

# Barrier properties and mechanical strength of bio-renewable, heat-sealable films based on gelatin, glycerol and soybean oil for sustainable food packaging

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## ABSTRACT

In this work we studied the mass transfer of renewable films based on gelatin (Ge), glycerol (Gly) and epoxidized soybean oil (ESO) for application in food packaging. Films were tested for water vapor absorption and diffusion at various water activities ( $a_w$ ), oxygen and water vapor permeability. The absorbed vapor mass increased with  $a_w$ , as expected, to 0.25–0.3 g/g<sub>pol</sub> ( $a_w = 0.8$ ). The isotherms were fitted by five different mathematical models. The apparent diffusion coefficient showed an increasing tendency with humidity, up to  $a_w = 0.6–0.7$ , where a maximum was reached. Oil addition caused a reduction in the diffusion coefficient of Ge based films, associated to a greater amount of dispersed hydrophobic phase. Moreover, heat seal and tear of Ge based films were studied. All films were able to be thermosealed. The partial replacement of Gly by 20% ESO increased significantly the heat seal strength, reaching values higher than those reported for synthetic polymers. Gelatin sample containing 20% Gly and 20% ESO presented an appropriate balance between gas barrier properties as well as the resistance of the heat sealing and the tearing.

## 1. Introduction

The mass transfer between packaged foods, packaging material and external atmosphere is the key for assessing products shelf-life in reference to consumer safety [1]. Permeation, migration, and sorption processes must be well established when polymers are used as packaging materials of products that are sensitive to environmental conditions, as occurs with food [2]. In the last decades, attention has turned to the use of biogenic polymers to produce biodegradable plastic films due to several advantages related with their natural and renewable origin, abundance, low cost, and inherent eco-compatibility [3]. Nevertheless, many of these polymers (i.e. proteins and polysaccharides) and/or the plasticizers that are usually used are hygroscopic. Thus, their properties depend strongly on environmental conditions, such as temperature and especially relative humidity. Therefore, the determination of moisture content and mass transport parameters in biogenic films at different relative humidity is always interesting and, in these cases, of extreme importance [4].

Proteins are interesting biopolymers since they have specific

structures derived from the amino acid composition, which confer a wide range of functional properties. Gelatin (Ge) is a water soluble protein derived from animal sources, obtained from the hydrolysis of bone-collagen or connective tissues skin of mammalian and fish [3]. This protein has received much attention for the design of food packaging films because of its relatively low cost, high availability as byproduct of agriculture and food industry as well as by its excellent film forming ability [3,5–8]. Gelatin films generally present excellent oxygen barrier properties at low or intermediate relative humidity and good mechanical properties. However, due to the hydrophilic nature of this protein and the plasticizers usually used, gelatin films are very susceptible to water vapor, compromising their industrial application. For that reason, many attempts have been undertaken to overcome this issue including cross-linking, compounding with nano-sized fillers, and blending with hydrophobic substances [3,4,7,9,10]. Particularly, epoxidized soybean oil (ESO) has been used to reduce biopolymers hydrophilicity, based on its low cost, biodegradable and environmentally friendly character and its renewable origin. In this sense, Belhassen et al. (2014) modified thermoplastic starch with ESO to

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enhance its mechanical strength and to increase its hydrophobicity [11]. Zhang et al. reported that the hydrophobicity of wheat gluten materials was improved significantly by using ESO as an additive [12].

Tear and heat seal strength are important properties of polymer films for their successful industrial application as flexible packages [13,14]. Generally, films are exposed to diverse mechanical stresses during their usage and handling. Most of films are durable under tensile stresses while they are prone to failure upon tearing. In this sense, it is relevant to know film tear behavior for an appropriate material design approach. On the other hand, heat sealing capability is one of the most important requirements for industrial application of polymer films as starting materials for making sachets, pouches or bags to contain liquids or dry food. For this purpose, heat seal must be strong enough to keep the products from leaking, during handling or storage conditions [15]. The main forces responsible for the sealed joint formation of plasticized protein films are the increment of hydrogen and covalent bonds, therefore the contribution to seal joint is given by hydrogen bonding between protein and plasticizers, as well as, between the plasticizer or protein molecules [16,17]. The knowledge of the failure mode of heat sealed films is also a critical parameter for packaging applications since it provides information about the quality of heat sealing. There are several modes of films failure for peel test: (I) adhesive seal failure; (II) cohesive seal failure; (III) failure at seal edge; and (IV) failure at film body [13,15].

This work was focused on studying and modeling the water vapor sorption in films based on gelatin, glycerol and epoxidized soybean oil as well as on assessing their water vapor permeation and oxygen permeability. Moreover, the effect of the partial replacement of glycerol with ESO was analyzed. Considering a potential application as food packaging materials, tear and heat sealing strength of gelatin based films were studied.

