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Effects of spelt and wheat bran on the performances of wheat gluten films

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Abstract

The individual and interactive effects of the spelt and wheat bran as well as glycerol, on the properties of wheat gluten based edible films were investigated in this work using response surface methodology. Tests were run to determine water vapour permeability (WVP), mechanical and dynamical properties and colour of the films as well as the rheological properties of the film forming solutions. Results highlight that the glycerol presence had a negative effect on water vapor permeability values of the films (increase of WVP), whereas the bran presence had a positive influence (decrease of WVP). The Elastic modulus (E_c) of the composite films increased with the increase of bran concentration and with the decrease of glycerol. The tenacity increased with the increase of glycerol and spelt bran up to a threshold value after which a decrease was observed. The complex modulus (E^*) of the composite films increased with the decrease of the glycerol concentration and with the increase of the wheat bran. All film forming solutions presented pseudoplastic behaviour; moreover, the apparent viscosity increased with the increase of bran concentration due to the fact that a greater number of water molecules are immobilized. The complex viscosity (η^*) was affected by a positive interaction between spelt bran and wheat bran. Results also showed that Yellow Index (YI) and *b* parameter of Hunter scale increased with the bran concentration, whereas the *L* values decreased. The glycerol increase determined a decrease in the YI and *b* value and an increase in *L* value.

Keywords: Edible films; Wheat gluten; Spelt bran; Wheat bran; Response surface methodology

1. Introduction

Production and utilization of edible, biodegradabile films and coatings prepared from various biological polymers such as polysaccharides, proteins, lipids or combinations of those components have received great interest in recent years. Edible films and coatings have been particularly considered in food preservation and technology, because of their capability of improving global quality and safety (Franssen and Krochta, 2003). The films can be used to cover food surfaces, separate incompatible zones and ingredients, or perform as pouches or wraps; forming an actual barrier against oxygen, aroma, oil or moisture. Others important features are: carrying of functional substances such as antioxidants or antimicrobials, and improving appearance and handling. Edible films elaboration

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from natural and abundant biodegradable polymers as cellulose, gums, starches or proteins, is also convenient concerning its lower environmental consequences in comparison with common synthetic packaging materials (Cutter, 2006).

Wheat gluten is a biodegradable and crop renewable agropolymer with interesting film-forming properties for the production of biopackaging materials. Wheat gluten is unique among cereal and other plant proteins in its ability to form a cohesive blend with viscoelastic properties once plasticized. In general, gluten-based materials require addition of plasticizer agents. Glycerol is one the most popular plasticizer used in filmmaking techniques due its stability and compatibility with hydrophilic biopolymeric chain (Pommet et al., 2005).

Similar to other protein films, wheat gluten films are excellent oxygen and carbon dioxide barriers at low relative humidities with selective permeability to gases (Mujica-Paz and Gontard, 1998). Moreover, Pochat-Bohatier et al. (2006) have shown that the wheat gluten films permselectivity was based on the rise of carbon dioxide solubility and diffusivity with the increase in relative humidity. The poor water vapour resistance of protein films and their lower mechanical strength in comparison with synthetic polymers limit their application in food packaging. Several studies have been carried out in an attempt to improve the performance of protein films. One extensively used method to enhance the water vapour barrier of films has been the incorporation of hydrophobic compounds such as lipids into the film-forming solution. McHugh (2000) and Morillon et al. (2002) have thoroughly reviewed the aspects concerning these methods. Other way to improve protein film functionality is to modify the polymer network through cross-linking of the polymer chains. The presence of reactive functional groups in the amino acid side chain of protein makes this cross-linking process possible through chemical, enzymatic or physical treatments.

An interesting alternative to improve the properties of biodegradable films is to add stiffening material in the film-forming solution. The so-called 'biocomposites' (biodegradabile composites) consist of biodegradable polymers as the matrix material and biodegradabile fillers, usually biofibres (e.g. lignocellulose fibres). Some authors (Wollerdorfer and Bader, 1998) have tested complex associations such as cellulose fibres with both, biopolyester and plasticized starch; most of studies are merely based on the biopolyester matrix (Netravali and Chabba, 2003). Polyhydroxyalkanoate (PHA) has been combined with cellulose fibres (Wollerdorfer and Bader, 1998), jute fibres (Wollerdorfer and Bader, 1998; Mohanty et al., 2000a), abaca fibres (Shibata et al., 2002) or lignocellulosic flour (Dufresne et al., 2003). Polylactic acid (PLA) has been associated to paper waste fibres, kenaf (Nishino et al., 2003), jute (Plackett et al., 2003) or flax fibres (Oksman et al., 2003). Another important biocomposites category is based on agro-polymers matrixes, mainly focussed on starchy materials. Various types of fibres, microfibrils or whiskers have been tested such as microfibrils from potato pulp (Dufresne et al., 2000), bleached leafwood fibres (Avérous et al., 2001), fibres from bleached eucalyptus pulp (Curvelo et al., 2001), flax and ramie fibres (Wollerdorfer and Bader, 1998) and wood pulp (De Carvalho et al., 2002). They have found high improvements of the performances (e.g. tensile and impact tests results), which are in part linked to an usual matrix reinforcement (Bledzki and Gassan, 1999). Another part of the mechanical properties increase is brought by the interrelations fibre–matrix. The main attributes are higher moduli (Dufresne et al., 2000; Avérous et al., 2001; Curvelo et al., 2001), reduced water sensitivity due to fibre–matrix interactions and to the higher hydrophobic character of the cellulose, which is linked to its high cristallinity (Avérous et al., 2001; Curvelo et al., 2001). Fibres addition induces variation of properties, due to the formation of a 3D network between the different carbohydrates, through hydrogen bonds.

The main objective of this study was to investigate the possibility of incorporation of spelt bran and wheat bran into the wheat gluten matrix to improve the water vapour barrier of the films; the influence of the bran addition on the mechanical and dynamic-mechanical properties of the films and on the rheological properties of the film-forming solutions was also determined. An experimental design and a response surface methodology analysis were used in order to point out the individual and interactive effects of the selected variables.

