

## Properties of Wheat Gluten/Poly(lactic acid) Laminates

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Laminates of compression-molded glycerol-plasticized wheat gluten (WG) films surrounded and supported by poly(lactic acid) (PLA) films have been produced and characterized. The objective was to obtain a fully renewable high gas barrier film with sufficient mechanical integrity to function in, for example, extrusion-coating paper/board applications. It was shown that the lamination made it possible to make films with a broad range of glycerol contents (0–30 wt %) with greater strength than single unsupported WG films. The low plasticizer contents yielded laminates with very good oxygen barrier properties. In addition, whereas the unsupported WG films had an immeasurably high water vapor transmission rate (WVTR), the laminate showed values that were finite and surprisingly, in several cases, also lower than that of PLA. Besides being a mechanical support (as evidenced by bending and tensile data) and a shield between the WG and surrounding moisture, the PLA layer also prevented the loss of the glycerol plasticizer from the WG layer. This was observed after the laminate had been aged on an “absorbing” blotting paper for up to 17 weeks. The interlayer adhesion (peel strength) decreased with decreasing glycerol content and increasing WG film molding temperature (130 °C instead of 110 °C). The latter effect was probably due to a higher protein aggregation, as revealed by infrared spectroscopy. The lamination temperature (110–140 °C) did not, however, have a major effect on the final peel strength.

**KEYWORDS:** Wheat gluten; poly(lactic acid); glycerol content; laminate; oxygen permeability; water vapor transmission rate; biopolymer

### INTRODUCTION

Wheat gluten (WG) protein films are derived from a renewable source, and they are potentially interesting as future alternatives to petroleum-based packaging materials, with excellent barrier properties to nonpolar gases under dry conditions. It is especially interesting to obtain WG as a byproduct from the production of ethanol from wheat, a market that is expected to increase in the near future and lead to an increasing amount of WG as a low-cost material (1, 2).

Interest in developing WG-based packaging materials has increased in recent years. Most of the research has been performed on solution-cast films, but some work has also been done on edible coatings (3–9). Thermoforming, such as extrusion (10–14), does not require the time-demanding drying procedures associated with casting (15, 16) and could be of interest for, for example, paper coating and sheet production. The extruded sheets can later be compression molded into, for example, trays (17).

A plasticizer is needed to avoid brittleness and to enhance the processability of WG. Glycerol from oil plants is probably the most common plasticizer used in protein films, but several other plasticizers have also been studied (18–20). One issue that has to be considered in the development of protein-based films is the aging due mainly to plasticizer loss. The loss/migration is high when the protein film is in contact with an absorbing medium, for example, paper (21). A possible way to limit this migration would be to laminate the protein film with a nonabsorbing material.

Several other aspects also have to be considered when packaging is developed, one of the most important being the water vapor transmission rate (WVTR). The water vapor barrier has to be improved to make WG-based films interesting in food packaging (22). It should, however, be kept in mind that a petroleum-based oxygen barrier polymer such as poly(ethylene-co-vinyl alcohol) (EVOH) needs to be protected by/laminated with a moisture-proof polymer layer. The aim of the present work was to make a fully renewable laminate, and this limited significantly the number of available polymers to protect WG from a moist environment. Both poly(lactic acid) (PLA) and renewable polyethylene are of interest (23) but, because of the limited availability of the latter, PLA was used here. PLA is far from being moisture-proof, but relative to WG it is much better.

This is, to our knowledge, the first study of WG laminated with PLA using compression molding. Bi- or trilayered films with PLA and proteins (vital WG and soy protein isolate) have been made and studied earlier, but the PLA was then coated from a chloroform solution (24, 25). Those studies showed the potential of adding a PLA layer; the WVTR was reduced by a factor of ca. 40, compared to the uncoated protein film. Nevertheless, lamination by thermoforming is perhaps a more interesting method because it is a solvent-free process.

The overall purpose of this study was to assess the potential of WG/PLA laminates as packaging films, the assessment being made by evaluating bending stiffness index, peel strength, tensile properties, WVTR, and oxygen permeability under dry and humid conditions. In addition, the migration of plasticizer (glycerol) was evaluated.

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**Table 1.** Mechanical Properties of the Gluten, PLA, and Laminate Films

