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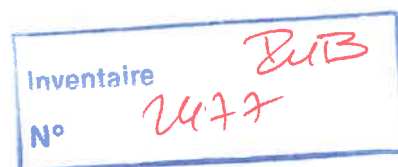
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Films were prepared by casting alkaline solutions of gliadin, a major wheat storage protein fraction. Their compositions and mechanical and surface properties were analyzed. Five polyols of the ethylene glycol series and glycerol were compared as plasticizers. The plasticized film-forming solutions exhibited viscosities almost independent of shear rate. Glycerol-containing protein solutions had, however, a higher viscosity than others. After drying, concentrations of plasticizers in films were explained mainly, but not uniquely, by their volatility. At equal concentrations in films, glycerol and tetraethylene glycol were more efficient than the other plasticizers studied. A wide range of elongation (10–600%) was obtained when the plasticizer contents were varied, but the tensile strength (2–12 MPa) was always lower than that of usual synthetic polymer films. A negative relationship, independent of the plasticizing molecules used, was found between tensile strength and elongation at break of gliadin films. Surface hydrophobicity of films was high and no influence of plasticizers was observed.

Keywords: *Film; gliadins; wheat; plasticizer; polyols*

INTRODUCTION

In recent years, environmental concerns have increased the interest in using renewable agricultural resources to prepare packaging materials. Most efforts were originally devoted to cellulose and starch. These polysaccharides are of prime interest as biopolymers because of their availability and rather low cost. However, the resulting biomaterials show some drawbacks, such as great water sensitivity and low elasticity, even after chemical modification, which limit their uses. Thus, it is necessary to investigate the film-forming potential of other biopolymers. Among proteins, some have properties desirable in the preparation of biomaterials, such as ability to form fibers or network, plasticity, and elasticity. This might explain the increasing interest for using commercially available proteins to prepare biomaterials, especially films. Biopolymers were used to prepare edible films (Kester and Fennema, 1986; Torres, 1994; Krochta and De Mulder-Johnston, 1997). The film properties of different plant proteins were studied: soy proteins (Gennadios and Weller, 1991; Gennadios et al., 1993b; Stuchell and Krochta, 1994; Kunte et al., 1997), corn zein (Gennadios and Weller, 1990; Gennadios et al., 1993a; Yamada et al., 1995; Parris and Coffin, 1997), wheat gluten (Gontard et al., 1992, 1993; Gennadios et al., 1993c,d), sorghum kafirin (Buffo et al., 1997), rice bran and peanut protein (Gennadios et al., 1997), cottonseed protein (Marquié et al., 1995), and pea protein (Guéguen et al., 1995; Viroben et al., 1995).

Proteins associate by intermolecular interactions (electrostatic, hydrogen, and hydrophobic). Protein structure and conformation influence the intermolecular interactions necessary for formation of a gel-type net-

work, which is then dehydrated (Miller and Krochta, 1997). The strength of protein–protein and protein–water interactions determines the properties of the materials and can be controlled by means of the film-forming conditions and by the presence of a plasticizer. Plasticizers decrease the protein interactions and increase polymer chain mobility and intermolecular spacing, decreasing also the glass transition temperature of proteins. A plasticizer is required to avoid brittleness and to increase the flexibility of the films. The plasticizers must have low molecular weights, high boiling points, compatibility with the polymers, and solubility in the solvent (Banker, 1966). Oligosaccharides, polyols (polyhydric alcohols), and lipids are different types of plasticizers, and the most frequently used is glycerol. The type and concentration of plasticizer influence properties of protein films (Gennadios et al., 1993d; McHugh et al., 1994; McHugh and Krotchka, 1994; Cuq et al., 1997b; Guéguen et al., 1998).

Because the raw material is produced in large amounts at a reasonable price, several studies were done on wheat gluten films (Gennadios and Weller, 1990; Gontard et al., 1992, 1993; Gennadios et al., 1993a–d; Cherian et al., 1995; Herald et al., 1995; Gontard and Ring, 1996; Ali et al., 1997; Rayas et al., 1997). By contrast, there have been only a few descriptions of films made of gliadins, the monomeric fraction of glutamine- and proline-rich wheat storage proteins (Okamoto, 1978; Gontard, 1991). Because gliadin is less complex than the polydisperse protein mixture composing gluten and contains no contaminating starch and few lipids, the aim of the present work was to study gliadin films, looking especially at the influence of plasticizers on the rheological properties of the film-forming solutions and on the surface and mechanical properties of the films. Glycerol and polyols from the ethylene glycol series were

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chosen as plasticizers, regardless of their edibility, because protein films should be intended for nonfood uses.

