

Improving Wheat Gluten Materials Properties by Kraft Lignin Addition

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ABSTRACT: The industrial production of wheat gluten (WG)-based biomaterials implies to improve their actual mechanical properties as well as to reduce their water sensitivity. In this study, the effect of Kraft lignin (KL) content on the processability and on the physical properties of WG materials was investigated. WG plasticized with glycerol was blended with KL, and processed into materials by mixing and thermomolding. Materials were characterized by dynamic mechanical thermal analysis, tensile test, and water absorption measurements. The introduction of KL in plasticized WG resulted in an increase of the mate-

rial glass transition temperature (T_g) and in a strong decrease of the rubbery storage modulus, which will favor industrial processing. The increase in T_g did not follow a simple mixing rule, demonstrating specific interaction between KL and WG. The resulting materials effectively showed improved properties when compared with pure WG-based materials: they exhibited higher tensile strength and lower water sensitivity in ambient conditions. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1391–1399, 2012

Key words: biomaterials; biopolymers; viscoelastic properties

INTRODUCTION

Wheat gluten (WG) is the coproduct of the starch industry, whose production is expected to strongly increase with bioethanol demand. It is mainly composed of two types of protein, namely gliadin and glutenin, which are responsible for its unique viscoelastic properties. WG is used as food additive; however, due to celiac disease, a considerable interest is given on nonfood applications such as the production of biodegradable materials for short-lived applications and nonfood packaging. An adequately plasticized WG can be processed using extruders or injection molding presses.¹ WG-based materials are fully biodegradable² and their mechanical properties which can be modulated according to the plasticizer content³ or to the crosslinking level.⁴ However, these mechanical properties remain lower than those of synthetic materials, and WG materials present a strong sensitivity to relative humidity and water absorption.

Blending of WG with other biodegradable polymers such as polyester⁵ did not significantly improve the properties, because of the nonmiscibility of those macromolecules. The chemical modification

of the polyester, for example, by grafting,⁶ gave better results in terms of mechanical properties and water sensitivity, i.e., the tendency of materials to absorb large quantities of water when directly immersed in an aqueous liquid, but significantly increased the final production cost.

The blending of WG with others natural resources could thus be envisaged as a new way to improve its properties while preserving its biodegradability. Lignin is a suitable candidate: it is one of the most abundant agro-polymers present in wood and plants. It is considered to be a three-dimensional amorphous polyphenolic macromolecule consisting of three types of phenylpropane units, which are forming a complex, highly branched, and amorphous structure.⁷ Native lignin is difficult to obtain, but the paper industry produces large quantities of modified lignin. Commercial lignin obtained from the conventional pulping process is divided into two types. The first type is Kraft lignin (KL), the most produced in the world, which is the by-product of the alkaline pulping process. It is soluble in alkaline solution, but poorly soluble in water at acid or neutral pH. The second one is lignosulfonate (LS) obtained from the acid (sulfite) pulping process. LS is soluble in acid, and due to its sulfonic group,⁸ it can also be soluble in water.⁹

Lignin presents some interesting characteristics to improve material properties, as a filler or as a main component. Huang et al. (2003)¹⁰ showed that the introduction of 10–20 parts of KL as a filler in soy

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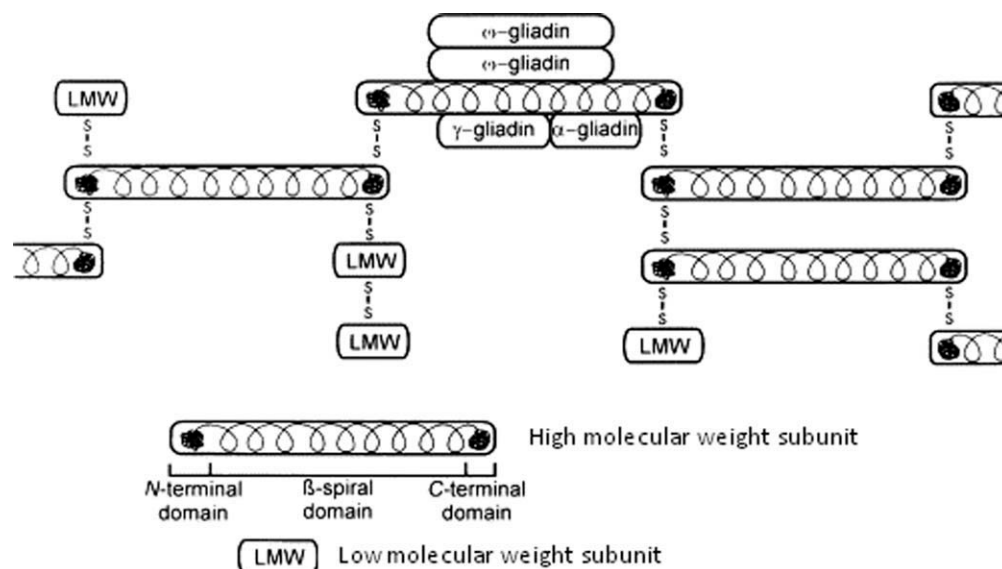


