' solubility also increased. Factors affecting solubility are the molecular structure of plasticizers, the structure formed when combined with rye flour and water, and the residence time in the solvent.

While packaging materials with high opacity are preferred to protect food from sunlight; edible films with low opacity (high transparency) are preferred to emphasize the visual quality of the food. In our study, the films having higher opacity were the ones made with ethylene glycol with values between 10.23 and 12.74. Slightly more transparent films were obtained when glycerol was used as a plisticizer, where opacity values between 5.88 and 6.58 were calculated (Figure 1).

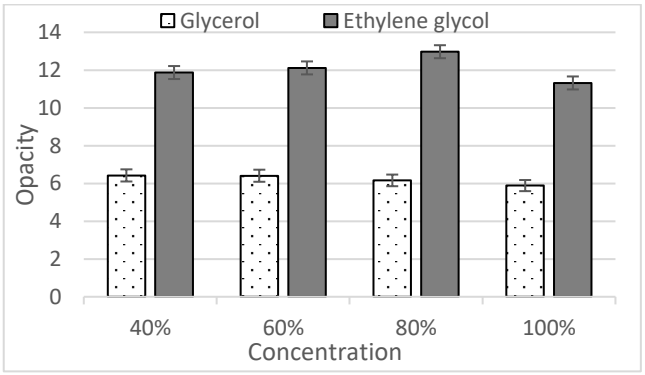


Figure 1. Opacity of rye flour films containing different plasticizers

3.2 Mechanical Properties

The main task of a packaging material is to protect and preserve the integrity of a food. This implies that the material itself should be able to withstand physical damage caused by external factors such as pressure or vibration during transportation (Akşehir, 2013).

Both the type and concentration of plasticizers had a substantial effect on mechanical properties of the rye flour films

(Table 2). In particular, ethylene glycol-containing films exhibited superior mechanical properties compared to glycerol-containing films. The tensile strength in presence of ethylene glycol and glycerol varied between 2.91 and 7.47 MPa, and 0.42 and 1.68 MPa, respectively. For both plasticizers, the increase in plasticizer concentration decreased the films' tensile strength and Young's modulus, but increased the elongation at break values.

Table 2. Mechanical properties of rye flour films

Film composition	TS[1] MPa	EAB[2] %	YM[3] MPa
R5G%40	1.68±0.28	39.75±3.69	42.23±9.98
R5G%60	0.67±0.05	57.55±6.58	3.29±0.88
R5G%80	0.50±0.09	53.95±14.21	1.57±0.20
R5G%100	0.42±0.063	69.3±6.44	1.07±0.13
R5EG%40	7.47±0.89	31.32±4.67	355.06±53.82
R5EG%60	4.9±0.46	37.5±2.38	136.99±37.53
R5EG%80	3.44±0.94	32.4±6.23	89.99±31.95
R5EG%100	2.91±0.15	34.42±9.95	80.75±17.81

[1]TS-tensile strength; [2]EAB-elongation at break; [3]YM- Young's modulus.

The elasticity of edible films constitutes an essential requirement in their utilization as packaging materials. Elongation at break values provide useful information about the potential of the produced films in food packaging applications. Comparing the effect of plasticizer type, the presence of glycerol in film compositions resulted in a favorable elasticity, with elongation values between 39.75 and 69.3%. Films containing ethylene glycol, on the other hand, exhibited greater firmness, since the elongation values were limited between 31.31 and 37.5%.

3.3 Fourier Transform Infrared Spectroscopy

Figure 2 shows FTIR spectra of rye flour films containing 60% (w/w rye flour) of both plasticizers.

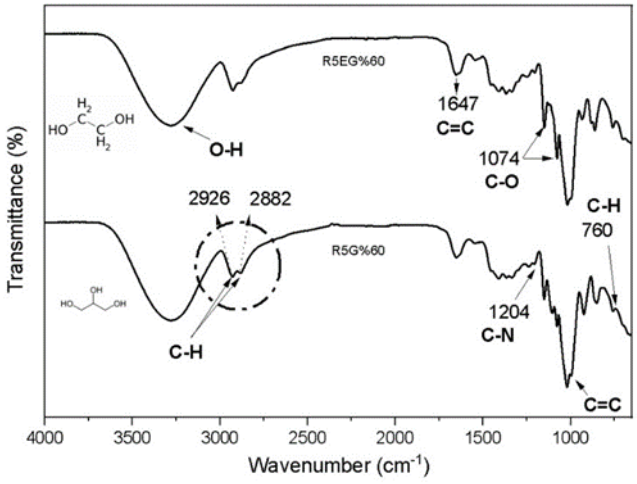


Figure 2. Typical FTIR spectra of rye films containing ethylene glycol (upper spectrum) and glycerol (bottom spectrum) as plasticizers.

A wide peak, corresponding to stretching of O-H and N-H bonds, around 3300 cm-1 (Akşehir, 2013; Erdoğan, 2020; Martins & Cerquira, 2021) was observed. This peak was not that intense in ethylene glycole film (upper spectrum) compared to glycerol-containing film (bottom spectrum). This was, obviously, due to the higher amounts of hydroxyl (-OH) groups present in glycerol (Toth & Halasz, 2019).The peak seen at 2924 cm-1 indicated the presence of methyl groups (-CH) vibrations (Shi & Zhang, 2007; Sucheta & Rai, 2019).

3.4 Thermal Stability

Thermogravimetric analysis plays a crucial tool for understanding the thermal properties, thermal degradation, and weight loss of material with variation in temperature (Shivangi & Shetty, 2021). The thermogravimetric (TG) curves of produced films are shown in Figure 3. The temperature peaks, weight loss and residual weight of films are shown in Table 3.