MATERIALS AND METHODS

Materials. A gliadin-rich fraction (86.4% proteins, $N \times 5.7$) was obtained by fractionation of industrial vital gluten (Roquette, Lestrem, France) at the pilot scale, following the method of Bérot et al. (1994), based on an acetic acid extraction, followed by centrifugation and ultrafiltration of the supernatant. The gliadin retentate was spray-dried.

Ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TEEG), diethylene glycol-monomethyl ether (DEGMET), as a more hydrophobic derivative of DEG, and glycerol (GLY) were purchased from Fluka or Sigma. All other reagents and chemicals were of analytical grade.

Preparation of Films. Gliadins were dispersed into 0.1N NaOH solution by using a Polytron homogenizer (25 000 rpm for 90 s). A second mixing (25 000 rpm for 60 s) was performed after a rest of 60 s to limit heating of the sample. After addition of the plasticizer (plasticizer/protein ratios = 0.26–0.51 w/w), the mixture was stirred three times (25 000 rpm for 90, 60, and 60 s) with rests of 60 s between each stirring, and then centrifuged (115g, 30 min) to eliminate the air bubbles. The protein content of the film-forming solution was 16% (w/w) and its pH 11. Alkaline conditions for gliadin film-forming solutions were chosen here because Gennadios et al. (1993b) showed that casting films of gluten proteins at alkaline pH resulted in higher tensile strengths than at acidic casting conditions with no significant differences in elongation. The deaerated solution was spread over a glass plate (260 × 150 × 0.5 mm) covered with a Gel Bond sheet (a polyester film) to help the peeling of the dried film and then dried in a ventilated oven at 70 °C during 1 h. The gliadin film was peeled off from the plate and equilibrated for 3 days in a cabinet under standard conditions of temperature (20 °C) and relative humidity (RH = 60%, produced by a saturated solution of sodium bromide). The gliadin films were in all cases transparent, with a light yellowish color.

Loss of Weight. The loss of weight of the films was determined by weight difference (± 0.1 mg) of the film before and after drying for 1 h at 70 °C.

Plasticizer Content. The residual amount of plasticizer in films was determined by high-performance liquid chromatography. Film samples (500 mg) were extracted twice with deionized water (25 mL) for 60 and 30 min. The supernatant was applied on an ion-exchange column (Shandon Cl⁻ MCA) heated at 60 °C. The plasticizer was eluted by water and detected by a differential refractometer (Jobin-Yvon). The concentration was calculated by reference to a calibration curve of the same plasticizer.

Residual Water. Film samples (500 mg) were dried under reduced pressure during 24 h in a desiccator containing P₂O₅, because preliminary assays had shown that no change of weight occurred after this time. The water content in films was determined from weight difference of the samples before and after drying.

Viscosity Measurements of Film-Forming Solutions. Flow curves of film-forming solutions, plasticizer solutions, and protein solutions were recorded at 20 °C at shear rates 0–100 s⁻¹ with a RFS2 Rheometrics rheometer, using a coaxial cylinder device. Viscosity was calculated by dividing shear stress by shear rate. For each condition, two solutions were analyzed in duplicate.

Mechanical Properties. Mechanical properties of films were investigated on film specimens of 75 mm length with a dumbbell shape (5A type, ISO 527-2 standard). Five replicates were tested for each film assay. Film thickness was measured at five points with a hand-held micrometer (Morton-Blet, Prolabo France; range of measurements = 1–1000 μm). Elongation at break (EL) and tensile strength (TS) were measured at 20 °C with a traction-compression device (model

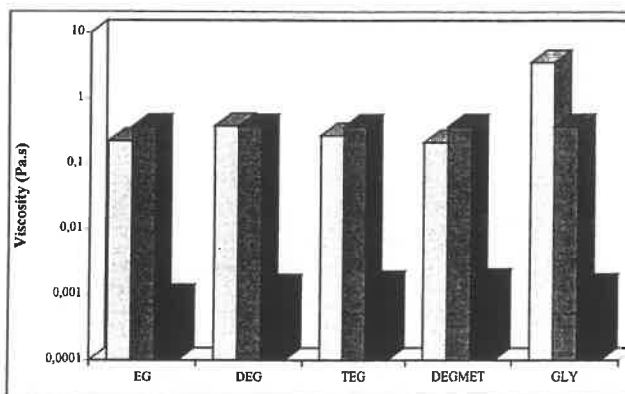


Figure 1. Viscosity of film-forming solutions at 5 s⁻¹ shear rate, in the presence of different plasticizers. For reference are also shown the viscosities of gliadin solutions and plasticizer solutions at the same concentrations as in the film-forming solutions. Bars represent, from left to right within each grouping, film-forming solution, protein solution, and plasticizer solution.