## 2. Materials and methods

### 2.1. Materials

Bovine gelatin, Ge (type B, 150 Bloom), with an isoelectric point  $I_p = 5.1$ , was kindly provided by Rousselot (Buenos Aires, Argentina). Epoxidized soybean oil (ESO) with an oxirane functionality of 3.5, was purchased from Unipox (Argentina). Glycerol (Gly) and buffer solution pH 10 (BS) were supplied by Cicarelli (Argentina).

### 2.2. Film processing

Pre-mixtures of Ge, Gly (20–40% w/w), ESO (0–20% w/w) and BS (30% w/w) on dry gelatin basis, were manually mixed for 15 min at room temperature. To analyze the effect of Gly partial replacement by ESO, five different combinations were considered, keeping the BS concentration constant: 40% Gly-0% ESO; 35% Gly-5% ESO; 30% Gly-10% ESO; 25% Gly-15% ESO; 20% Gly-20% ESO. Samples were named Ge-XGly-YESO, where X, and Y referred to Gly, and ESO concentrations (% w/w, dry Ge basis), respectively. Pre-mixtures were fed into a mixing-injection machine (Atlas-Laboratory MiniMixer/Minimolder, USA), mixed at 60 °C, under 100 rpm, for 45 min. All formulations were kept at 4 °C before further processing. Mixtures were hot pressed into films in a hydraulic press (Cavern, USA) between two Teflon-coated aluminum foils at 120 °C and 15,000 lb<sub>f</sub>. Target film thickness was 150 μm. Films were kept at 4 °C, for a maximum of 7 days, before testing.

### 2.3. Film characterization

#### 2.3.1. Thickness

Film thickness (L) was measured in five points using a manual micrometer (0–25 ± 0.01 mm, Venier, China). For each formulation, the average thickness was calculated based on three films.

#### 2.3.2. Water vapor mass transport properties

**2.3.2.1. Water vapor sorption isotherms.** Sorption studies were performed at 30 °C using a quartz spring balance with a coupled CCD camera [18]. The spring elongation, and therefore the mass evolution of a sample exposed to a pure water vapor at a certain activity ( $a_w$ ), was measured as a function of time. Temporal evolution of water absorbed mass was recorded until samples reached the equilibrium, repeating the procedure at different water activities (approximately ten values between 0.1 and 0.8). Absorption isotherms were obtained by plotting the equilibrium solubility as a function of water vapor activity.

**2.3.2.2. Sorption isotherms fitting.** Water vapor absorption isotherms were fitted using different mathematical models widely used for food and natural polymers: Guggenheim–Anderson–DeBoer (GAB, Eq. (1)), Brunauer–Emmett–Teller (BET, Eq. (2)), Oswin (Eq. (3)), Modified Oswin (Eq. (4)) and D'Arcy and Watt (Eq. (5)):

$$M = \frac{M_m \cdot C_G \cdot K_G \cdot a_w}{(1 - K_G \cdot a_w) \cdot (1 - K_G \cdot a_w + C_G \cdot K_G \cdot a_w)} \quad (1)$$

$$M = \frac{M_m \cdot C_B \cdot a_w}{(1 - a_w) \cdot (1 + a_w \cdot (C_B - 1))} \quad (2)$$

$$M = m \cdot a_w^n \cdot (1 - a_w) \quad (3)$$

$$M = K_O \cdot m \cdot a_w^n \cdot (1 - K_O \cdot a_w) \quad (4)$$

$$M = \frac{K_1 \cdot K_2 \cdot a_w}{1 + K_1 \cdot a_w} + K_3 \cdot a_w + \frac{K_4 \cdot K_5 \cdot a_w}{1 - K_4 \cdot a_w} \quad (5)$$

where  $M$  is the water content absorbed in equilibrium per gram of dry film at a water activity  $a_w$ ;  $M_m$  is the moisture content in the monolayer;  $C_G, K_G$  and  $C_B$  are the constants of GAB and BET models, respectively;  $m$  and  $n$  are the constants of Oswin model, which was modified by multiplying water activity ( $a_w$ ) by another constant  $K_O$ . Finally, D'Arcy and Watt model comprises a first term with constants  $K_1$  and  $K_2$  related to a Langmuir-type isotherm for surface monolayer absorption, a second term which involves a linear absorption with relative pressure (Henry's law,  $K_3$ ), and a third term that describes the formation of a multilayer through a modified Langmuir equation with  $K_4$  and  $K_5$  constants.