2. Material and methods

2.1. Preparation of edible films forming solutions

Wheat gluten (10 g) (Sigma–Aldrich, Milan, Italy) was solubilised in distilled water–glycerol solution. The solution was stirred continuously using a magnetic stirrer hotplate until powders were completely dissolved. Then the wheat and spelt bran (Molino Bongiovanni, Mondovì, Cuneo, Italy) was added to the wheat gluten–water–glycerol solution and stirred again. The amount of glycerol (J.T. Baker, Milan, Italy), wheat bran and spelt bran (granulometry <200 μm), which were expressed as percentage on solution weight, varied according to three variables-five levels central composite design (CCD). The coded and real values of the independent variables of the experimental design are reported in Table 1. Each solution was adjusted to pH 11 using 1 M NaOH and then was heated at 70 °C for 15 min on hotplate. Finally, vacuum was applied to remove air from the system.

2.2. Edible film preparation

Edible films were obtained by casting technique: 8 ml of film forming solution were dispensed on the surface of Petri dishes (diameter 15 cm) and dried at room temperature for 24 h. Films were peeled from the plates and conditioned for 72 h at room temperature inside desiccators containing

Table 1
Composition of the 17 runs of the central composite design, colour parameters (L, a, b and YI) and independent variables of the wheat gluten-based edible films

Coded values				Real values			Hunter Scale				Independent variables				
Run	X1	X2	X3	Glycerol (%)	Spelt bran (%)	Wheat bran (%)	L	a	b	YI	E_c (MPa)	Tensile strength (MPa)	Elongation at break (%)	E^* (MPa)	WVP (g/m s Pa)
1	−1	−1	−1	3	2.15	2.15	82.42	−0.210	23.09	50.17	32.39	2.128	2.128	384.14	2.062E−11
2	−1	−1	+1	3	2.15	5.25	72.52	3.150	27.20	70.43	86.38	3.139	3.139	767.20	5.645E−12
3	−1	+1	−1	3	5.25	2.15	76.73	1.542	25.86	61.96	99.43	3.115	3.115	639.65	4.056E−12
4	−1	+1	+1	3	5.25	5.25	71.48	3.305	27.00	71.12	137.52	4.930	4.930	1051.40	3.079E−12
5	+1	−1	−1	5	2.15	2.15	84.07	−0.665	21.32	45.07	2.74	0.679	0.679	42.25	1.312E−-1
6	+1	−1	+1	5	2.15	5.25	73.80	2.865	27.93	70.76	5.35	1.012	1.012	123.84	1.914E−11
7	+1	+1	−1	5	5.25	2.15	83.49	0.027	21.50	46.30	6.82	1.131	1.131	148.52	1.332E−11
8	+1	+1	−1	5	5.25	5.25	71.36	3.602	27.54	72.90	12.68	1.547	1.547	300.27	1.973E−12
9	0	0	−2	4	3.7	0.6	82.54	0.150	22.55	49.38	15.17	1.637	1.637	244.72	1.125E−11
10	0	0	+2	4	3.7	6.8	69.89	3.947	27.26	74.10	44.85	2.739	2.739	612.33	6.237E−12
11	0	−2	0	4	0.6	3.7	79.55	0.577	25.17	57.39	6.72	1.089	1.089	177.80	1.964E−11
12	0	+2	0	4	6.8	3.7	76.10	1.880	25.49	61.91	39.55	2.969	2.969	661.48	5.734E−12
13	−2	0	0	2	3.7	3.7	73.99	2.252	26.07	65.49	405.99	5.312	5.312	1662.16	4.747E−12
14	+2	0	0	6	3.7	3.7	77.19	1.772	25.43	61.29	2.82	0.718	0.718	51.09	4.263E−11
15	0	0	0	4	3.7	3.7	75.91	2.227	25.96	63.66	47.69	2.512	2.512	529.52	7.214E−12
16	0	0	0	4	3.7	3.7	75.72	1.822	26.48	64.52	25.22	2.524	2.524	409.94	9.109E−12
17	0	0	0	4	3.7	3.7	75.33	1.757	25.89	63.42	6.50	1.142	1.142	75.36	1.115E−11

saturated saline solutions of NaBr which provided relative humidity of 57.5–57.7%, prior to testing.

2.3. Water vapour permeability

Water permeability was determined by means of Permatran (Mocon, Model W 3/31, Neuwied, Germany). Samples with a surface area of 5 cm^2 were tested at 25 °C. The permeation tests were conducted by keeping the water activity on the downstream side of the film equal to 0, and keeping the water activity at the upstream side of the film at the constant value of 0.5. A flow rate of 100 ml/min of a nitrogen was used.

2.4. Mechanical and dynamic-mechanical analyses

The mechanical and viscoelastic properties of the films were determined using a stress-controlled Dynamic Mechanical Analyzer (DMA-Q 800, TA Instruments, New Castle, DE, USA) equipped with a tension clamp. Mechanical tests under static, transient and dynamic conditions were performed, i.e. uniaxial tension, stress relaxation and oscillatory stress, respectively.

The film samples used for the mechanical and dynamical-mechanical test had a length of 20 mm, width of 5.6 mm and thickness varying between 0.08 and 0.10 mm. For each test five repetitions were carried out.

2.5. Uniaxial tension tests

In order to determine the elastic modulus, the tensile strength and deformation at break of samples, the stress–strain curves were acquired and analyzed. Tests were carried out according to the following conditions: preload force of 10^{-2} N, force ramp rate of 1 N min^{-1}.

The elastic modulus was evaluated from the initial slope of the stress–strain curve using the following exponential equation (Del Nobile et al., 2007):

$$\sigma_T = E_C \cdot \varepsilon_T \cdot \exp(-\varepsilon_T \cdot K) \quad (1)$$

where ε_T and σ_T are the true strain and the true stress, respectively, calculated according to Mancini et al. (1999); E_C is the elastic modulus or Young's modulus; K is a constant value, regarded as a fitting parameter. Eq. (1) was used to reduce the error that affect the estimation of E_c from a stress–strain curve. E_c is generally calculated as the slope of the straight line that best fit the experimental data. However, in the case of a polymeric film the stress–strain curve usually shows a downward concavity due to the necking effect. Therefore, it is necessary to select only the first part of the data, the one having a trend close to a straight line, to calculate the value of E_c. The above choice could introduce a not negligible error in the E_c determination. Using Eq. (1) the above problem is overcome and equation can be directly fitted to the data. Moreover, the tensile strength and elongation at break were expressed as MPa and percentage, respectively (Ninnemann, 1968). In order to determine the tenacity of the selected films, the area under the stress–strain curve was calculated by an integration procedure.