DY34, Adamel-Lhomargy Testing Instrument, Ivry, France) equipped with a 10 N load cell. Initial grip separation was set at 50 mm, while cross-head speed was set at 20 mm min⁻¹. TS was calculated by dividing maximum stress by the cross-sectional area of the film and EL was expressed in percentage of the initial length of the elongating part of the specimen (20 mm).

Surface Hydrophobicity. Surface hydrophobicity of films was evaluated through contact angle measurement using an image analysis system DigiDrop, GBX. After a drop of deionized purified water (Milli-Q system) was placed above the film, the angle of the tangent to the basis of the drop (contact angle) was measured and expressed in degrees.

Statistics. The results were compared by analysis of variance and Duncan's multiple-range test. Statgraphics Plus software was used for this purpose.

RESULTS AND DISCUSSION

Viscosity of Film-Forming Solutions. The addition of EG, DEG, TEG, and DEGMET to protein solutions (plasticizer/protein ratio = 0.37 w/w) decreased the viscosity, and no large difference was observed among these plasticizers. Only glycerol increased considerably the viscosity, although the viscosity of the glycerol solution alone was not higher than that of other plasticizers (Figure 1). In the absence of plasticizer, the viscosity of protein solutions was decreasing with increasing shear rate. In the presence of plasticizer, viscosity was almost independent of shear rate (Figure 2). The differences between film-forming and protein solutions were mainly observed at low shear rate. The lower viscosity of film-forming solutions at 0.1 s⁻¹ might be interpreted as a weakening of protein-protein interactions due to the plasticizer. Higher shear rates destroyed these interactions, resulting in similar behaviors in the presence as in the absence of plasticizer. Mate and Krochta (1996) described the same shear-thinning behavior of film-forming solutions of whey protein as we observed for gliadins (Figure 2). Viscosities of gliadin film-forming solutions were in the range indicated by Cuq et al. (1995) as convenient for an easy film casting, that is, <700 mPa·s.

Reproducibility of Film Preparation. Three film-forming solutions were prepared using diethylene glycol as plasticizer (plasticizer/protein ratio = 0.37 w/w), and two films were cast from each one. Results of all tests performed are shown in Table 1. Evaporation of water

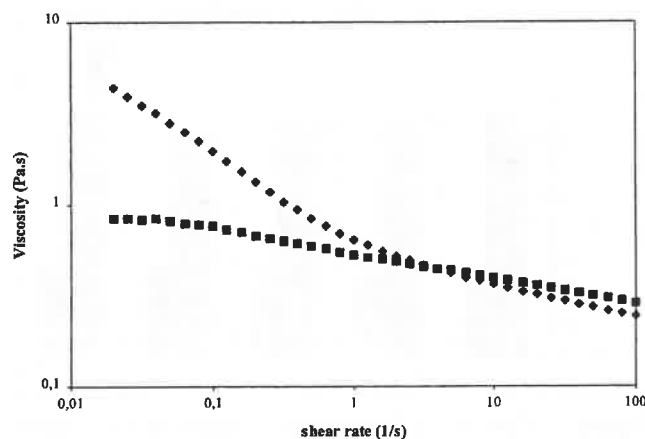


Figure 2. Viscosities as a function of the shear rate of a gliadin solution (◆) and of a film-forming solution in the presence of DEG (■). Protein concentration in film-forming solutions was 16%, and the plasticizer/protein ratio was 0.37.

and plasticizer during drying was very reproducible. Film thickness after drying was more variable. The higher variability of TS measurements was possibly due to thickness variability, although Cuq et al. (1996) reported that film thickness had no influence on TS of protein films. EL showed less variability. In all of the experiments reported below, four films were prepared from two film-forming solutions and the numbers of analyses per film were those indicated in Table 1.