**2.3.2.3. Water vapor diffusivity.** Water vapor apparent diffusion coefficient ( $D_{H_2O}$ ) was calculated from the best fit of the data measured using the well-known expression for one-dimensional isometric Fickian diffusion in a thin plate:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp\left(\frac{-D_{H_2O} \cdot (2n+1)^2 \cdot \pi^2 \cdot t}{L^2}\right) \quad (6)$$

where  $M_t$  and  $M_\infty$  is the mass absorbed at time  $t$  and at the equilibrium, respectively;  $L$  is the film thickness and  $D_{H_2O}$  is the diffusion coefficient. The apparent diffusion coefficient of water vapor for each considered  $a_w$  was calculated by minimizing the root of the square deviations between the simulated and experimental data.

**2.3.2.4. Water vapor permeation (WVP).** This barrier property was measured for gelatin films at different relative humidity percentages, ranging from 35 up to 90%. Assays were performed according to ASTM F 1249-13 [19] in a PERMATRAN-W 3/33 equipment (Mocon Inc., Minneapolis, USA) at 23 °C. Films were masked with aluminum foil and mounted on test cells. The effective exposed area of gelatin film was 5 cm<sup>2</sup>. Measurements were performed three times for each selected film formulation (Ge-40Gly-0ESO, Ge-30Gly-10ESO and Ge-20Gly-20ESO), reporting the mean values of water vapor permeation.

#### 2.3.3. Oxygen permeability

Oxygen transmission rate (OTR) of gelatin films was determined using a Mocon OX-Tran2/20 (Mocon Inc., USA), following the ASTM

3985-05 standard method [20]. Films were placed in an aluminum mask, resulting in a 5 cm<sup>2</sup> active sample area. Tests were performed at 23 °C, using different relative humidity percentages (35, 50, 70 and 90% RH) and 100% oxygen as test gas. Three specimens of each selected film formulation (Ge-40Gly-0ESO, Ge-30Gly-10ESO and Ge-20Gly-20ESO) were assayed, reporting the mean values of oxygen transmission rate. Oxygen permeability (OP) was calculated from the oxygen transmission rate as:

$$OP \left[ \frac{\text{cm}^3 \cdot \mu\text{m}}{\text{m}^2 \cdot \text{day} \cdot \text{kPa}} \right] = \frac{OTR \cdot L}{\Delta P} \quad (8)$$

where L is the film thickness and  $\Delta P$  is the partial pressure gradient of oxygen through the film.

### 2.3.4. Heat sealing and seal strength measurement

Heat sealing was carried out by an impulse heat sealer machine (Lipari, Model CC 300) provided with a seal bar of 1.5 mm width. Rectangular strips of gelatin films, each measuring 75 mm in length and 25.4 mm in width, were cut using a precision sample cutter. Previously, these strips were conditioned in a chamber at 50% relative humidity (RH) and 25 °C at least 48 h in order to achieve stabilization before testing. For heat sealing, two conditioned strips were placed one over another, held in the jaw of machine and heat sealed together. The same dwell time of the sealing bar was set for all gelatin formulations. After heat sealing, strips were allowed to cool to room temperature.

Heat seal strength of gelatin based films was evaluated using the peel test according to ASTM F88-09 standard [21], using an Instron Universal Testing machine (model 3369, Instron Corporation, USA). For seal strength measurement, sealed sample was held unsupported (T peel test mode) and the two tail ends of the test specimen were clamped in the tensile tester. The heat seal area of the sample was kept at equidistance between the clamps, so that the seal remained perpendicular to the pull direction. Tensile assays were performed using a constant crosshead speed of 200 mm/min and a gap between grips of 25 mm. Ten specimens of selected film formulation

(Ge-40Gly-0ESO, Ge-30Gly-10ESO and Ge-20Gly-20ESO) were assayed at 23 °C. Seal strength was calculated as the value of peak force required to peel/tear apart the seal divided by the film width, expressed in Newtons/meter (N/m). Reported values were calculated from the average of ten measurements for each film formulation.

### 2.3.5. Tear strength

Tear test was performed using an universal testing machine (Instron model 3369), according to ASTM D 1938-08 standard test method [22]. Samples (25 × 75 mm), with a slit at 12.5 mm, were prepared from different film formulations (Ge-40Gly-0ESO, Ge-30Gly-10ESO and Ge-20Gly-20ESO). At least ten specimens of selected film formulations were assayed at 23 °C, using a constant crosshead speed of 250 mm/min and a gap between grips of 50 mm. Load-extension curves were recorded, reporting values of tearing force according to ASTM 1938-08.

### 2.3.6. Statistical analysis

Experimental data were statistically analyzed by one-way analysis of variance (ANOVA) along with Tukey's tests at 95% confidence interval ( $\alpha = 0.05$ ).

## 3. Results and discussion

Macroscopically, translucent and flexible gelatin films were obtained, regardless the studied relative proportions of Gly and ESO. Obtained materials presented a homogeneous appearance with a slight amber hue and uniform thicknesses around  $125 \pm 25 \mu\text{m}$ . Particularly, mixtures with higher concentration of ESO (Ge-20Gly-20ESO) showed a slight oily exudation during their processing. However, films did not result sticky or oily after thermocompression.