Figure 1 Proposed structural model for wheat gluten.¹⁸

protein plastics enhanced the tensile strength, Young's modulus, thermal stability, and water resistance. Baumberger et al. (1998)⁸ studied the properties of wheat starch films containing 0–30% of commercial KL: up to 20% lignin, a slight increase of elongation and stress at break was observed. Ali et al. (1997)¹¹ used lignin as a main component to fabricate lignin-based blend with poly(vinyl acetate). Recently, El-Wakil (2009)¹² studied the properties of KL-based materials, reinforced with both WG and sodium silicate. This reinforcement improved the diametric tensile strength, and increased the T_g , but this study did not elucidate the role of each of those compounds taken independently.

In a recent study,¹³ we showed that an introduction of KL in WG-based material resulted in a protein depolymerization during processing. The specific role of phenolic groups in this depolymerization was evidenced.¹⁴ However, how the addition of KL affected WG materials mechanical and physical properties has not been investigated, while this information is essential in view of biomaterials production. This present work therefore studied the effect of these interactions on the materials processability, and on their resulting physical properties. In a first step, the properties of both agropolymers, and especially their plasticization with glycerol were characterized separately. Then, plasticized materials were prepared and characterized by mechanical spectroscopy, tensile test, microstructure analysis, and water absorption measurements.

EXPERIMENTAL PROCEDURES

Commercial vital WG was obtained from Amylum Group (Aalst, Belgium). Its protein content was 77% (dry matter) according to the manufacturer. Its mois-

ture content, determined by weighing after heating at 104°C for 24 h, was 10.6% (wet basis). Its density is 1.31 g/cm³.¹⁵ WG is a blend of various types of proteins, being mainly the monomeric gliadin and the polymeric glutenin. The gliadin molecular weight ranges from 30 to 75 kDa, while the glutenin subunits range from 30 to 90 kDa.^{16,17} In WG, polypeptides linear chain are assembled in a supramolecular structure stabilized by covalent disulfide bonds and noncovalent interactions, which gives rise to the organization proposed in Figure 1.¹⁸ Anhydrous glycerol was purchased from Fluka Chemie (Buchs, Switzerland) in p.a. quality. Industrial KL was provided by Westvaco (Charleston, SC). Its M_w and M_n were estimated by gel permeation chromatography to be respectively, 4080 g/mol and 850 g/mol.¹⁹ Lignin is a highly branched polymer formed by the polymerization of three different phenylpropane units,⁷ whose elementary structure is shown in Figure 2 (a complete

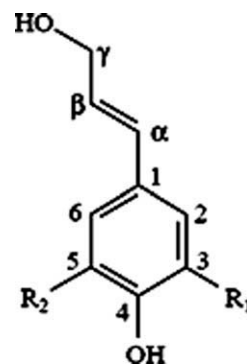


Figure 2 The three building blocks of lignin.⁷ Coniferyl alcohol/guaiacyl: R1 = OMe, R2 = H; Sinapyl alcohol/syringyl: R1 = R2 = OMe; *p*Coumaryl alcohol: R1 = R2 = H.

description of the characteristics of the KL is given in Pouteau et al. 2003¹⁹).

Sample preparation

Gluten, KL, and glycerol were used as such and mixed in a two blades counter-rotating batch mixer turning at a 3 : 2 differential speed (Plasti-corder W50, Brabender, Duisburg, Germany). The total amount of matter introduced in the mixer was always 50 g, to ensure similar filling up. Samples compositions given here are based on the weight of each compounds introduced in the mixer. Torque and product temperature were continuously recorded during mixing. Temperature of the mixing chamber was regulated at 80°C using a regulation temperature unit (Julabo F34, Seelbach, Germany) that provided water circulation in the double jacket of the mixer. Mixing speed and mixing time were 100 rpm and 15 min, respectively. The samples compositions are given in weight percentage (%) of gluten, KL, and glycerol.