sample <sup>a</sup>	modulus (MPa)	max stress (MPa)	elongation at max stress (%)	thickness ( $\mu\text{m}$ )	grammage ( $\text{g}/\text{m}^2$ )	bending stiffness index ( $\text{Nm}^2/\text{kg}^3$ )
WG-110-0	2641 (261) <sup>b,c</sup>	14.04 (9.2) gh	0.50 (0.27) d	227 (20)	310 (27) c	0.152 (0.024) a
WG-110-5	2231 (61) c	15.46 (3.41) gh	0.72 (0.15) d	249 (9)	289 (5) cd	0.104 (0.003) de
WG-110-10	1197 (96) i	14.50 (1.8) gh	1.84 (0.56) d	233 (7)	290 (7) cd	0.032 (0.001) f
WG-110-20	118 (18) k	4.82 (0.67) i	58.28 (10.86) b	206 (11)	253 (14) de	ND <sup>d</sup> g
WG-110-30	26 (5) k	2.52 (0.2) i	115.9 (15.05) a	177 (8)	224 (2) e	ND g
WG-130-0	2623 (213) b	20.68 (7.48) fg	0.64 (0.35) d	264 (14)	309 (10) c	0.140 (0.007) ab
WG-130-5	2486 (41) b	24.22 (5.6) ef	1.02 (0.33) d	233 (6)	304 (21) c	0.134 (0.016) abc
WG-130-10	2086 (84) cd	24.50 (3.82) ef	1.42 (0.29) d	227 (12)	295 (10) cd	0.093 (0.011) e
WG-130-20	392 (27) j	8.52 (0.79) hi	34.55 (13.81) c	223 (9)	267 (12) cde	0.011 (0.000) fg
WG-130-30	62 (9) k	4.31 (0.55) i	108.6 (9.2) a	187 (5)	235 (14) e	0.002 (0.000) g
PLA	3200 (106) a	63.67 (1.88) a	2.38 (0.1) d	122 (10)	154 (9) f	0.148 (0.011) a
L-110-0	2034 (66) cde	33.87 (1.01) cd	2.57 (0.09) d	380 <sup>e</sup> (16) 136 <sup>f</sup>	476 (20) ab	0.137 (0.005) ab
L-110-5	1918 (31) def	30.98 (5.25) de	2.05 (0.57) d	391 (19) 147	472 (16) ab	0.128 (0.008) abc
L-110-10	1731 (36) fg	41.82 (5.96) bc	2.25 (0.33) d	387 (10) 143	465 (20) ab	0.123 (0.007) bcd
L-110-20	1545 (49) gh	41.05 (1.01) bc	2.97 (0.07) d	374 (11) 130	450 (22) ab	0.116 (0.002) bcde
L-110-30	1526 (64) gh	37.39 (1.3) cd	2.79 (0.09) d	347 (19) 103	444 (24) b	0.110 (0.004) cde
L-130-0	2049 (91) cd	35.96 (3.09) cd	2.25 (0.49) d	383 (10) 139	497 (10) a	0.140 (0.001) ab
L-130-5	2111 (21) cd	32.65 (2.83) d	1.56 (0.16) d	383 (10) 139	499 (6) a	0.135 (0.001) abc
L-130-10	1814 (69) ef	47.21 (4.82) b	2.47 (0.34) d	408 (34) 164	499 (40) a	0.137 (0.008) ab
L-130-20	1450 (28) h	40.74 (1.39) bc	2.97 (0.13) d	390 (11) 146	474 (11) ab	0.118 (0.007) bcde
L-130-30	1398 (25) hi	36.65 (0.83) cd	2.78 (0.09) d	376 (12) 132	435 (7) b	0.118 (0.002) bcde

<sup>a</sup> Samples are denoted as follows: The first abbreviation indicates whether it is the pristine wheat gluten (WG), poly(lactic acid) (PLA), or laminate film (L). The following number is the thermoforming temperature for the gluten film, and the last number is the plasticizer content in the gluten layer. <sup>b</sup> The values in parentheses are standard deviations. <sup>c</sup> Levels not followed by the same letter are significantly different, according to the Tukey–Kramer's HSD test ( $p = 0.05$ ). <sup>d</sup> ND, not detectable. <sup>e</sup> The average total thickness of the laminate. <sup>f</sup> The average thickness of the WG layer in the laminate.

## EXPERIMENTAL PROCEDURES

**Materials.** The vital WG powder was kindly supplied by Reppe AB, Lidköping, Sweden. According to the supplier, the gluten protein content (according to Mod NMKL nr6, Kjeltec,  $N \times 6.25$ ) was 85.2%, the starch content (according to Mod. NMKL Nr 6, Kjeldahl, Ewers) was 5.84%, the concentration of fats (according to Soxtec, Lidfett.OA.19, tecator AN 301) was 1.2%, and the ash content (according to NMKL 173 s ed) was 0.86%, all on a dry weight basis. The water content (according to NMKL 23 1991) was 6.9% on a total weight basis. Glycerol with a concentration of  $\geq 99.5$  wt % and a water content of  $\leq 0.5$  wt % was supplied by Karlshamns Tefac AB, Karlshamn, Sweden. The WG/glycerol films are hereinafter referred to as “WG”. Polylactide (PLA, NatureWorks 4042D) was kindly obtained from NatureWorks LLC, Blair, MN.

**Sample Preparation.** The WG/PLA laminates were prepared in a two-step procedure, in which the materials were compression molded separately to films in a Table-Top Press, Polystat 200T (Servitec Maschinenservice GmbH, Germany). In the first step a dough was prepared by mixing wheat gluten with 0, 5, 10, 20, or 30 wt % glycerol (based on the total weight of protein and glycerol) for 5 min at 150 rpm, with a mortar agate (VWR International GmbH, Germany). Six grams of the dough was subsequently placed in an aluminum frame ( $125 \times 125 \times 0.1$  mm<sup>3</sup>) between Mylar foils, which in turn were placed between metal plates. The compression molding of the dough was then performed at 100, 110, 120, and 130 °C during 10 min using a 400 bar pressure set on the machine gauge. After the molding, the plate assembly was removed from the press and the WG film was separated from the frame by a scalpel. The same hot-press and molding frame were used to compression mold 3 g of the PLA pellets to thin films using a set pressure of 200 bar for 5 min at 190 °C.

The second step involved laminating the WG film (prepared at 110 or 130 °C) between two PLA films by applying a pressure of 100 bar at 110 °C for 10 min. For the peel test, other temperatures were also used (see below). The pressed laminates were removed from the press and stored on Mylar foils at 23 °C and 50% relative humidity (RH) for at least 2 days prior to the measurements.

Samples are denoted as follows: the first letters indicate whether it is the pristine wheat gluten (WG), the poly(lactic acid) (PLA), or the laminate

film (L). The second number is the thermoforming temperature for the WG film, and the last number is the plasticizer content in the WG layer. Hence, L-130-30 means a laminate film in which the WG layer, containing 30 wt % glycerol, was thermoformed at 130 °C.