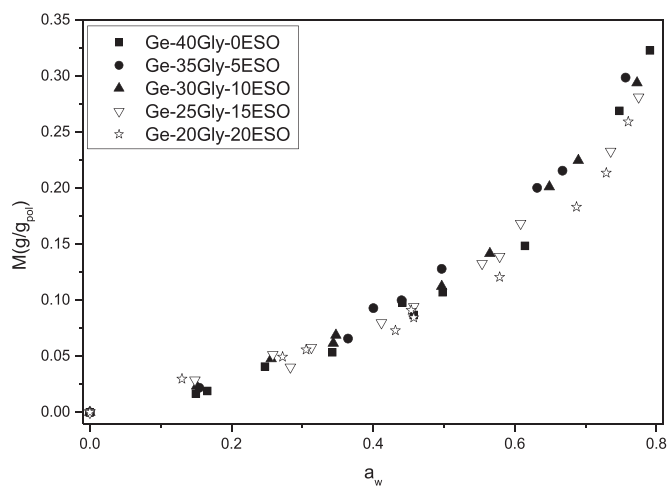


Fig. 1. Water vapor isotherms of Ge-Gly-ESO based films.

### 3.1. Water vapor absorption and diffusion

Gas transport phenomena of gelatin films are crucial in the design as flexible packaging materials where the content is sensitive to environmental conditions. Water vapor absorption isotherms at 30 °C, obtained from equilibrium solubility at different water activity ( $a_w$ ) values, are presented in Fig. 1. These isotherms showed the characteristic behavior of moisture-sensitive polymers [2]. In general, the observed trend given by the gradual increase of water absorbed with the relative humidity was similar in all studied films. Hydrophilic groups, both from gelatin and glycerol, can associate with water molecules through hydrogen bonds, resulting in high water vapor absorption [23,24]. However, the rate of variation was higher for  $a_w > 0.5-0.6$ , in all studied cases. This increment in isotherms slopes was related to the presence of water in the free, non-associated state [24]. Concerning plasticizers content (Gly and ESO concentration), all the films showed a similar behavior, except for Ge-20Gly-20ESO film, for which absorption was slightly lower (Fig. 1). The partial replacement of Gly by ESO in this film formulation could be responsible for the reduction in water absorption, in agreement with Zhang et al. [12] and Belhassen et al. [11] for wheat gluten based materials and thermoplastic starch, respectively.

Experimental values of water vapor absorption were fitted by different mathematical models (Eq. (1)–(5)). All the considered expressions adequately adjusted the sorption curves, obtaining, in general, high  $R^2$  values (Fig. 2, Supporting information). However, Oswin model (Eq. (3)) showed the greatest deviation from the measured values ( $R^2 = 0.98$ ), while the D'Arcy and Watt empirical isotherm (Eq. (5)) allowed the data adjustment only by zeroing the first term ( $K_1$  and  $K_2 = 0$ ). In particular, GAB (Eq. (1)) and modified Oswin (Eq. (4)) models presented the highest  $R^2$  values ( $R^2 = 0.994-0.998$  in both cases), and were considered as the best fitting expressions to describe the water vapor sorption from the obtained Ge-Gly-ESO based films. Parameters obtained with modified Oswin model are presented in Table 1. Similar results were reported by Carvalho et al. [23] for films based on gelatin.

Fig. 3 shows the adjustment of the experimental absorption data by Eq. (6) of a representative curve corresponding to Ge-40Gly-0ESO film. It is clearly observed that samples reached equilibrium more rapidly at high water vapor activities (i.e.  $a_w = 0.70-0.80$ ), as expected. The apparent diffusion coefficient ( $D_{H_2O}$ ) obtained by Fick law was in the order between  $1 \times 10^{-8}$  and  $1 \times 10^{-7} \text{ cm}^2/\text{s}$  (Fig. 4). This coefficient showed an increasing tendency with the relative humidity up to  $a_w = 0.6-0.7$ , where a maximum followed by the opposite trend was observed. The evolution of water diffusion coefficient with  $a_w$  may be related to changes in the mobility of protein chains by the plasticizing effect of water, the saturation of polymer free sites and the formation of