Mixed blends were separated in two parts of about 25 g each, successively thermomolded in a square mold (9 cm × 9 cm) at 80°C. A pressure of 9.3 MPa was applied in the hot mold for 15 min. However, at high KL concentrations (around 30% KL), a sample outflow from the mold occurred. The outflowing product had the same visual appearance as the sample remaining in the mold, suggesting this outflow was not specific to the KL component, but originated in a change in the material viscoelastic properties. Therefore, a spacer (2.3 mm of thickness) was used for all studied samples to avoid the direct pressure. This post-treatment was performed in a heated press (PLM 10 T, Techmo, Nazelles, France).

Material properties

Mechanical spectroscopy was performed by applying a strain controlled deformation, using two protocols depending on the material composition and mechanical behavior. In both case, dried materials were used to avoid any water loss during analysis.

Blends with low KL content and gluten/glycerol samples (without KL) were cut to form rectangular samples (10 × 3 × 1 mm³) and then were placed in controlled atmosphere with 0% relative humidity (RH) until their weights were constant. Samples were directly analyzed with a dynamic mechanical thermal analyzer (DMTA IV, Rheometric Scientific, Piscataway, NJ) equipped with a cryogenic system fed with liquid nitrogen. A tensile test was performed with a temperature ramp from -50 to 150°C at a heating rate of 3 °C min⁻¹. A variable sinusoidal mechanical stress was applied to the sample (frequency = 1 Hz) to produce a sinusoidal strain am-

plitude of 0.05%. It was verified that these conditions ensured measurements in the linear viscoelastic domain. During analysis, the storage modulus (E'), the loss modulus (E''), and $\tan \delta$ ($=E''/E'$) were recorded and plotted against temperature for further evaluation of thermal transitions. The glass transition temperature (T_g) was identified as the $\tan \delta$ maximum. Each sample was analyzed in duplicate.

Samples with high KL content, as well as materials from plasticized KL alone, cannot be cut in a rectangular sample due to their high brittleness, and thus cannot be analyzed with the previous method. They were reduced into powder by grinding in presence of liquid nitrogen using a laboratory ball mill (Prolabo, France). Then, they were placed in controlled atmosphere with 0% RH until their weights were constant. About 50 mg of the obtained powder were packed into the material pocket (Triton technology) as described by Garea et al. (2007)²⁰ before dynamic mechanical analysis (Tritec 2000 DMA). Material pocket is a suitable apparatus for the determination of a powder glass transition temperature, without any pretreatment. It consists in a stainless steel envelope, one face being fold on the other, confining the powder in between two stainless steel plates. While the overall mechanical properties determined with this technique are dominated by the stainless steel envelope ones, any significant thermal transition of the powder located in between exhibit a specific signature, and can therefore be identified: it allowed the determination of the product glass transition temperature. A single cantilever bending test was performed with a temperature ramp from ambient temperature to 120°C at a heating rate of 3 °C min⁻¹, a frequency of 1 Hz and a strain of 0.05%. In this case to achieve better precision, T_g was identified as the peak of the first derivative of the storage modulus variation with temperature as proposed by Kasapis (2004).²¹ In addition, WG and KL powder T_g s were also determined using the same protocol, after being placed in a controlled dry atmosphere (0% RH) until reaching a constant weight. Each sample was analyzed in four replicates.

Those two different protocols gave slightly different values for the T_g . The glass transition is a continuous phenomenon occurring on a large range of temperature, so the determination of the T_g relies significantly on the methodology, and on the experimental sample conditioning. The determination of the T_g on a same set of sample with the two protocols showed that the two methods gave a slightly constant difference of about 40°C. Therefore, the first protocol, which is the more conventional method used in thermomechanical analysis, was taken as the reference method, and the values determined with the second protocol were corrected (reduced by

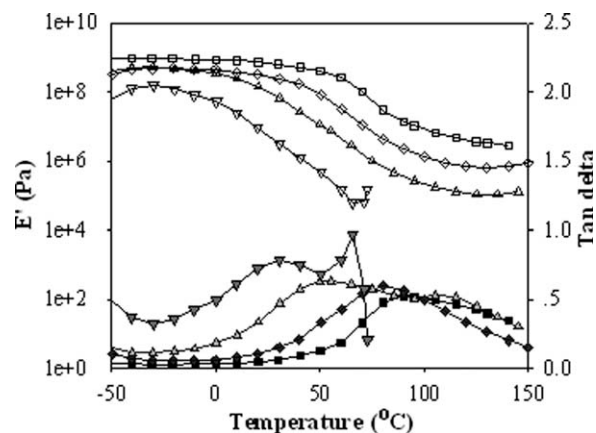


Figure 3 Storage moduli (empty symbols) and $\tan \delta$ (full symbols) of WG-based materials plasticized with 20% (squares), 30% (diamonds), 40% (triangles), and 50% (down triangles) glycerol content, molded at 80°C.