2.6. Dynamic low-amplitude oscillatory tests

Frequency sweep tests in tension were performed applying an oscillatory stress using DMA-Q 800, in order to determine the viscoelastic properties of tested edible films. Some fundamental dynamic-mechanical properties, such as storage modulus (E') and loss modulus (E'') were determined in order to calculate complex modulus (E^*). Instrumental settings were as follows: preload force 10^{-2} N and frequency range 0.02–200 Hz. The strain value was obtained from preliminary strain sweep (0.2–0.5%) oscillatory trials to determine the linear viscoelastic region. In order to compare the E^* values, among the investigated films, an oscillatory frequency of 40 Hz was chosen as reference since starting from this value E^* does not depend at a great extent on the frequency.

2.7. Stress relaxation tests

Mechanical transient tests were performed to evaluate the spectrum of the relaxation times from relaxation curves. The relaxation data were obtained using DMA-Q 800 by setting the following experimental conditions: preload force 10^{-2} N, quasi-instantaneous strain (0.5–1%), displace time of 5 min. The relaxation modulus was calculated as the time-dependent stress divided by the imposed strain. The relaxation behaviour of the investigated films was described using the Maxwell's Generalized Model, according to Bruckner et al. (2001):

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} = E_0 + \int_0^\infty E(\lambda) \cdot \exp\left(-\frac{t}{\lambda}\right) \cdot d\lambda \tag{2}$$

where $E(t)$ is the relaxation modulus expressed in MPa, i.e. the elastic modulus at the decay time t; $\sigma(t)$ is the stress at time t, expressed in MPa; ε_0 is the imposed strain; $E(\lambda)$ [MPa] is the continuos distribution function (spectrum) of relaxation time (the number of Maxwell elements approaches to infinity); λ is the relaxation time in sec; E_0 is the modulus of the single spring in parallel to Maxwell elements. The relaxation spectrum is a fundamental quality in the linear theory of viscoelastic materials (Honerkamp and Wesse, 1993) that does not depend on the experimental conditions but only on the physical nature of the specimen. To describe the continuous distribution function of relaxation time a modified version of the expression proposed by Del Nobile et al. (2007,), to represent the dynamic-mechanical behavior of several viscoelastic foods, was used:

$$E(\lambda) = G_1 \cdot \left\{ \frac{1}{\delta_1 \cdot (2 \cdot \pi)^{0.5}} \exp\left[-\frac{1}{2}\left(\frac{\lambda}{\delta_1}\right)^2 \right] \right\} \tag{3}$$

Eq. (3) is the normal distribution function with the mean value equal to zero and the standard deviation equal to δ_1, multiplied by a constant value (G_1). The parameters appearing in Eq. (3) account for the height (G_1) and width (δ_1) of the relaxation time distribution curve. By substituting Eq. (3) in Eq. (2) the following expression is obtained:

$$E(t) = E_0 + \int_0^\infty G_1 \cdot \left\{ \frac{1}{\delta_1 \cdot (2 \cdot \pi)^{0.5}} \exp\left[-\frac{1}{2}\left(\frac{\lambda}{\delta_1}\right)^2 \right] \right\} \cdot \exp\left(-\frac{t}{\lambda}\right) d\lambda \tag{4}$$

2.8. Rheological measurements

The rheological behavior of each film forming solution was investigated using a controlled-strain rotational rheometer (ARES model, TA Instruments, New Castle, DE, USA) equipped with a force rebalance transducer (model 1K-FRTN1, 1–1000 g cm, 200 rad/sec, 2–2000 gmf) and a couette tool with concentric cylinder geometry (diameter of cup and bob, 34 mm and 32 mm, respectively). A steady temperature was ensured with an accuracy of ±0.1 °C by means of a controlled fluid bath unit and an external thermostatic bath. Two repetitions for the flow experiment were performed for each sample. Steady shear stress over a range of shear rates of 0–1000 s^{-1} was measured. Flow experiments were carried out at 25 °C. In order to prevent water evaporation, a suitable cover tool sealing the top of the couette tool was used during test. The rheological behaviour is studied using the following power law model which satisfactory fitted the experimental data

$$\tau = K \cdot \dot{\gamma}^n \tag{5}$$

where τ is the shear stress [Pa], K is the consistency index [Pa ^{n}], the $\dot{\gamma}$ is the shear rate and n is flow index (dimensionless). The apparent viscosities were calculated at 37, 74, 150, 300, 600 and 1000 s^{-1} shear rate using the following power law model (Bertuzzi et al., 2007):

$$\eta = K \cdot \dot{\gamma}^{n-1} \tag{6}$$

Dynamic strain sweep tests were performed at a frequency of 1 s^{-1} to determine the linear viscoelastic region. Dynamic frequency sweep tests at interval frequency of 0.01–30 Hz and strain amplitude of 0.6% and 1.0% were performed to determine the complex viscosity (η^*), expressed as Pa s. In order to compare the η^* values, among the investigated film forming solutions, an oscillatory frequency of 1 Hz was chosen as reference.

Rheological transient tests were performed to evaluate the spectrum of the relaxation times from relaxation curves. The relaxation data were obtained by setting the following experimental conditions: quasi-instantaneous strain (10%), displace time of 3 min. The relaxation modulus was calculated as the time-dependent stress divided by the imposed strain. The relaxation behaviour of the investigated film forming solutions was described using in Eq. (4).

2.9. Colour evaluation

Films disks of appropriate diameter were rested on white background standard (Trezza and Krochta, 2000). Measurements were performed using a Minolta CR-400 colorimeter (Tokyo, Japan). The exposed area was sufficiently great relative to the illuminated area to avoid any light trapping effect. The Hunter parameters L, a and b, and the yellow index (YI) were measured according to a standard test method (ASTM D1925, 1995), in at least three positions randomly selected for each sample. Colour parameters range from $L = 0$ (black) to $L = 100$ (white),

$-a$ (greenness) to $+a$ (redness), and $-b$ (blueness) to $+b$ (yellowness). Standard values considered were those of the white background. Measurements were made for C illuminant and 2° observer.

2.10. Statistical analysis

The influence of the glycerol, wheat bran and spelt bran on the gluten-based film properties was studied by modulating the three selected variables according to a three factor, five level CCD, as reported in Table 1. The real values of the independent variables were used in this work. The lowest and highest levels of independent variables studied were chosen from results of preliminary laboratory tests.