**Thickness Measurement.** The film thickness was measured at a pressure of 100 kPa in accordance with SCAN-P 7:96 (26) and determined as an average of five different measurements on each individual specimen, four along the perimeter and one at the center using a Lorentzen & Wettre (Kista, Sweden) Type 21 micrometer. The sample designations with average film thicknesses are presented in **Table 1**.

**Tensile Test.** A Zwick Z010 tensile tester, controlled by a testXpert 7.1 operation program (Zwick GmbH & Co., Germany) and equipped with a 500 N load cell, was used to determine the Young's modulus, the maximum stress, and the strain at maximum stress of the WG and the PLA films, as well as of the WG/PLA laminates. The measurements were performed at 23 °C and 50% RH, according to ASTM D 882-02, on specimens cut to a rectangular shape (10 mm width and 60 mm length) with a scalpel (27). The rectangular shape was used because the WG samples with  $< 15$  wt % glycerol were too brittle to be punched into dumbbell-shaped specimens. An initial grip-to-grip distance of 40 mm and a crosshead speed of 100 mm/min were used. At least five replicates (usually 10 replicates) cut from each sample were tested.

**Peel Test.** The adhesion strength between the WG and PLA layers was assessed according to ASTM F 88-05 (28) for samples made at the different lamination temperatures. Additional laminates for the peel test with WG containing only 30 wt % glycerol were prepared at temperatures between 110 and 150 °C, with a 10 °C increment, using the lamination method described above. The peel strengths were determined at 23 °C and 50% RH using the Zwick Z010 tensile tester and load cell. An initial grip distance of 50 mm and a crosshead speed of 200 mm/min were used. At least five replicates from each sample were measured.

**Bending Resistance Test.** The stiffness index was assessed for single films and laminates according to SCAN-P 29:95 (29) at 23 °C and 50% RH using a Lorentzen & Wettre stiffness tester. A rectangular specimen, cut with a scalpel to  $38 \times 50$  mm<sup>2</sup>, was mounted with the short side in a clamp so as to allow bending in the horizontal direction. The distance between the

clamp and the blunt edge by means of which the force was applied was 25 mm. The force needed to bend the specimen  $7.5^\circ$  was determined. The bending stiffness index ( $S_i$ ;  $\text{Nm}^7/\text{kg}^3$ ) was obtained from the force ( $F$ , Nm) and the grammage ( $w$ ,  $\text{kg}/\text{m}^2$ ) (cf. **Table 1**),  $S_i = F/w^3$ , and was calculated as the average of three replicates.

**Infrared Spectroscopy (IR).** Infrared spectra were obtained using a Perkin-Elmer Spectrum 2000 FTIR spectrometer (Perkin-Elmer Inc.) equipped with an MKII Golden Gate and single-reflection ATR system with a diamond crystal and controlled by the program Spectrum version 2.00, from Graseby Specac Ltd., U.K. The spectra were taken as an average of 16 scans between 4000 and  $600\text{ cm}^{-1}$  at intervals of  $1\text{ cm}^{-1}$  and with a resolution of  $4\text{ cm}^{-1}$ .

**Field-Emission Scanning Electron Microscopy (FE-SEM).** Cross sections of the laminates, prepared by cryofracturing, were examined in a Hitachi S-4800 FE-SEM. The test specimens were stored in a Denton vacuum under 0.1 mbar vacuum pressure and then coated for 60 s with a gold powder layer using an Agar high-resolution sputter coater (model 208RH), equipped with a gold target/Agar thickness monitor controller. Micrographs with different magnifications were taken using the video capture computer program InterVideo WinDVR from InterVideo Inc.

**Glycerol Mass Loss.** Laminates were placed on a blotting paper (Blotting Paper 1600, 220 diameter, from VWR International), and kept for 3 days or 1, 2, 3, 4, 10, 17 weeks at  $23^\circ\text{C}$  and 50% RH. The laminates were placed on the paper support, a moderately fast absorbing medium, because several future packaging applications may involve WG laminated/coated onto paper or paperboard. The mass loss of the films due to migration of glycerol was determined gravimetrically (AT261 Delta Range, Mettler Toledo GmbH, Germany) at the same conditions. Three replicates from each sample were weighed.

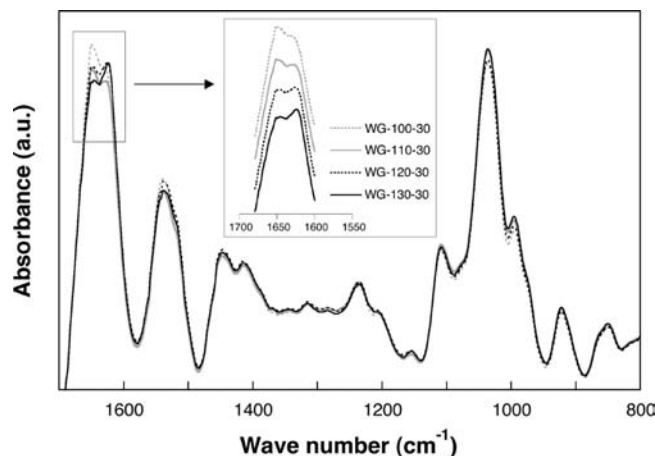
**Oxygen Permeability (OP).** The oxygen transmission rate (OTR) was determined using a Mocon Ox-Tran 2/20 apparatus equipped with a coulometric oxygen sensor (Modern Controls Inc.). The measurements were performed at  $23^\circ\text{C}$  and 0 or 50% RH according to ASTM D3985-95 (30). The WG/PLA laminates were tightly sandwiched between two pieces of aluminum foil mask to give a circular exposure area of  $5\text{ cm}^2$  and mounted in isolated diffusion cells that were subsequently purged with nitrogen gas (2% hydrogen) to obtain the background oxygen leakage. After background correction, one side of the sample was exposed to flowing oxygen (gas purity = 99.95%) at atmospheric pressure, and the rate of flow of oxygen through the sample was measured until a steady state was reached. To be able to compare data the OTR was normalized with respect to the oxygen pressure and the thickness to yield an OP.