Effect of the Plasticizer Chemical Structure. Films with the Same Weight of Plasticizer in the Film-Forming Solution. All films were prepared with a plasticizer/protein ratio of 0.37 (w/w) and were dried at the same conditions. Only the water content of the film with DEGMET was significantly different from the others, but all of the films differed significantly in their plasticizer contents (Table 2). No glycerol [boiling point (bp) = 290 °C] was evaporated, but 66% of the DEGMET (bp = 193 °C) was lost. Losses for EG (bp = 198 °C), DEG (bp = 244 °C), TEG (bp = 287 °C), and TEEG (bp = 307 °C) were 46, 23, 13, and 17%, respectively. Considering that initial contents were the same for all plasticizers, these differences could be explained partially by their different boiling points. However, this is not the sole explanation, because more TEG and

TEEG than GLY was lost, although they have similar or even higher boiling points; interactions between glycerol and proteins cannot be excluded. Thus, to maintain equal contents of plasticizer in films for comparison, specific drying conditions must be adapted for each plasticizer or plasticizer contents of film-forming solutions must be adjusted.

Tensile strength and elongation at break of films are shown in Table 2. It was not possible to characterize films plasticized with glycerol, because they were very sticky and impossible to peel off from the glass plate. This behavior was due to an excessive content of plasticizer, because experiments performed later with 20% of glycerol resulted in films easy to manipulate. The stress–elongation curves were in all cases not linear, indicating a plastic behavior. TS of films were between 1.6 and 11.3 MPa and EL between 3.8 and 557%. Smaller TS values corresponded to higher EL values. Because the residual contents of each plasticizer were different, differences in mechanical properties could not be attributed to the structure of the plasticizer molecules rather than to their concentrations in the films. Volatility must be taken into account in the choice of a plasticizer, because it influences the cost and the safety of the process and the stability of film properties with aging.

Protein films similar to polysaccharide films are known for their hydrophilic character, but the gliadin films exhibited contact angles between 85° and 105°. The angle increased with the number of carbons in the EG series, but plasticizer contents varied, too. Nevertheless, contact angles of pea protein films were in the range of 14–40° (Guéguen et al., 1998). This means that gliadin films were less readily wetted, suggesting a higher surface hydrophobicity, which can be related to the water insolubility of gluten proteins. Indeed, their values of contact angle were similar to those observed currently with polystyrene or poly(tetrafluoroethylene) (Extrand and Kumagai, 1997). In contrast with synthetic polymer films, angles on gliadin films decreased rapidly with contact time (not shown), suggesting a rapid change of surface properties.

Films with the Same Amount of Residual Plasticizer. To compare with confidence the effects of the plasticizer molecules on hydrophobicity and mechanical properties

Table 1. Reproducibility of the Different Measures on Films Prepared with DEG^a

	loss of wt (%)	residual water (%)	plasticizer content (%)	thickness (μm)	contact angle (deg)	TS (MPa)	EL (%)
no. of films	6	6	6	6	6	6	6
repeat/film	1	2	2	25	5	5	5
av	76.9	9.5	20.0	67.5	90.4	2.6	479
SD	1.5	0.9	0.6	8.5	3.6	0.2	32
CV (%)	1.9	1.0	3.0	12.5	4.0	9.3	6.6

^a Protein concentration in film-forming solutions was 16% and plasticizer/protein ratio was 0.37.

Table 2. Residual Water and Plasticizer Contents and Mechanical and Surface Properties of Films Prepared with the Same Initial Contents of Different Plasticizers in the Film-Forming Solution

plasticizer	residual water (%)	plasticizer content (%)	TS (MPa)	EL (%)	contact angle (deg)
EG	10.3 (1.5) ^a d ^b	14.6 (1.3) b	4.1 (1.2) b	243 (47) b	85 (4) a
DEG	9.5 (0.9) b	20.0 (0.6) c	2.5 (0.2) ab	479 (32) c	90 (4) b
TEG	9.5 (1.4) b	23.6 (1.5) e	2.8 (0.7) ab	504 (112) c	94 (5) c
TEEG	9.8 (0.3) c	22.3 (1.3) d	1.6 (0.2) a	557 (38) d	105 (4) e
DEGMET	7.2 (0.05) a	10.0 (1.9) a	11.3 (5.2) c	3.8 (1.5) a	95 (2) c
GLY	9.0 (2.2) b	28.1 (0.8) f	nd ^c	nd	99 (11) d

^a Values in parentheses indicate standard deviation. ^b Values in one column followed by the same letter were not significantly different at the risk 5.0% (analysis of variance and Duncan's multiple-range test). ^c nd, not determined.