A statistical software (Statistica for Windows, StatSoft, Tulsa, OK, USA) was used to fit a second-degree polynomial function (Eq. 7) to the independent variables using the following equation:

$$\psi = B_0 + \sum_{i=1}^{3}(B_i \cdot x_i) + \sum_{i=1}^{3}(B_{ii} \cdot x_i^2) + \sum_{i=1}^{3}\sum_{\substack{j=1\\ j\neq 1}}^{3}(B_{ij} \cdot x_i \cdot x_j) \tag{7}$$

where ψ is the generic dependent variable examined in this work; B_0 is the value of fitted response at the centre point of the design, i.e. (0,0,0); B_i, B_j and B_{ij} are the linear, quadratic and cross-product regression terms, respectively; x_i and x_j are the independent variables (glycerol, wheat bran and spelt bran) accounted in this work. Eq. (7) permitted evaluation of the effects of linear, quadratic and interactive terms of the independent variables on the selected dependent variables. Contour plots were generated by fixing investigated variables at the center value of CCD. Moreover, the interactions among the rheological properties of the film forming solutions and the mechanical and dynamical–mechanical properties of produced films were evaluated using the principal component analysis (PCA).

3. Results and discussion

3.1. Film properties

3.1.1. Water vapor permeability

The best equation that describes the relationship between water vapor permeability and the independent variables (glycerol, spelt bran and wheat bran) is shown in Table 2. The glycerol, spelt bran and wheat bran concentrations were denoted by XG, XSB and XWB, respectively. It can be see that the WVP values are affected by a positive quadratic effect of the glycerol and by a negative interaction glycerol–spelt bran. Fig. 1 shows the contour plot of the interaction glycerol–spelt bran on the water vapor permeability. The plot reveals that permeability values were strongly influenced by glycerol presence, being higher as

Table 2
Best fit equations of the individual, quadratic and interactive effects of glycerol, spelt bran and wheat bran on the properties of the edible films and the maximum and the minimum independent variables value

	Best fit equations	Max	Min	F[a]	SE	R^2
Ec (MPa)	−134.498 * XG + 110.647 * XSB + 101.750 * XWB + 31.045 * XG^2 − 25.176 * XG * XSB − 23.308 * XG * XWB	XG = 2.0 XSB = 6.8 XWB = 6.8	XG = 6.0 XSB = 6.8 XWB = 6.8	9.63	55.14	0.84
Tenacity	0.733405 * XG − 0.353339 * XSB − 0.127585 * XG^2 + 0.073966*XG * XSB	XG = 3.05 XSB = 0.6	XG = 6.0 XSB = 0.6	28.91	0.22	0.89
Tensile strength (MPa)	0.3371 * XSB + 1.4469 * XWB − 0.295 * XG * XWB	XG = 2.0 XSB = 6.8 XWB = 6.8	XG = 6.0 XSB = 0.6 XWB = 6.8	139.24	0.51	0.96
Elongation at break (%)	42.8279 * XG − 9.8694 * XSB − 10.5764 * XWB − 2.3370 * XG^2	XG = 6.0 XSB = 0.6 XWB = 0.6	XG = 2.0 XSB = 6.8 XWB = 6.8	136.91	11.38	0.97
E^* (MPa)	−362.664 * XG + 349.990 * XSB + 447.142 * XWB + 78.912 * XG^2 − 67.979 * XG * XSB − 92.533 * XG * XWB	XG = 2.0 XSB = 6.8 XWB = 6.8	XG = 6.0 XSB = 6.8 XWB = 6.8	32.98	176.43	0.94
G_1 (MPa)	−147.733 * XG + 112.504 * XSB + 110.790 * XWB + 33.444 * XG^2 − 24.930 * XG * XSB − 25.322 * XG * XWB	XG = 2.0 XSB = 6.8 XWB = 6.8	XG = 6.0 XSB = 6.8 XWB = 6.8	7.08	66.71	0.79
δ_1 (MPa)	6.57087 * XWB + 1.62526 * XG * XSB − 1.54363 * XSB * XWB	XG = 6.0 XSB = 6.8 XWB = 0.6	XG = 2.0 XSB = 0.6 XWB = 0.6	54.84	9.02	0.92
E_0 (MPa)	71.1495 * XWB − 15.3457 * XG * XWB	XG = 2.0 XWB = 6.8	XG = 6.0 XWB = 6.8	6.63	78.59	0.68
WVP (g/m s Pa)	0.00000000000115658 * XG^2 − 0.00000000000056751 * XG*XSBg	XG = 6.0 XSB = 0.6	XG = 2.0 XSB = 6.8	34.18	7E−8	0.82

[a] F, Fisher test value; SE, standard error; R^2, regression coefficient.

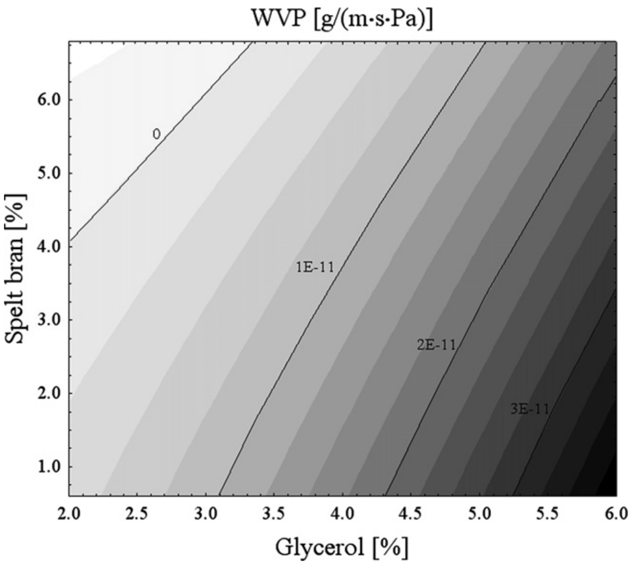

Fig. 1. Effect of the interaction XG–XSB on the WVP [g/(m s Pa)].

plasticizer concentration increase, whereas spelt bran affected negatively the permeability. The positive effect of the glycerol on water vapor permeability values of the films is in agreement with previous results of other authors. Park and Chinnan (1995) attributed the permeability increment to plasticizing effect of glycerol, which reduce polymer packaging density. The negative effect of the bran on water vapor permeability values is probably due to the fact that bran posses a lower water permeability. Therefore, an increase in its concentration brings about a decrease in the water permeability value of the composite film. As expected, the minimum value of the permeability was observed at the lowest concentration of the glycerol (2.0%) and at the highest concentration of the spelt bran (6.8%) (Table 2).