**Water Vapor Transmission Rate.** The WVTR was measured on each sample at  $38^\circ\text{C}$  and 90% RH using a Mocon Permatran-W 3/31 according to ASTM F 1249-90 (31). Specimens were tightly sandwiched between two pieces of aluminum foil to give a  $5\text{ cm}^2$  exposure area. The WVTR presented were steady state values normalized with respect to the sample/laminate thickness.

**Statistical Analysis.** Statistical analysis was carried out with a statistical software program JMP version 5 (SAS Institute Inc.). Unless stated otherwise, a Tukey–Kramer HSD (honestly significant difference) test, which performs a statistical means comparison for all pairs, was used at a significance level of 0.05.

## RESULTS AND DISCUSSION

**Properties of WG Films.** The effects of molding temperature and glycerol concentration on the mechanical properties have been well characterized elsewhere (17, 22). Nevertheless, the specific WG film properties had to be determined here for comparison with the properties of the final laminates. The choice of the compression molding temperatures used in this study was based on findings from previous studies (17, 22), where it was shown that wheat gluten films molded below  $100^\circ\text{C}$  yielded insufficient denaturation and gliadin polymerization, resulting in a sticky and dough-like film, whereas those molded above  $130^\circ\text{C}$  resulted in a dark-brown partly degraded film. **Figure 1** displays the infrared spectra of gluten films. The absorbance in the amide I region results mainly from the stretching vibrations of the carbonyl groups and is a good fingerprint of the secondary

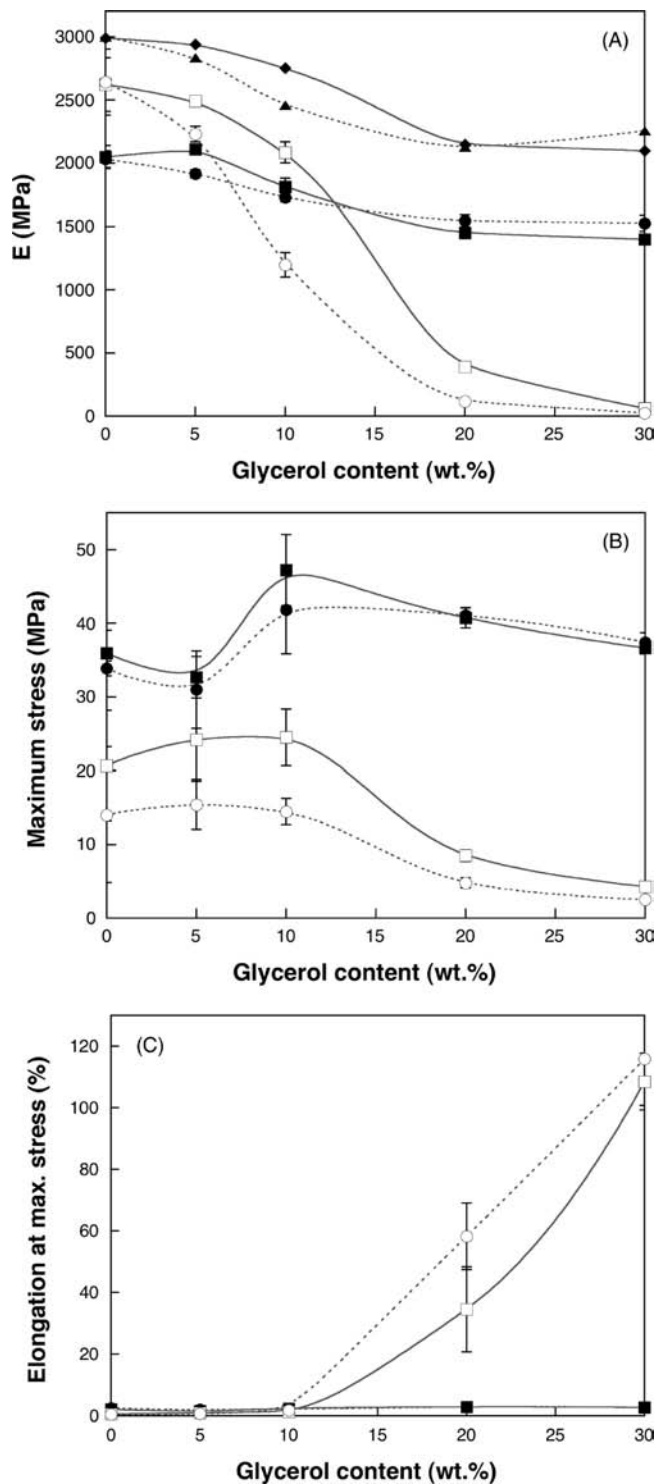


**Figure 1.** Effects of the thermoforming temperature on the WG protein secondary structure as revealed by changes in the amide I infrared region ( $1600\text{--}1700\text{ cm}^{-1}$ ).