Table 3. Residual Water and Plasticizer Contents and Mechanical and Surface Properties of Films Prepared with the Same Residual Contents of Different Plasticizers

plasticizer	plasticizer/protein ratio	residual water (%)	residual plasticizer (%)	TS (MPa)	EL (%)	contact angle (deg)
EG	0.51	9.6 (1.3) ^a b ^b	21.5 (2.4) bc	2.7 (0.4) b	393 (32) a	90 (7) a
DEG	0.37	9.5 (0.9) b	20.0 (0.6) ab	2.5 (0.2) b	479 (32) b	90 (4) a
TEG	0.31	7.6 (0.4) a	19.4 (1.6) a	3 (1.1) c	423 (11) ab	100 (2) b
TEEG	0.33	10.3 (0.1) c	22.2 (0.7) c	1.5 (0.4) a	595 (120) c	112 (7) d
GLY	0.26	9.4 (0.1) b	19.0 (2.8) a	1.8 (0.9) a	562 (120) c	104 (3) c

^a Values in parentheses indicate standard deviation. ^b Values in one column followed by the same letter were not significantly different at the risk 5.0% (analysis of variance and Duncan's multiple-range test).

Table 4. Residual Water and Plasticizer Contents and Mechanical and Surface Properties of Films Prepared with Different Residual Contents of DEG and DEGMET

plasticizer	residual plasticizer (%)	residual water (%)	TS (MPa)	EL (%)	contact angle (deg)
DEG	14.3	8.8 (0.6) ^a b ^b	5.2 (0.9) d	188 (78) a	97 (3) b
	17.1	9.6 (0.5) c	4.4 (0.2) c	209 (73) a	101 (3) c
	18.5	8.3 (0.2) a	3.8 (0.3) b	362 (69) b	98 (6) b
	20.0	9.5 (0.9) c	2.5 (0.2) a	490 (32) c	90 (3) a
DEGMET	10.0	7.2 (0.5) b	11.3 (5.2) b	3.8 (1.5) a	95 (2) b
	12.5	7.7 (0.4) b	8.5 (5) ab	195 (65) b	97 (3) b
	14.9	5.4 (0.4) a	3.8 (0.9) a	291 (20) c	91 (7) a

^a Values in parentheses indicate standard deviation. ^b Values in one column followed by the same letter were not significantly different at the risk 5.0% (analysis of variance and Duncan's multiple-range test).

of films, we strove to prepare films containing the same amounts of residual plasticizer (20%). The weight of plasticizer added to film-forming solutions was estimated by assuming that the residual content was directly proportional to initial amounts for fixed drying conditions. It was impossible to prepare a film with DEGMET because a phase separation occurred in the film-forming solution for concentrations lower than that required. With other plasticizers, the chosen final content of 20% was obtained by varying the initial plasticizer/protein ratio between 0.56 (EG) and 0.26 (GLY) (Table 3). Except for EG and TEEG, no significant difference of plasticizer content was observed. The water contents were similar except with TEG, for which it was lower. A lower water content is expected to decrease plasticity (Baumberger et al., 1997), because water also acts like a plasticizer.

The mechanical properties of films with the same amounts of residual plasticizer are shown in Table 3. Considering the series of plasticizers EG-TEEG, TS values were similar for EG and DEG and higher for TEG. In contrast, TEEG resulted in lower TS. EL increased when the chain length increased. TEG yielded EL lower than expected, not significantly different from EG and DEG; however, the TEG content in film was lower, too. GLY provided properties similar to TEEG, that is, the greatest EL and the lowest TS in the series. Expressing the TS and EL versus the molar concentration of plasticizers did not abolish the differences among plasticizers (not shown), in opposition to results obtained on fish myofibrillar proteins (Cuq et al., 1997b). The results on gliadin films were different, too, from what was reported on pea proteins by Guéguen et al. (1998), that is, decreased EL and TS of films with increased plasticizer chain length. This probably arises from the specific structures and properties of pea globulins and wheat prolamins, leading to different behaviors in the presence of plasticizers. In the case of wheat gliadin, it appeared that TEEG and glycerol had a higher "plasticizing activity" than other plasticizers tested.