3.2. Mechanical properties: small deformations

Fig. 2 shows the stress–strain curves relative to three combinations (run 1, 3, 15) of the experimental design. The curves shown in the above figure is the best fit of Eq. (1) to the experimental data. As can be inferred from the data shown in the above figure Eq. (1) satisfactorily describe the stress–strain data. Therefore, it can be advantageously used to determine the film elastic modulus. The best-fit equation describing the effects of the glycerol, wheat bran and spelt bran on E_c values is reported in Table 2; in the same table, the maximum and the minimum values of the independent variables and the summary of the multiple regression analysis is also reported. As can be inferred from the data, E_c values is affected by the individual positive terms of glycerol, wheat bran and spelt bran, by the positive quadratic effect of glycerol and by a negative interaction glycerol-spelt bran, glycerol–wheat bran. The maximum value of E_c was observed at 2.0% of glycerol and 6.8% of wheat bran and spelt bran, whereas the minimum value was observed at 6.0% of glycerol and at the same percentage of bran (6.8%). In order to better understand the individual and interactive effects of glycerol, wheat bran and spelt bran on the mechanical parameters, the surface response plots were analyzed. Fig. 3 shows the contour plot of the interaction glycerol–spelt bran on the E_c values. It can be observe that the higher concentrations of spelt bran and the lower concentrations of glycerol corresponded to higher E_c values of the composite films. As reported in literature, the plasticizers are intended to decrease the intermolecular forces along polymer chains, imparting increased film flexibility while decreasing the barrier properties of films (Caner et al., 1998). Moreover, the bran acts as stiffing agent when the adhesion between fibre and polymeric matrix is good leading to higher modules.

3.3. Mechanical properties: large deformations

Table 2 reports the best-fit equations of the individual and interactive effects of the independent variables on tenacity values (i.e., the area under the stress–strain curve),

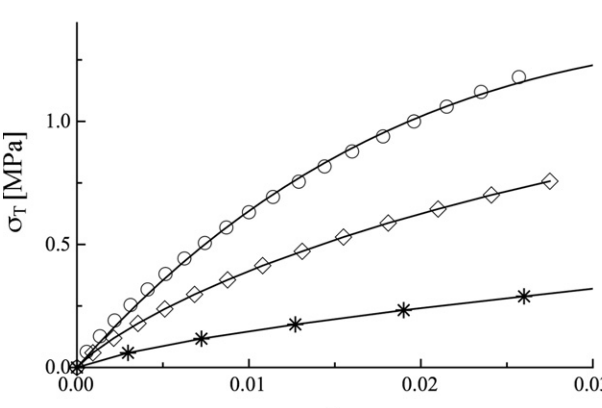

Fig. 2. Tensile true stress plotted as a function of tensile true strain in a tension stress strain test. (∗) run 1, (○) run 3, (◇) run 15.

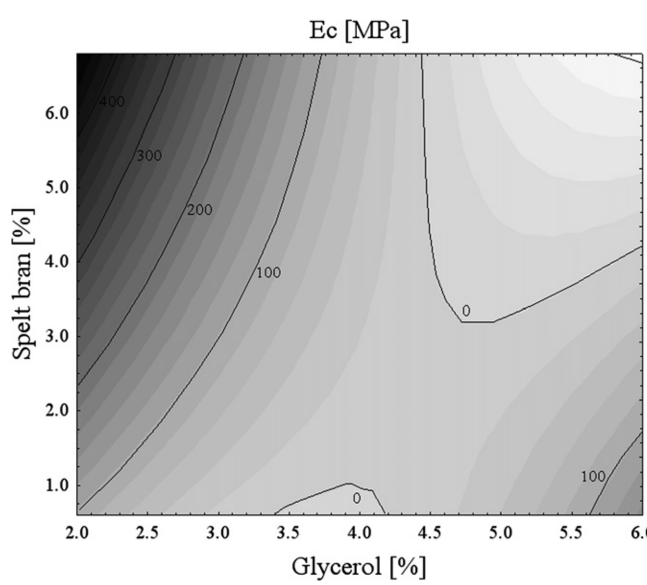

Fig. 3. Effect of the interaction XG–XSB on the E_c [MPa].

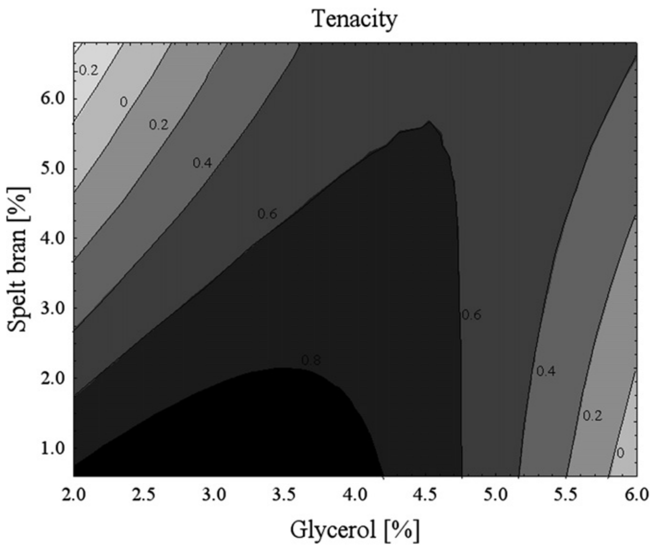

Fig. 4. Effect of the interaction XG–XSB on the Tenacity.

tensile strength and elongation at break. The tenacity was influenced by an individual positive term of the glycerol and negative of spelt bran and by the negative quadratic effect of the glycerol. Moreover, a positive interaction glycerol-spelt bran was observed. As can be observed from Fig. 4, the tenacity values increased with the increase of glycerol and spelt bran up to a threshold value after which a decrease was observed. The maximum value of tenacity corresponded at 3.05% and 0.6% of glycerol and spelt bran, respectively, whereas the minimum value was observed at 6.0% of glycerol and 0.6% of spelt bran (Table 2). Regarding to the tensile strength, it was affected by the individual positive term of the spelt bran and wheat bran, and by the negative interaction glycerol–wheat bran. The maximum value of tensile strength was observed at the lowest glycerol value (2.0%) and the highest spelt bran and wheat bran value (6.8%); the minimum value was observed at 6.0% of glycerol and at the lowest and highest value of spelt bran and wheat bran, respectively. The elongation at break values were influenced by the individual positive term of the glycerol and by the individual negative term of the spelt bran and wheat bran; moreover, they were affected by the negative quadratic effect of the glycerol. The maximum value of elongation at break was observed at the highest glycerol value and at the lowest value of the spelt bran and wheat bran; the minimum value of the above variable was obtained at the lowest glycerol value and at the highest value of spelt bran and wheat bran. Concerning glycerol, the classical effect of a plasticizing molecule was noticed, i.e. an increase of the elongation at break and a decrease of the tensile strength when the glycerol content increased (Mangavel et al., 2002). Concerning the bran, the influence of spelt bran or wheat bran on the dependent variables values is probably due to the fact that the quality of the interface fillers-matrix could not be equal for two types of bran; the spelt bran seems to bring higher adhesion with the matrix compared to the wheat bran.