protein structure (32). The bands in the vicinity of 1650, 1632, and  $1618\text{ cm}^{-1}$  can be assigned to, respectively,  $\alpha$ -helical conformations/unordered structure, intramolecular  $\beta$ -sheets, and intermolecular  $\beta$ -sheets with a high level of hydrogen bonding. The band at  $\sim 1618\text{ cm}^{-1}$  was prominent in the film molded at 120 and  $130^\circ\text{C}$ , whereas the band at  $1650\text{ cm}^{-1}$ , featuring  $\alpha$ -helices and random coil structures, dominated in the spectra of the films molded at 100 and  $110^\circ\text{C}$ . Hence, the higher temperatures induced greater aggregation/polymerization in the WG films. To limit the number of samples in the subsequent laminate studies, only the 110 and  $130^\circ\text{C}$  molding temperatures were used. The mechanical properties of single films compression molded at 110 and  $130^\circ\text{C}$  are given in **Figure 2** and **Table 1**. The higher molding temperature often yielded the highest average modulus and maximum stress and the lowest maximum strain, a result that can be explained on the basis of the IR data in **Figure 1** (a higher degree of protein polymerization at the higher temperature). The standard deviation in the Young's modulus and strength data of the WG films with 0% glycerol was high, due to the difficulty in measuring such brittle materials with a tensile tester. As expected, at least when considering average values and the entire glycerol range, glycerol lowered the stiffness and strength and increased the extensibility (**Figures 2** and **Table 1**). Glycerol also reduced the grammage of the samples (**Table 1**), a direct effect of the decrease in dough viscosity leading to a more even filling of the mold and more flash.

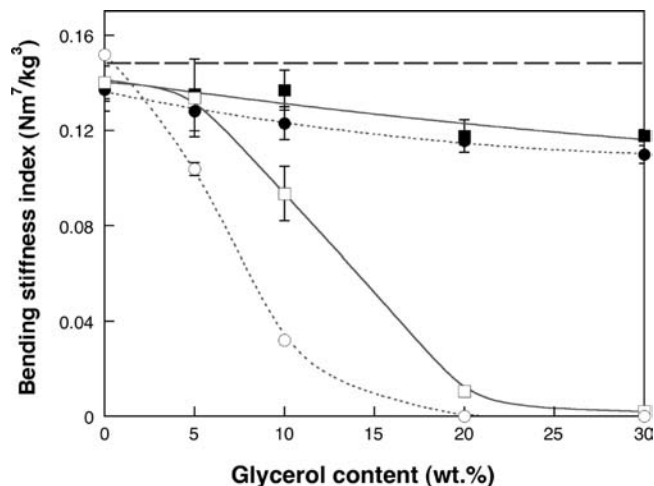
**Mechanical Properties of Laminates.** In the laminate, both materials contribute to the Young's modulus and maximum stress. For the modulus, it should be possible to use an "additive" relationship:  $E_{\text{tot}} = V_{\text{WG}} \times E_{\text{WG}} + V_{\text{PLA}} \times E_{\text{PLA}}$ , where  $V$  is the relative layer thickness (calculations are not shown, but input values were taken from **Table 1** and the thickness of the PLA was assumed to be unaffected by the lamination). As shown in **Figure 2A**, the calculated modulus was consistently higher than the measured value, the difference decreasing marginally with increasing glycerol concentration. The figure also shows that the decrease in laminate modulus with increasing WG layer glycerol content is modest in relation to what is observed for the single WG films. One hypothesis for why the laminate modulus was lower than the calculated value, and in fact was lower than both the WG and PLA values at lower glycerol contents, is that the layers were able to glide relative to each other during the tensile testing. The strength (maximum stress) was increased when the WG films were laminated, due to the higher strength of PLA (**Table 1** and **Figure 2B**). The difference between laminated and single WG film strength





**Figure 2.** Influence of glycerol content in the WG layer on the laminate tensile properties: (A) Young's modulus; (B) maximum stress; (C) elongation at maximum stress (■, L-130; ●, L-110; ◆, L-130 calculated; ▲, L-110 calculated; □, WG-130; ○, WG-110). The calculated modulus was obtained on the basis of the measured value of each layer given in Table 1.

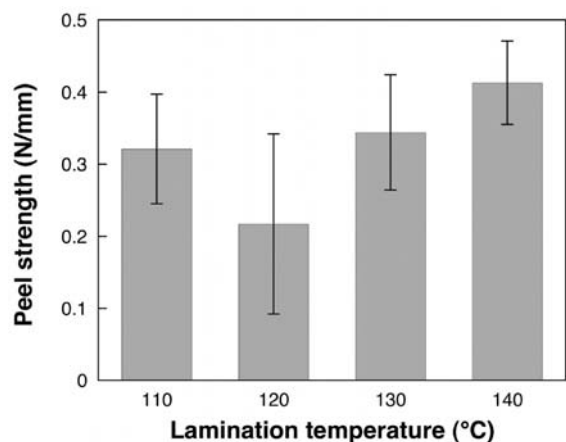
values was particularly high at the higher glycerol contents. Interestingly, whereas the lamination yielded stronger films, the extensibility was also somewhat greater for the low glycerol content laminate films, although the difference was not significantly different (Tukey–Kramer HSD) (Table 1 and Figure 2C). At a high plasticizer content ( $\geq 20$  wt %), however, a large increase in extensibility was observed only for the single WG films.