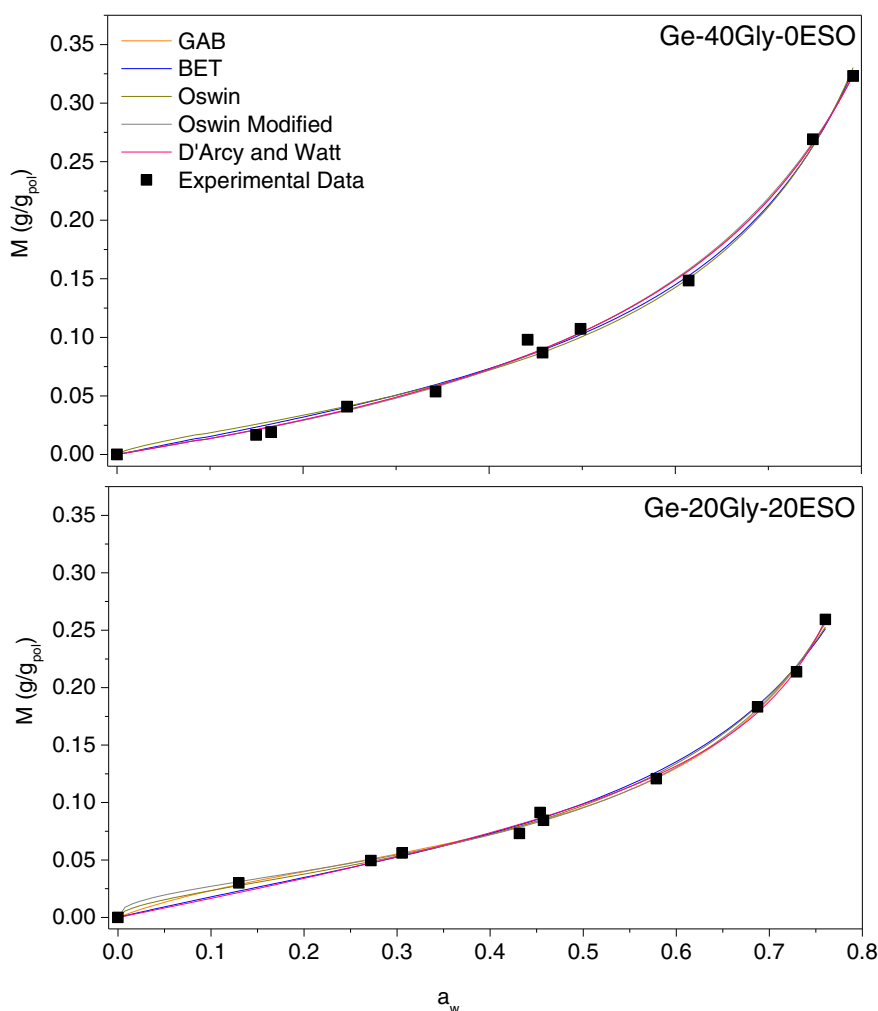


Fig. 2. Experimental and fitted water vapor isotherms of Ge-40Gly-0ESO and Ge-20Gly-20ESO films.

water molecule clusters [2,24]. This observation is consistent with the slope increment of sorption isotherms. In hydrophilic films the formation of clusters can be expected if the number of water molecules is greater than the amount that can be associated with the polymer [2].

Regarding ESO concentration, its incorporation into gelatin films caused a reduction in the diffusion coefficient, which is associated with a greater amount of dispersed hydrophobic phase. Particularly, Ge-20Gly-20ESO film did not show a local maximum in the diffusion coefficient, instead  $D_{H_2O}$  increased in the whole studied range of water vapor activities (Fig. 4).

### 3.2. Water vapor permeation and oxygen permeability

Water vapor permeation showed a marked increasing tendency with water vapor activity (Table 2), being in accordance to the results previously reported for gelatin and other protein based films [2]. All gelatin formulations developed in the present work showed this trend, i.e.

water vapor permeation raised 70 times (from 111 to 7720 g-mil/[m<sup>2</sup>·day]) when relative humidity was increased from 35 to 90% in Ge-40Gly-0ESO films. The decrease in water vapor resistance with RH is associated to the hydrophilic character of gelatin and glycerol [2]. Interestingly, the incorporation of ESO into gelatin films caused a reduction in the water vapor permeation. This can be related to an increased hydrophobic character, as it was discussed before, but probably also to a major presence of disperse oil droplets within the matrix that could hinder the transport of water molecules along the film. The water permeation of the obtained Ge-Gly-ESO films was in the same order of other biobased films, i.e. cassava starch-Gly films (Table 2) [25], but was much higher than the water permeation of synthetic polymers, such as polyethylene terephthalate (PET), polypropylene (PP) or nylon (Table 2), specially at high water activity, limiting the use of Ge based films at high HR.