3.4. Dynamic-mechanical properties

Table 2 reports the best-fit equations of the effects of glycerol, spelt bran and wheat bran on the E^* values, along to the multiple regression analysis. The E^* values were negatively affected by the individual term of the glycerol and positively by the individual term of the spelt bran and wheat bran; moreover, a positive quadratic effect of the glycerol and a negative interaction glycerol–spelt bran and glycerol–wheat bran was recorded. The above data are reported in Fig. 5 to better illustrate the dependences between the selected variables. As can be inferred from the above figure, E^* values increased with the decrease of the glycerol concentration and with the increase of the wheat bran. In the same table, it can be see the maximum value of the E^* at 2.0% of glycerol and at 6.8% of spelt bran and wheat bran; the minimum value was observed at 6.0% of glycerol and at 6.8% of spelt bran and wheat bran. As already said, the presence of glycerol decreased the protein–protein interactions increasing the mobility of polymeric chains allowing the films less resistant (do A. Sobral et al., 2005).

3.5. Stress relaxation

As reported above, the viscoelastic properties of polymeric materials can be expressed by different fitting parameters (G_1, δ_1 and E_0). Fig. 6 shows the stress relaxation tests relative to three combinations (run 1, 6, 8) of the experimental design. As expected there is first a sharp decrease in the stress after which the stress level off to constant value. This behaviour was in accord with that found by Mancini et al. (1999), who pointed out an asymptotically decaying trend for the alginate gels tested. The curves shown in the above figure was obtained by fitting Eq. (4) to the experimental data. As can be see from figure the

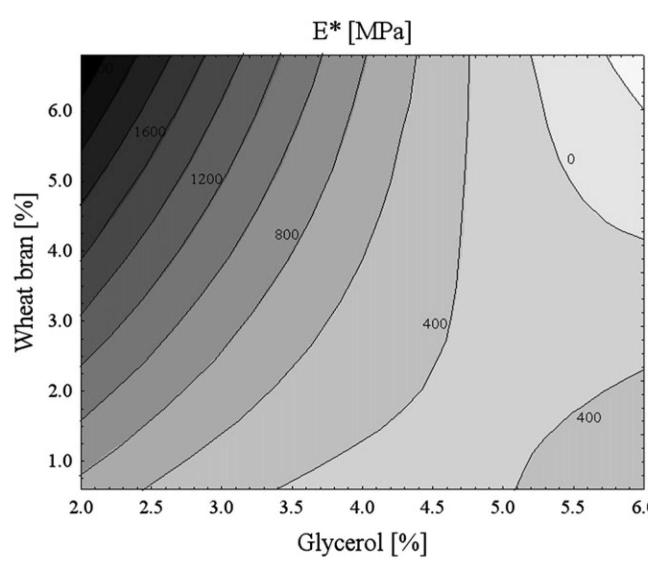

Fig. 5. Effect of the interaction XG–XWB on the E^* [MPa].

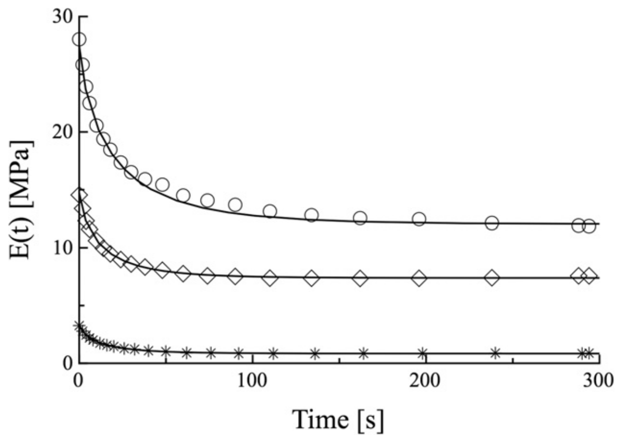

Fig. 6. $E(t)$ plotted as a function of decay time in a stress relaxation test. (○) run 1, (∗) run 6, (◇) run 8.

monomodal Generalized Maxwell model excellently fits the experimental data. The best-fit equations describing effects of glycerol, spelt bran and wheat bran on G_1 values, δ_1 and constant E_0 are reported in Table 2, along to the multiple regression analysis. The values of the parameter G_1 were negatively affected by the individual term of the glycerol and positively by the individual term of the spelt bran and wheat bran; moreover, they were influenced by a positive quadratic effect of the glycerol and by the negative interaction glycerol–spelt bran and glycerol–wheat bran. The maximum and the minimum value of the G_1 was observed at 2.0% and 6.0% of the glycerol, respectively, and at 6.8% of the spelt bran and wheat bran. The $\delta_1$values were affected by the individual positive term of wheat bran, by a positive interaction glycerol–spelt bran and by a negative interaction spelt bran–wheat bran. From the above table, it can be observed that the maximum value of the δ_1 corresponded at 6.0% of the glycerol, at 6.8% of the spelt bran and at 0.6% of the wheat bran; while the minimum value was observed at 2.0% of the glycerol and at the lowest value of the spelt bran and wheat bran. As can be inferred from the data the bran acts as stiffing agent determining an increase of elastic response (higher G_1 values) whereas the plasticizer effect of the glycerol increases the viscous response of the investigated films (higher δ_1 values). Regarding to the constant E_0, an individual positive term of the wheat bran and a negative interaction glycerol–wheat bran was recorded. The maximum and the minimum value of the E_0 was observed at 2.0% and 6.0% of the glycerol, respectively and at 6.8% of the wheat bran. These results reflect the typical behaviour of an elastic modulus. Indeed, the increase of the glycerol concentration increased the flexibility of the films (lower E_c values) whereas the bran acted as reinforcing material.