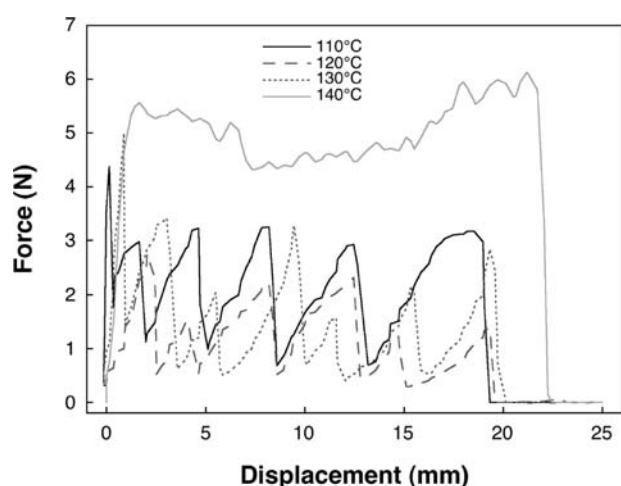
**Figure 3.** Bending stiffness index of the laminate films (■, L-130; ●, L-110) and WG films (□, WG-130; ○, WG-110) as a function of glycerol content and WG layer thermoforming temperature. The dotted line indicates the PLA value.

The bending data showed, as expected, that the plasticizer had a significantly lower impact on the stiffness when the WG film was laminated with PLA than it had in a single WG film (Table 1 and Figure 3). It seemed with few exceptions (although the differences were small and mostly insignificant) that the higher molding temperature (130 °C) promoted a higher bending stiffness in both the single and laminated films. The tensile stiffness data were, however, less conclusive; indeed, the 130 °C single films were generally stiffer (although often not significantly different) than the 110 °C films; however, for the laminates, the 110 and 130 °C strength values were indistinguishable. A hypothesis is that the WG/PLA interlayer adhesion strength decreased with increasing molding temperature because the degree of protein denaturation/aggregation became higher and that this reduced the WG layer “tackiness”. At the same time, an increase in protein polymerization yields a stiffer WG layer. It was reported earlier that the peel strength of WG films containing 30 wt % glycerol decreased by  $> 50\%$  when the molding temperature was increased from 110 to 130 °C (22).

The peel strength of heat-sealed WG has been reported to increase in the presence of glycerol (22), and we noticed here, through delamination, an inferior interlayer adhesion at low glycerol contents. The peel strength of the laminates also increased with increasing glycerol content (not shown). The average peel strength increased by ca. 20% when lamination was carried out at 140 °C instead of at 110 °C (Figure 4). However, Tukey–Kramer's HSD test ( $T = 110$  °C (ab), 120 °C (b), 130 °C (a), 140 °C (a), values at temperatures with the same letter were not significantly different) indicated that the differences were basically independent of the lamination temperature. Visual determination of the mode of specimen failure revealed that adhesive failure occurred in all of the laminates regardless of the actual lamination temperature. The load–displacement curves indicated that the force for the sample laminated at 140 °C was relatively constant and smooth during the peeling operation, indicating “normal” peeling (Figure 5). However, the peeling was discontinuous for the samples laminated below 140 °C. Even though the peel strength was greater using a 140 °C lamination temperature, the mechanical integrity and thickness uniformity of the laminate were poor. As a result, the temperature at which the laminate was most homogeneous and uniform in thickness (110 °C,



**Figure 4.** Effects of lamination temperature on peel strength of L-110-30. The bars indicate the standard deviation.



**Figure 5.** Typical load–displacement curves of the laminate films during the peel test. The lamination temperature ranged from 110 to 140 °C.

**Figure 6**) was thereafter used as lamination temperature in subsequent studies.

**Migration.** The effects of mass loss, which is basically due to a loss of glycerol, on the mechanical properties have been studied previously (21). The loss of plasticizer (glycerol) is indeed a problem in keeping the mechanical properties stable during storage. Here, however, it was found that by laminating WG with PLA the loss was suppressed/absent (**Figure 7**). The problem with a migrating plasticizer may, consequently, be avoided by lamination with a nonabsorbing material, a finding that opens the way to a possible future scenario in which WG is used in laminates (e.g., PLA/WG/PLA) extrusion coated onto paperboard. The glycerol content remained unchanged during the evaluation period of up to 4 months, even for the samples with the highest glycerol concentration (30 wt %). Unexpectedly, a small mass gain was observed in all of the test samples, probably because of small fluctuations in temperature and humidity in the climate room with its target climate of 23 °C and 50% RH. Even very small fluctuations ( $\pm 1$ –2% RH) may affect the samples as well as the paper support.

**Oxygen and Water Vapor Transmission Rates.** **Table 2** shows the oxygen and water vapor transport properties of the laminates and of the PLA and one of the WG films (WG-110-30). The laminate oxygen transmission rate generally decreased with decreasing glycerol concentration. Between 30 and 10 wt %

glycerol the decrease was always monotonic. It was interesting to note that even at 50% RH the low-glycerol laminates showed relatively low permeabilities. The thickness of the gluten layer in this case was 100–150  $\mu\text{m}$  (**Table 1**). Using the PLA data and the laminate relationship

$$L_t = P_t \sum_i L_i/P_i$$

( $L$  and  $P$  are thickness and permeability, index  $i$  is the number of layers, and  $t$  indicates the total laminate values), it was possible to estimate the WG layer oxygen permeability. It ranged between ca. 0.007 and 6.9  $\text{cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$  at 50% RH, all depending on sample series, glycerol content, and actual thicknesses used, and from 0.002 to 0.4  $\text{cm}^3 \cdot \text{mm}/(\text{m}^2 \cdot \text{day} \cdot \text{atm})$  at 0% RH.

The WVTR values show that the PLA layers protect the WG layer from moisture. The average WVTR of most laminates was  $< 10 \text{ g} \cdot \text{mm}/(\text{m}^2 \cdot \text{day})$  at 38 °C and 90% RH, whereas the value of the pure WG films was out of range (**Table 2**).