Oxygen permeability also increased significantly with water activity. Water can be easily incorporated between protein molecules,

**Table 1**  
Parameters of fitted water vapor isotherms with modified Oswin model.

	Ge-40Gly-0ESO	Ge-35Gly-5ESO	Ge-30Gly-10ESO	Ge-25Gly-15ESO	Ge-20Gly-20ESO
R <sup>2</sup>	0.9959	0.9967	0.9979	0.9941	0.9975
K <sub>0</sub>	0.12 ± 0.02	0.24 ± 0.09	0.18 ± 0.03	0.14 ± 0.03	0.06 ± 0.01
M	0.93 ± 0.04	0.74 ± 0.10	0.81 ± 0.05	0.85 ± 0.06	1.04 ± 0.02
N	0.94 ± 0.15	1.20 ± 0.19	1.05 ± 0.11	0.89 ± 0.14	0.40 ± 0.08

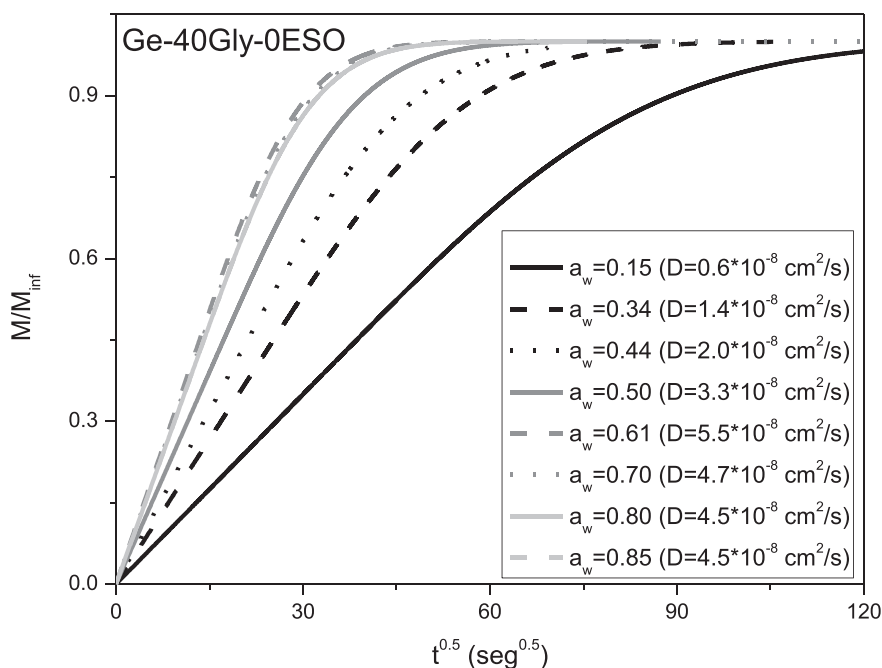


Fig. 3. Water vapor absorption of Ge-40Gly-0ESO film as a function of time.

increasing the matrix free volume and mobility of chains, favoring oxygen transport through the film [26]. On the other hand, oxygen permeability of gelatin formulations did not show a significant difference due to the oil incorporation (Table 2). As other biobased films, Ge based films showed excellent oxygen barrier properties at low and intermediate HR (Table 2) [27–29]. At relative humidity up to 70%, the oxygen permeability of Ge-Gly-ESO films was lower than the corresponding value of many synthetic polymers traditionally used in food packaging (Table 2). These results suggest the potential use of gelatin based films to control the oxygen transfer between food and the environment, at least for products with low water activity.

### 3.3. Heat seal strength

All gelatin based films developed in this work were heat sealable, regardless of the glycerol-ESO proportion. This result reveals a simultaneous interdiffusion and entanglement of gelatin chains from both the melted layers at the interface allows obtaining a joint upon cooling. Despite glycerol has been reported as heat-sealing promoter [30], the partial replacement of Gly by ESO did not modify the heat sealing capability of gelatin films. The visual inspection of the sealed interface after rupture revealed that the seal area remained intact but film tears at the edge of the sealed region, corresponding to the Mode III [15]. This failure mode indicated a good seal strength since there is no