3.6. Colour evaluation

Colour attributes are of prime importance because they directly influence consumer acceptability. Gluten films, containing different amounts of glycerol and bran, resulted enough homogeneous and opacity development appears to be related to the increase of bran. The results obtained from the measure are summarized in Table 1. Yellow Index and *b* parameter of Hunter scale increased with the bran concentration, especially with wheat bran; on the contrary, they decreased with the increase of glycerol. Moreover, a parameter increased with the increase of the glycerol and bran concentrations. In contrast, *L* increased as bran concentration decreased; this effect was also observed when the spelt bran concentration was higher of the wheat bran concentration. So, bran presence gave origin to darker films. It was also observed that, in general, the increase of glycerol produced an increase in *L*.

3.7. Film-forming solution properties

3.7.1. Apparent viscosity

The film forming solutions showed a non-Newtonian behaviour and their apparent viscosity was highly dependent on the shear rate at which shear stress was measured (Steffe, 1992). In particular, all film forming solutions presented pseudoplastic behaviour ($n < 1$) and the apparent viscosity was calculated according to Eq. (6). Flow index for all analyzed samples were calculated using Eq. (5) and ranged between 0.73 and 0.90. A decrease in flow behaviour index with bran concentration was observed. As bran concentration is lowered very dilute solution will exhibit almost Newtonian behaviour ($n = 1$) while departure is noticed as soon as free water molecules become to interact with the fibre–matrix system. Regarding to the consistency index *K*, it was observed an increase of this parameter with the bran concentration. As the bran concentration increases, the solution is more viscous and the consistency index increase. The best-fit equation describing effects of glycerol, spelt bran and wheat bran on the apparent viscosity is reported in Table 3, along with the multiple regression analysis. As can be observed, the selected variable was positively affected by the individual term of the glycerol and negatively by the individual term of spelt bran and wheat bran; moreover, the apparent viscosity was influenced by a negative quadratic effect of the glycerol, by a positive quadratic effect of the spelt bran and wheat bran and by a positive interaction spelt bran–wheat bran. The maximum value corresponded at 4.24% of the glycerol and at 6.8% of the spelt bran and wheat bran, while the minimum value was observed at 2.0% of the glycerol, at 3.33% of the spelt bran and at 0.6% of the wheat bran. The increase of apparent viscosity with the bran concentration is probably due to the fact that the bran presence and its interaction with the matrix decrease the mobility of water molecules. Thus, as the bran concentration increase a greater number of water molecules are immobilized, leading to the increase of apparent viscosity. Regarding to the glycerol concentration, its behaviour is probably related to the interaction with the other component. Fig. 7 shows the apparent viscosity-shear rate plot for 4.3%, 7.4% and 10.5% of bran concentration. As can be observed, the apparent viscosity increased with

Table 3
Best fit equations of the individual, quadratic and interactive effects of glycerol, spelt bran and wheat bran on the properties of the film forming solutions and the maximum and the minimum independent variables values

	Best fit equations	Max	Min	F^a	SE	R^2
Viscosity (Pa s)	0.026087 * XG – 0.016187 * XSB – 0.014881 * XWB – 0.003072 * XG^2 + 0.001849 * XSB^2 + 0.001968 * XWB^2 + 0.006441 * XSB * XWB	XG = 4.24 XSB = 6.8 XWB = 6.8	XG = 2.0 XSB = 3.33 XWB = 0.6	32.19	0.039	0.87
η^* (Pa s)	0.020581 * XSB * XWB	XSB = 6.8 XWB = 6.8	XSB = 0.6 XWB = 0.6	283.84	0.08	0.94
G'_1 (MPa)	2.659796 * XSB * XWB	XSB = 6.8 XWB = 6.8	XSB = 0.6 XWB = 0.6	932.09	5.70	0.98
δ'_1 (MPa)	11.40867 * XG – 0.84985 * XG^2 – 0.66483 * XG * XSB – 0.60906 * XG * XWB + 0.41955 * XSB * XWB	XG = 6.0 XSB = 0.6 XWB = 0.6	XG = 6.0 XSB = 6.8 XWB = 6.8	292.12	1.97	0.99
E'_0 (MPa)	0.331471 * XG – 0.244418 * XSB – 0.236454 * XWB – 0.041201 * XG^2 + 0. 102504 * XSB * XWB	XG = 4.02 XSB = 6.8 XWB = 6.8	XG = 2.0 XSB = 6.8 XWB = 0.6	34.06	0.13	0.93

[a] F, Fisher test value; SE, standard error; R^2, regression coefficient.

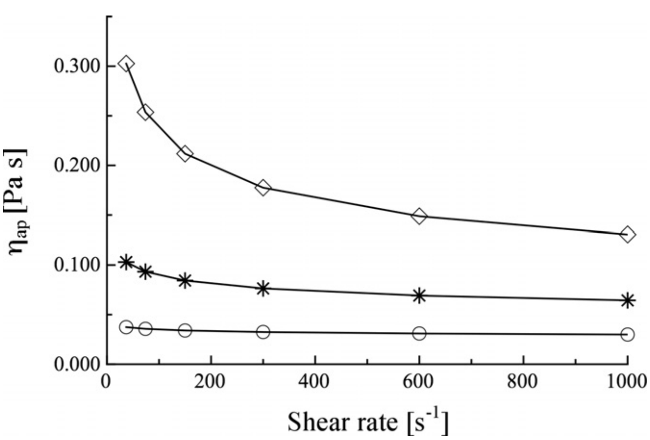

Fig. 7. Effect of the bran concentration on the apparent viscosity of film forming solutions. Experimental data for: (○) 4.3%, (∗) 7.4% and (◇)10.5% of bran concentration.

the increase of the bran. Moreover, at high shear rate values apparent viscosity reaches a constant value related to completion of structure reorganization (Bertuzzi et al., 2007).

3.8. Dynamic properties

Table 3 reports the best-fit equation of the effects of the glycerol, spelt bran and wheat bran on the η^* values. The complex viscosity (η^*) was affected by a positive interaction spelt bran–wheat bran; moreover, the maximum value of this parameter was observed at the highest value of the spelt bran and wheat bran, while the minimum value corresponded at the lowest value of the independent variables.