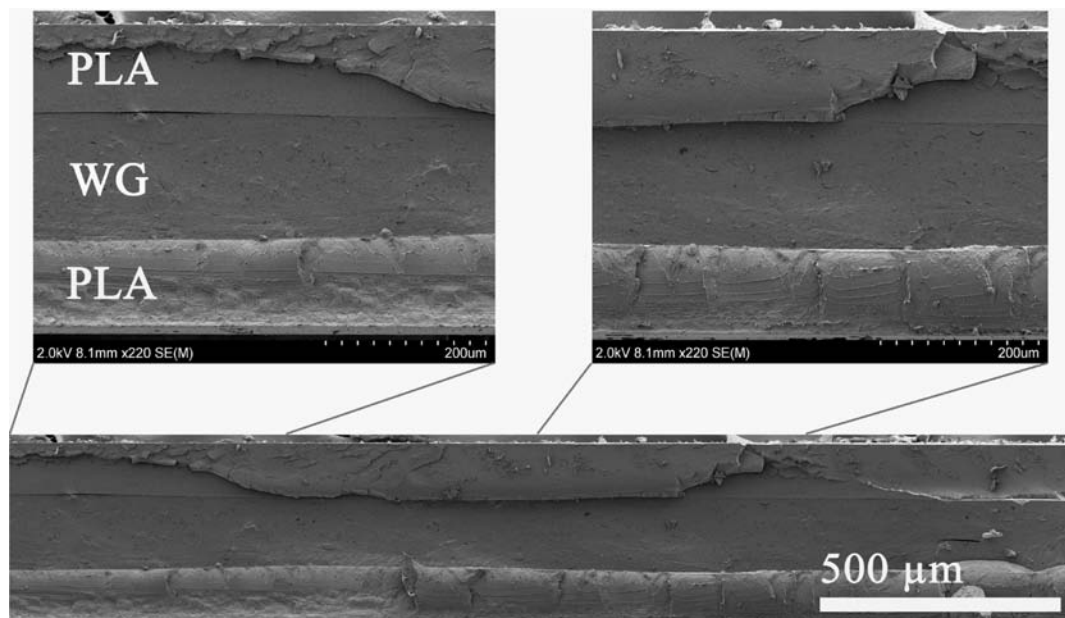
Some comments should be made regarding the measurements of the transport properties. To begin with, it is important to note that, for the sake of limiting the number of measurements, comparisons between the laminates and WG were made with WG-110-30 representing the WG films. Of course, the other films may have had different transport properties, but for an overall qualitative view of the trends we believe this was sufficient. The 0% RH OP and the first set of WVTR measurements (including all values on pure WG-110-30 and PLA) were performed on comparatively new ( $< 1$  month old) laminates, whereas the 50% RH OP and the second set of WVTR were performed on films that had been stored for  $> 1$  year on blotting paper. The laminate WVTR data revealed that the older samples had always higher values than the new samples (compare the first and second sets of WVTR measurements in **Table 2**). This suggests that time-induced material changes, other than those associated with plasticizer loss, may have occurred. It is possible that changes in the protein structure, due to, for example, oxidation of sulfhydryl groups, could occur. Morel et al. (33) showed that storage time and conditions (temperature and RH) affected thiol oxidation and that this led to the formation of protein polymers of large molecular size.

It is interesting to note that the laminate moisture barrier was, in several cases, better than that of the individual components (PLA and WG). Furthermore, it was interesting to compare the measured OP and WVTR data with data for conventional and “barrier” plastics. As can be seen in **Figure 8**, a laminate with 10 wt % glycerol in the WG layer had a WVTR value similar to that of polyamide 6 (PA 6). Its OP value at 0% RH was similar to that of the liquid crystalline polymer (Vectran), among the best oxygen barrier polymers on the market.

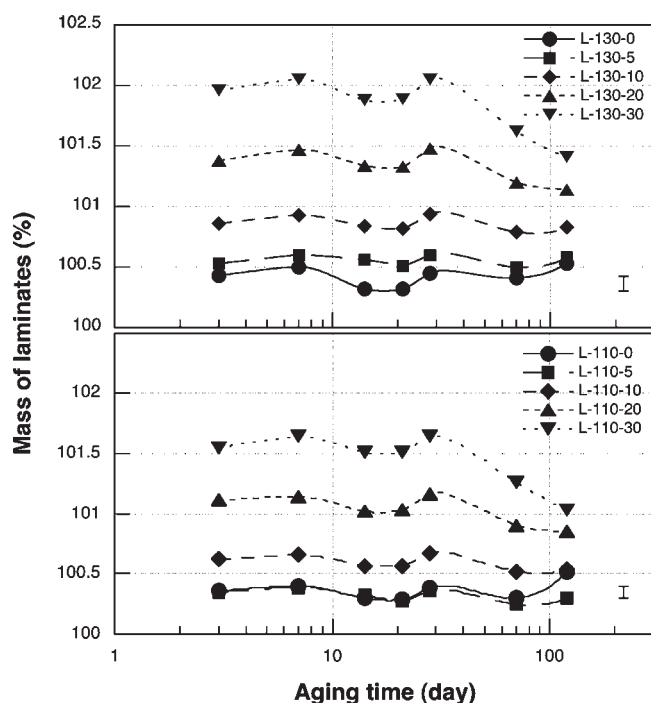
**Conclusions.** The major findings in this study were as follows.