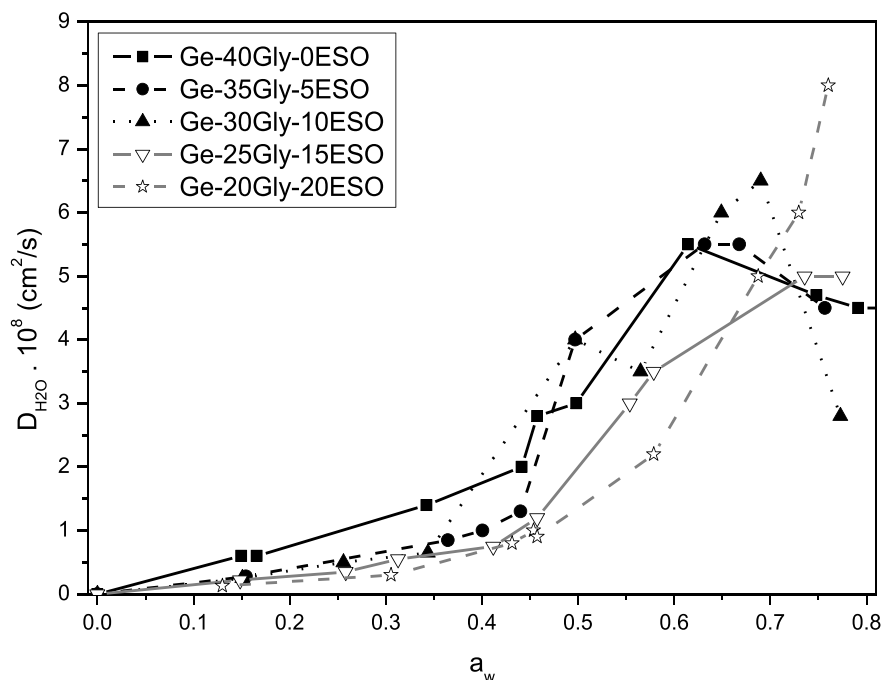


Fig. 4. Apparent diffusion coefficient ( $D_{\text{H}_2\text{O}}$ ) of Ge-Gly-ESO films as a function of water vapor activity.



**Table 2**

Comparison of water vapor permeation (WVP) and oxygen permeability (OP) values between Ge-Gly-ESO films and other films based on biodegradable and synthetic polymers.

	Test conditions		WVP [(g mm/m <sup>2</sup> day)]	Reference	OP [cm <sup>3</sup> μm/(m <sup>2</sup> ·day·kPa)]	Reference
	T [°C]	RH [%]				
Ge-40Gly-0ESO	23	35	111.4 ± 12.8	This work	6.1 ± 1.0	This work
		50	579.5 ± 46.5		20.2 ± 3.2	
		70	3061 ± 19		104.3 ± 7.6	
		90	7719 ± 35		1908 ± 372	
Ge-30Gly-10ESO	23	35	112.3 ± 2.2	This work	5.5 ± 0.6	This work
		50	567.3 ± 16.8		13.8 ± 1.0	
		70	3065 ± 132		136.9 ± 6.3	
		90	8365 ± 27		–	
Ge-20Gly-20ESO	23	35	39.2 ± 21	This work	6.0 ± 0.5	This work
		50	254 ± 18		8.1 ± 0.1	
		70	2009 ± 33		97.1 ± 4.4	
		90	6436 ± 198		3096 ± 442.9	
SPI-50% Gly	25	60	–	–	18.2	[36]
WG-30% Gly	30	0	–	–	17	[37]
Cassava starch-0-30% Gly			849–1577	[25]	23.8–31.0	[25]
Bioplast GF 102 (starch and polycaprolactone)	23	100	69	[38]	–	–
Skygreen (aliphatic polyester)	23	100	108	[38]	–	–
HDPE	20	75	0.1	[39]	390–780	[40]
LDPE	20	75	2.5		970–1400	
Nylon-6	20	75	8.7		7.8–11.6	
PET	20	75	1.8		12–16	
PP	20	75	0.39		580–970	
PS	20	75	–		970–1600	
PVC	20	75	–		19–78	

SPI, soy protein isolate; WG, wheat gluten; HDPE, high density polyethylene; LDPE, low density polyethylene; PET, polyethylene terephthalate; PP, polypropylene; PS, polystyrene; PVC, polyvinyl chloride.

disentanglement in the sealed area, rather film tore from edge under the application of pulling force. The presence of ESO allows conserving the failure mode of glycerol plasticized films.

Table 3 presents the heat seal strength for gelatin films, which is defined as the maximum force per unit specimen width required to separate progressively two films that have been previously heat sealed together (ASTM 2009). Partial replacement of 10% Gly (dry gelatin basis) by ESO in gelatin formulations did not significantly modify the seal strength respect to that containing 40% Gly. However, this mechanical property was significantly increased by the incorporation of 20% ESO. The obtained results can be related to an attenuated plasticization effect of Gly when it is partially replaced by ESO in gelatin formulations. In this sense, films became more rigid according as ESO concentration increased. This behavior was reflected on the increment in heat seal strength, being in accordance with the seal failure mode. Considering that all formulations failed at the seal edge, the stiffness of film formulations determines the strength required to break thermo-sealed samples.