3.9. Stress relaxation

The viscoelastic properties of the film forming solutions were expressed by different fitting parameters (G'_1, δ'_1 and E'_0); they were obtained by fitting Eq. (4) to the experimental data. The best-fit equations of the effects of the independent variables on G'_1, δ'_1 and E'_0 values are reported in Table 3. The G_1' values were influenced by a positive interaction spelt bran–wheat bran; the maximum and the minimum value was observed at the highest (6.8%) and lowest (0.6%) concentration of bran, respectively. The δ'_1 values were positively affected by the individual term of the glycerol and by its negative quadratic effect; moreover, the selected variable was affected by a negative interaction glycerol–spelt bran and glycerol–wheat bran and by a positive interaction spelt bran–wheat bran. The maximum value of the δ'_1 parameter was observed at 6.0% of the glycerol and at the lowest concentration (0.6%) of the spelt bran and wheat bran, while the minimum value was observed at 6.0% of the glycerol and at the highest concentration (6.8%) of bran. As already said, the elastic response of the film forming solutions incresed with the bran concentration (higher G_1 values) whereas the viscous response increased with the glycerol concentration (higher δ_1 values). Concerning to the constant E'_0, an individual positive term of the glycerol and an individual negative term of the spelt bran and wheat bran was recorded. The constant E'_0 was also affected by a negative quadratic effect of the glycerol and by a positive interaction spelt bran–wheat bran. The maximum value of the constant E'_0 corresponded at 4.02% of the glycerol and at 6.8% of spelt bran and wheat bran, while the minimum value was observed at 2.0% of the glycerol, 6.8% of the spelt bran and 0.6% of the wheat bran.

3.10. Principal component analysis

In order to evaluate the correlations among the films properties, such as water vapor permeability, mechanical and dynamic-mechanical properties, and the film-forming solutions properties a Principal Component Analysis was performed. The results obtained are showed in Table 4.

Table 4
Correlation coefficients of the investigated parameters

	η^*	E^*	G_1	E_0	G_1'	E_0'	Viscosity	Tensile strength	Elongation at break	E_c
η^*	1	0.3290	0.1166	0.0206	0.9964	0.9511	0.9945	0.4046	−0.5780	0.0887
E^*	0.3290	1	0.9097	0.8483	0.3201	0.3244	0.3160	0.9696	−0.8682	0.9221
G_1	0.1166	0.9097	1	0.9892	0.1119	0.1425	0.1021	0.8108	−0.6384	0.9895
E_0	0.0206	0.8483	0.9892	1	0.0186	0.0526	0.0083	0.7221	−0.5451	0.9769
G_1'	0.9964	0.3201	0.1119	0.0186	1	0.9292	0.9979	0.3897	−0.5845	0.0828
E_0'	0.9511	0.3244	0.1425	0.0526	0.9292	1	0.9204	0.4075	−0.4904	0.1129
Viscosity	0.9945	0.3160	0.1021	0.0083	0.9979	0.9204	1	0.3849	−0.5815	0.0706
Tensile strength	0.4046	0.9696	0.8108	0.7221	0.3897	0.4075	0.3849	1	−0.8998	0.8302
Elongation at break	−0.5780	−0.8682	−0.6384	−0.5451	−0.5845	−0.4904	−0.5815	−0.8998	1	−0.6665
E_c	0.0887	0.9221	0.9895	0.9769	0.0828	0.1129	0.0706	0.8302	−0.6665	1

Table 5
Optimal composition of wheat gluten-based edible film

Dependent variables	Goal	Observed value	Predicted value	Absolute residual error[a] (%)
E_c (MPa)	Maximum	405.99	282.27	30.47
Tensile strength (MPa)	Maximum	5.31	4.42	16.84
Elongation at break (%)	Maximum	115.77	111.75	3.47
E^*	Maximum	1662.16	1351.92	18.66
WVP (g/m s Pa)	Minimum	1.97E−12	1.40E−12	28.96

[a] The absolute residual error has been computed as: [(Observed value − Predicted value)/Observed value] $*$ 100.

Significant correlations among the film-forming solution parameters, except for δ_1', was observed. In fact, the more a solution is viscous, the more increase the resistance to flow of the material ($\eta*$). Moreover, the increase of the viscosity determines a viscoelastic solid behaviour of the material that gradually relaxes and reaches an equilibrium stress greater than 0 (higher value of E_0'). Regarding to the film properties, as expected the E_c is strongly correlated with the tensile strength that expresses the maximum stress developed in a film during a tensile test. The E_c is also correlated with the complex modulus (E^*) and the fitting parameters (G_1 and E_0). Thus, the more a film is elastic, the more decrease its resistance to deformation. It can be observed from table a negative correlation among E^* and the elongation at break; in fact, the more a film is resistant to the deformation, the less it strains. There are not significant correlations among the water vapor permeability and the other parameters.

3.11. Optimal composition of wheat gluten-based edible film

The results of the statistical analysis leading to the optimal composition of wheat gluten-based edible film were reported in Table 5. The absolute residual error for the dependent variables Ec, tensile strength, elongation at break, E^* and WVP ranged from 3.47% to 30.47%. The wheat gluten-based edible film optimization could be achieved using the composition corresponding to the lowest absolute residual errors (3.47%) of the dependent variables. This composition contains values of glycerol, spelt and wheat bran concentrations equal to 5%, 2.15% and 2.15%, respectively.

4. Conclusions

The purpose of this work was to investigate the water vapour barrier, the mechanical and dynamical properties and the rheological behaviour of the wheat gluten-based edible films in order to obtain the optimal formulation for peculiar applications.

The properties of composite edible films were influenced by glycerol, spelt bran and wheat bran concentrations. In particular, the glycerol had a negative effect on WVP values of the films in fact the permeability incremented with the increase of the glycerol concentration, whereas the bran presence had a positive influence (decrease of WVP). The positive effect of bran on WVP values is probably due to the fact that bran posses a lower water permeability. Therefore, an increase in its concentration brings about a decrease in the water permeability value of the composite film. As expected, the minimum value of the permeability was observed at lowest concentration of glycerol (2.0%) and at highest concentration of spelt bran (6.8%). E_c increased with the bran concentration increase and with the glycerol decrease. The effect of the bran concentration on apparent viscosity of the film forming solutions was investigated. As the bran concentration increase, a greater number of water molecules are immobilized resulting an increase of apparent viscosity. The complex viscosity (η^*) was affected by a positive interaction spelt bran–wheat bran. The colour results showed that Yellow Index and b parameter of Hunter scale increased with the bran concentration, in particular the wheat bran gave origin to darker films, whereas the L values decreased. Moreover, a parameter increased with the increase of the glycerol and bran concentrations. The glycerol increase determined a decrease in Yellow Index and b, and an increase in L. There may be several applications for edible coating/film. For instance, they can be used to reduce the migration of low molecular weight compound, such as water, from one phase to another in a multiphase food matrices or to provide mechanical protection. In consequence, the optimal composition of composite edible film for the characteristics demanded corresponded to a values of glycerol, spelt bran and wheat bran concentration equal to 5%, 2.15% and 2.15%, respectively.

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