With the use of two supports (PLA layers), it was possible to produce WG-based laminates with very low plasticizer content (0–10 wt %) that were stronger than the single/unsupported WG films. At these low glycerol contents, the barrier properties were close to those of oil-based barrier plastics. Hence, this may be considered as a first step toward producing competitive WG laminates. Further work is needed to improve the interlayer adhesion at the lowest glycerol loadings and to improve, if necessary, the laminate flexibility and toughness.

The laminate did not lose any plasticizer during a period of 17 weeks. Lamination may be the way to improve the long-term WG properties in “absorbing” environments, at least with regard to plasticizer-dependent properties. This is an important finding for



**Figure 6.** FE-SEM images of the cryofractured surface of the WG/PLA laminate film L-110-30. Note that the irregular PLA fracture surfaces were a consequence of the cryofracturing process.



**Figure 7.** Mass of the laminates placed on paper for up to 17 weeks. 100% corresponds to the mass of the unaged samples. The standard deviation was calculated for each data point in the figure, and for clarity only the maximum of these is shown in the bottom right corner.

future WG applications as, for example, barrier coatings on paper and paperboards.

The large drop in bending stiffness with increasing glycerol content, observed in the single WG films as a consequence of plasticization, was significantly smaller for the laminates, because of the stiffening effect of the two adjacent PLA layers. The tensile tests on the laminates showed that glycerol had only a small, if any, effect on the Young's modulus, maximum stress, and elongation at maximum stress, probably again due to the supporting adjacent PLA layers.

**Table 2.** Oxygen and Water Vapor Barrier Properties of the WG, PLA, and Laminate Films

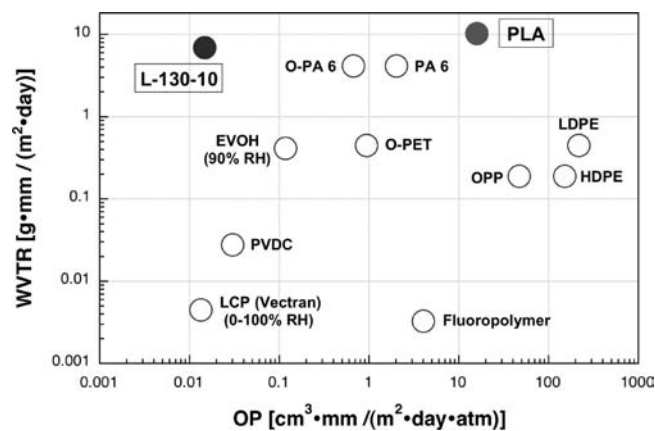
sample	OP ( $\text{cm}^3 \cdot \text{mm}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$ )		WVTR ( $\text{g} \cdot \text{mm}/\text{m}^2 \cdot \text{day}$ )
	at 23 °C, 0% RH	at 23 °C, 50% RH	at 38 °C, 90% RH
WG-110-30	0.117/0.329 <sup>a</sup>	7.771/8.156	OR <sup>b</sup>
PLA	18.093/15.872	18.115/16.691	10.95/9.20
L-110-0	0.007	0.362 <sup>c</sup> /0.452 <sup>c</sup>	4.62/8.63 <sup>c</sup>
L-110-5	0.092	0.024 <sup>c</sup>	5.91/8.18 <sup>c</sup>
L-110-10	0.029	0.271 <sup>c</sup> /0.116 <sup>c</sup>	4.95/9.31 <sup>c</sup>
L-110-20	0.153	3.478 <sup>c</sup> /4.822 <sup>c</sup>	7.66/12.58 <sup>c</sup>
L-110-30	0.977	10.498 <sup>c</sup> /11.175 <sup>c</sup>	8.00/12.51 <sup>c</sup>
L-130-0	0.036	0.056 <sup>c</sup>	6.23/8.86 <sup>c</sup>
L-130-5	0.087	0.256 <sup>c</sup> /0.083 <sup>c</sup>	6.29/7.98 <sup>c</sup>
L-130-10	0.015	0.856 <sup>c</sup> /0.841 <sup>c</sup>	4.48/9.06 <sup>c</sup>
L-130-20	0.043	5.163 <sup>c</sup> /5.344 <sup>c</sup>	4.94/12.79 <sup>c</sup>
L-130-30	1.038	10.186 <sup>c</sup> /9.967 <sup>c</sup>	7.90/13.01 <sup>c</sup>

<sup>a</sup> Double values correspond to duplicate measurements. <sup>b</sup> OR, out of range, i.e., >1200. <sup>c</sup> The measurements were performed on the laminates stored for >1 year on blotting paper.

Considering the whole glycerol range, the OPs of the laminates generally decreased with decreasing glycerol content. The WVTR values showed that the PLA layers did, to a considerable extent, protect the WG layers from moisture. In fact, the laminate values were often lower than those of any of the constituents (PLA and WG).

To conclude, the studied laminates showed potential to be used in drier food applications and environments where an oxygen barrier is of interest. The laminate properties obtained were promising, from a general perspective, but need to be compared with properties of existing packaging systems for the specific food product, before the overall interest and market competitiveness can be determined. The purpose of the present study was not to develop a packaging for a specific product, it was instead aiming to provide a base from where a second study could be initiated. The latter would include issues such as how to scale up the process, the actual packaging design, filling and sealing issues,





**Figure 8.** Permeability data of the laminate, PLA, and synthetic polymers. The permeability of the plastic materials was obtained from ref 34. Unless stated otherwise, the WVTR data were obtained at 38 °C and 90% RH and the OTR data at 23 °C and 0% RH.

and effects of distribution and handling. Also important are migration issues, end user aspects, and food quality as a function of storing conditions/times.

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