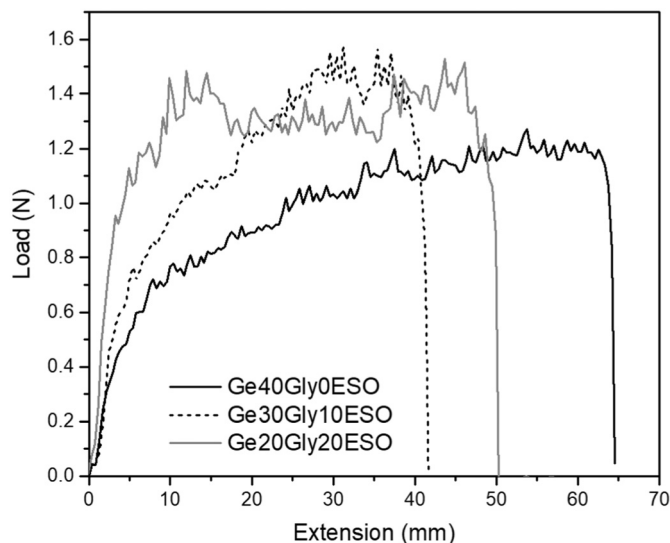
It is important to highlight that seal strength of gelatin films with glycerol-ESO combination (1:1) (Table 1) is higher than those reported for carrageenan films (130–137 N/m) [31], lactic-acid-casein-based films (153–247 N/m) [32], protein isolate/lipid emulsion films (301–323 N/m) [16] and starch films plasticized with sorbitol-glycerol (375 N/m) [17]. Even more, seal strength corresponding to gelatin based films was in the order of heat sealed synthetic polymers (730 N/

**Table 3**

Heat seal strength and tearing force of Ge-Gly-ESO films.

	Heat seal strength (N/m)	Tearing force (N)
Ge-40Gly-0ESO	264.8 ± 55.4 <sup>a</sup>	1.17 ± 0.08 <sup>a</sup>
Ge-30Gly-10ESO	358.3 ± 43.0 <sup>b</sup>	1.50 ± 0.10 <sup>b</sup>
Ge-20Gly-20ESO	685.0 ± 185.0 <sup>b</sup>	1.66 ± 0.24 <sup>b</sup>

Mean values ± standard deviations. Mean values within the same column followed by the same letter are not significantly different ( $p > .05$ , Tukey test).

**Fig. 5.** Tear curves of Ge-Gly-ESO films.

m) [33].

### 3.4. Tear curves

The knowledge of film tear behavior is relevant for an appropriate material design approach. Fig. 5 shows representative load-extension curves for gelatin films with different Gly-ESO combinations, but having the same total plasticizer content (40%, dry gelatin basis). All curves show a rapidly increase of force values, which correspond to the initial damage zone ahead of the propagating tear [34]. The incorporation of 40% Gly as unique plasticizer led to films with an extensible behavior, characterized by an increasing tendency in load-extension curve with a maximum value just prior to the catastrophic failure. Even though Rivero et al. [35] reported that gelatin films

containing glycerol lower than 40% p/p are considered as low-extensible materials, the addition of 10% ESO in presence of 30% Gly allowed conserving the extensible behavior. However, tear pattern of 20Gly-20ESO combination revealed a low extensible behavior, characterized by a constant load once the crack has initiated. The initial force increment corresponds to the load required to start the tear, then a constant force is needed to propagate it and the lineal load decrease indicates the final retraction of the specimen as the force is removed. From these results, it can be concluded that tear-propagation pattern of gelatin films depends on glycerol-ESO combination. Moreover, the load required for tear propagation significantly increased with ESO concentration (Table 3). This behavior could be attributed to the stiffness increment of gelatin based films because of partial replacement of Gly by ESO, as it can be discussed previously for heat seal strength results.

#### 4. Conclusions

The water vapor sorption isotherms of gelatin based films showed the characteristic behavior of moisture sensitive polymers, reaching a water absorption of about 0.25 g/g<sub>Ge</sub> for  $a_w = 0.75$ . Although all the studied mathematical models adequately fitted the experimental data, the GAB and modified Oswin expressions were the most appropriate to describe the sorption properties of gelatin films. Apparent diffusion coefficients were in the order between  $1 \times 10^{-8}$  and  $1 \times 10^{-7}$  cm<sup>2</sup>/s. In general,  $D_{H_2O}$  increased with  $a_w$ , until approximately an activity of 0.6–0.7, value from which the opposite tendency was observed. This behavior was associated to the plasticizing effect and the clusters formation of water molecules at high relative humidity. The incorporation of ESO in gelatin films caused a reduction in the water vapor apparent diffusion coefficient, attributed to a greater amount of dispersed hydrophobic phase. In particular, the presence of 20% ESO in Ge-20Gly-20ESO film slightly reduced the moisture absorption and diffusion.

Partial replacement of Gly by ESO in gelatin films significantly reduced the permeation to water vapor without significantly altering the oxygen permeability. The obtained results, both solubility and oxygen permeability, will be used to establish the structure-property relationship of gelatin films with different formulations and will help to a better understanding and improvement of these materials.

The incorporation of ESO did not affect the heat sealing ability of films plasticized with Gly, and good quality seals could be obtained. The heat seal strength increased significantly with the presence of 20% ESO, without modifying the film seal failure mode. On the other hand, although the partial replacement of Gly by 20% ESO conferred a non-extensible character to the films, the maximum tearing force increased significantly. It is possible to conclude the formulation Ge-20Gly-20ESO allowed to develop films with an appropriate balance between properties of gas barrier as well as the resistance of the heat sealing and the tearing.

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