The surface properties of films are shown in Table 3. The high values of contact angles confirmed the results

reported above. TEEG, the plasticizer with the longest carbon chain, provided the highest contact angle. Globally, the contact angles were similar to those obtained for methylcellulose-paraffin wax films (Martin Polo et al., 1992). However, as stated previously, this surface analysis should be completed in the future by kinetic studies to characterize in more detail the wetting of films.

Effect of Plasticizer Concentration. Films were prepared with final concentrations of plasticizer in the range of 14–20% for DEG and 10–15% for DEGMET. Water contents of films showed variations that were not linked to the amount of plasticizer (not shown). The mechanical properties at the different plasticizer concentrations are shown in Table 4. A decrease of TS and an increase of EL were observed when the concentration of DEG or DEGMET increased. By small changes of the plasticizer concentrations in gliadin films, it was therefore possible to modify considerably their mechanical properties. The amplitude of variation of TS was wider with DEGMET, but this may be due to the lower concentrations studied. Such concentration-dependent properties were expected in the case of plasticizing molecules. The same were described with different plasticizers for films of zein, a maize prolamin (Park et al., 1994), and of fish myofibrillar proteins (Cuq et al., 1997a) but, once again, gliadin films opposed to pea protein films, for which increasing DEG concentration resulted in reduced EL (Guéguen et al., 1995).

Contact angles were high and similar for both plasticizers (Table 4), as previously mentioned. They did not follow the variations of DEG or DEGMET concentrations, and the more hydrophobic DEGMET did not induce larger angles. This suggested that surface hydrophobicity of gliadin films arose from the properties of the constituting proteins and was not much influenced by the type and the plasticizer contents.

Relationship between TS and EL of Films. Different plasticizers were used in this study. All data on mechanical properties were tentatively combined in a synthetic plot showing EL versus log TS (Figure 3). The best fit was obtained with a linear model. The coefficient of correlation was -0.97 , which indicated a strong

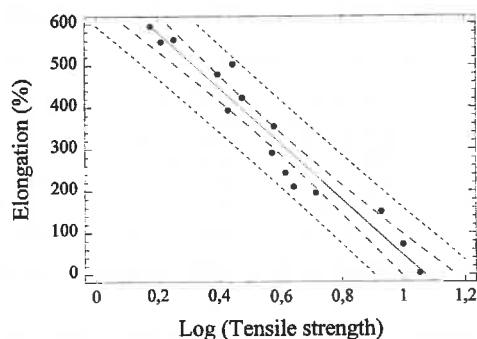


Figure 3. Plot of the best fit for EL versus log TS of gliadin films prepared with glycerol and different polyols of the ethylene glycol series. Coefficient of correlation was -0.97 .

relationship between the variables. The analysis of variance indicated it was significant at the 99% confidence level. This suggested the relationship between strain and stress of gliadin films is independent of the chemical structure of the plasticizer molecule incorporated in the film. This plot indicates that, regardless of plasticizer type, limit values of elongation at break and maximum strength of gliadin films will be about 700% versus 1 MPa and 0% versus 11 MPa, respectively. With the plasticizers studied here, the molecule structure influenced film properties by determining the amount required to obtain a given plasticization. This is expected if no specific interaction occurs between protein and plasticizer. Volatility of plasticizers affects their residual concentrations in films and the stability of films with aging.

The mechanical properties measured with gluten films prepared under alkaline conditions (Gennadios et al., 1993b,d) fell in the range of those recorded here with gliadins films. A direct comparison was prevented by conditions of mechanical testing (differing specimen shapes and cross-head speeds).

Conclusion. An alkaline casting process, excluding alcohol, was found to be convenient to prepare gliadin films. It yielded homogeneous solutions with the required viscosity for casting. Adjusting the plasticizer concentration in films led to a wide range of elongation values. This made gliadin an interesting alternative raw material for making films. However, it was not possible to reach TS values as high as those of low-density polyethylene with similar elongations, 8.6–17.3 MPa (Gennadios et al., 1993b). TS and EL of gliadin films were linked by a negative relationship. Changing the plasticizer modified the residual content of plasticizer in films but not the TS/EL relationship. Thus, the least volatile plasticizers are recommended, because the control of their concentration in films is easier and they ensure more constant properties with aging. In this study, tetraethylene glycol was more convenient than other polyols of the ethylene glycol series compared, because the loss during film drying was limited and it was more efficient at smaller concentrations. Glycerol resulted in similar film properties as tetraethylene glycol, except that the viscosity of film-forming solutions was then considerably higher. This offers a possibility to adapt the properties of the film-forming solution to the casting conditions.

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