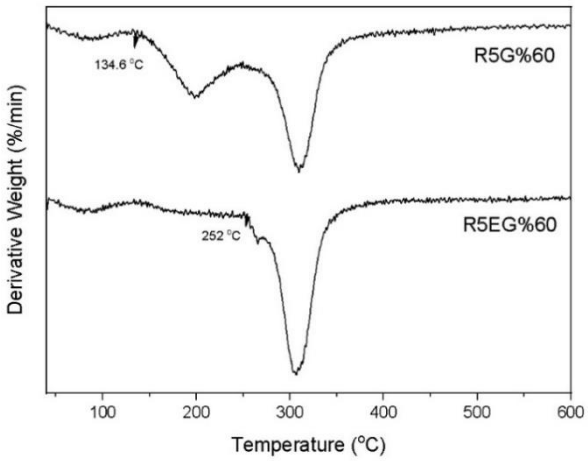


Figure 3. Differential thermogravimetric curves of rye films

The temperature at which initial degradation begins is important because the molecular structures in this film lose their integrity. The films containing glycerol exhibited degradation starting at as low as 153ºC. Another important parameter is the maximum temperature. It indicates that the film deteriorates faster and loses its function at maximum temperature. Films with ethylene glycol lost 44.13% weight between 250 ºC and 338 ºC. The ethylene glycol film started to degrade at the highest temperature and it was observed that the ethylene glycol film was the least decomposed in a short time.

Table 3. Thermogravimetric analysis results of rye films

Plasticizer	Solvent evaporation		T (ºC)		WL	RW
	T (ºC)	WL (%)	Min	Max	(%)	(%)
G	115	5.92	153	347	69.21	15.06
EG	125	7.94	250	338	44.13	19.22

T-temperature; WL-weight loss; RW-residual weight

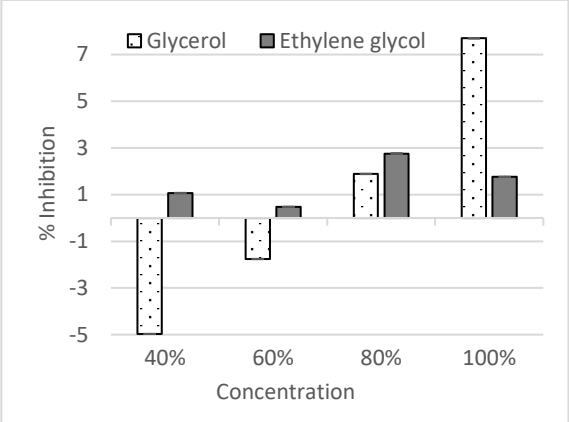
3.5 DPPH Radical Scavenging Capacity and Total Phenolic Content of Films

Antioxidants are defined as chemical components that prevent/reduce oxidation and have a protective effect against various agents by averting the harmful effects of free radicals formed in the food (Baykuş, 2019). The antioxidant capacity of the produced films was examined by measuring the release of antioxidant compounds into the reaction mixture, evaluated by the DPPH free radical scavenging method. The radical scavenging capacity and the total phenolic content of produced films are shown in Figure 4-a and Figure4-b, respectively.

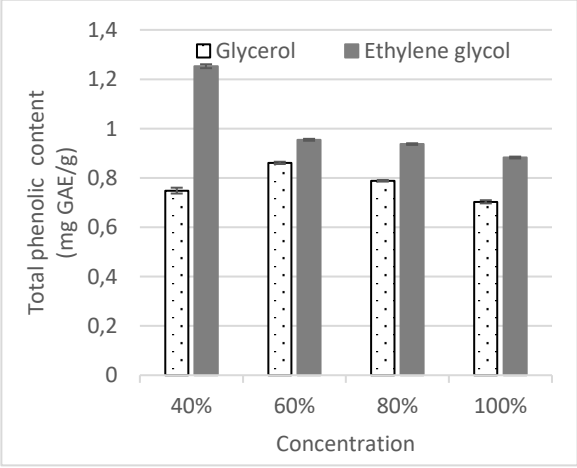
The radical scavenging ability of ethylene glycol films was relatively low and % inhibition values ranged between 0.48 and

2.76%. The antioxidant values of glycerol films, starting from negative values at low concentrations, increased as the amount of glycerol increased, reaching a maximum of 7.7%. These low antioxidant activities were due to the inability of the hydrophilic film composite to efficiently release the phenolics in methanolic DPPH solution (Priyadarshi et *al.*, 2022).

The highest total phenolic content was measured in the films containing 40% ethylene glycol (1.25 mg GAE/g). In general, the phenolic content of films was low. This was expected due to the exposure to high temperature during film preparation. Moreover, the increase in the amount of plasticizer reduced the total amount of phenolic substances per gram of film. This implied that as the rye flour was the source of phenolic compounds and addition of plasticizer most probably had a dilution effect in the composite, resulting in a decrease in the total phenolic compounds per gram film.



(a)



(b)

Figure 4. (a) DPPH radical scavenging capacity and (b) total phenolic content of rye films

4. Conclusions and Recommendations

The study was focused on production and characterization of rye-flour edible films to determine the effect two hydrophilic plasticizers on the physical, mechanical, and chemical properties of the composite films. The investigation revealed that as the concentration of both glycerol and ethylene glycol increased, the thickness, water vapor permeability and water solubility values of edible films increased. Good tensile strength of ca. 7.5 MPa was observed in ethylene glycol containing films, whereas glycerol containing exhibited an elongation of 69.3%. The total phenol content and the DPPH radical scavanging activity of films was substantially low implying that the preparation method might adversly affected the film composition. However, the presented formulations provided films with good mechanical properties and high biodegradability demonstrating their potential in food packaging applications. Further improvement can be attained by usage of bioactive additives, enriching the nutritional and antioxidant properties of the composites.

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