40°C). Besides, this approximation might generate an uncertainty (estimated to be less than 5°C) on the T_g value, it is still significantly less important than the observed differences between the samples for which those different methods have been applied. Moreover, it does not modify the observed tendencies, as the same correction is applied to the same data set. This procedure then allows the direct comparison of the data obtained with the two methods.

Mechanical properties were determined by tensile tests which were performed on a Rheo TAXT2 rheometer (Champlan, France). Samples were cut into dumb-bell-shaped specimens of 75 mm overall length and 4 mm width for the elongating part (5A type, standard ISO 527-2, 1993) and preconditioned at 25°C and 53% RH over a saturated salt solution of $\text{Mg}(\text{NO}_3)_2$ for 1 week. Specimen thickness was measured with a caliper. The initial grip separation was 50 mm and elongation speed was 1 mm s⁻¹. Stress values (MPa) were calculated by dividing the measured force values (N) by the initial cross-sectional area of the specimen (mm²). Strain values were expressed as percentage of the initial length of the elongating part of the specimen ($L_0 = 20$ mm). Young's modulus was determined as the slope of the linear regression performed on the first points taken at least until 3% strain on the stress-strain curve. The values of tensile strengths and elongations at break, as well as Young's moduli, are the means of at least four replicates.

Scanning electron microscopy (SEM) was used to examine the cryofracture surface of the materials. Each sample was laid on conductive carbon cement mounted on aluminum stubs, then sputter coated with platinum.²² They were then observed by SEM (HITACHI S-4500) using an accelerating voltage of 5 kV.

For the determination of water absorption properties,²³ samples (24 mm in diameter) were placed in

controlled atmosphere with 0% RH until their weights were constant (W_i). Then, they were immersed in 50 mL distilled water containing 0.05% NaN_3 (to avoid the microbial growth) at 25°C for 1 week. The swollen samples were wiped and weighed (W_w). Then, they were dried to 0% relative humidity (W_f). Due to the migration of glycerol in the water bath, W_f was always smaller than W_i . Measurements made on WG/glycerol samples demonstrate that after 1 week, all the glycerol has been exchanged with water. Water absorption can therefore be directly compared for sample with similar initial glycerol contents. Each sample was analyzed in duplicate. Water absorption was calculated with the following equation:

$$\text{Water absorption(\%)} = 100(W_w - W_f)/(W_i) \quad (1)$$

RESULTS AND DISCUSSION

Wheat gluten and Kraft lignin plasticization with glycerol

Glycerol is a well known plasticizer of WG, whose plasticizing efficiency was evidenced by a shift in material T_g . Figure 3 presents the evolution of the elastic modulus E' and $\tan \delta$ with the temperature, for WG-based materials with different glycerol content, from -50 to 150°C. At 20 and 30% glycerol content, only one peak of $\tan \delta$, characteristic of the glass transition, was observed in the studied range of temperature. At 40 and 50% glycerol content, two peaks of $\tan \delta$ were observed. The reason for such a reproducible behavior remained unclear, especially when considering the behavior of the elastic modulus at high glycerol content. It might show the limits of measuring the material properties at temperature above the T_g , where elastic moduli are relatively low and phenomena like the leaching out of glycerol may affect the measurement, or being a signature of the presence of a second phase in the sample or of a specific material internal reorganization allowed by the gain in molecular mobility above T_g . The T_g of those samples was identified as the temperature of the first peak, which was not affected by this behavior. The glass transition of KL-based materials plasticized with glycerol with the material pocket method were determined using, in that case, the first derivative of the storage modulus to determine T_g (Fig. 4).

Both KL and WG T_g s are represented on Figure 5 as a function of plasticizer content for comparison. In the native state (without plasticizer), the T_g of WG and KL were, respectively, equal to 193 and 177°C measured using the material pocket method as previously described. Those values are coherent

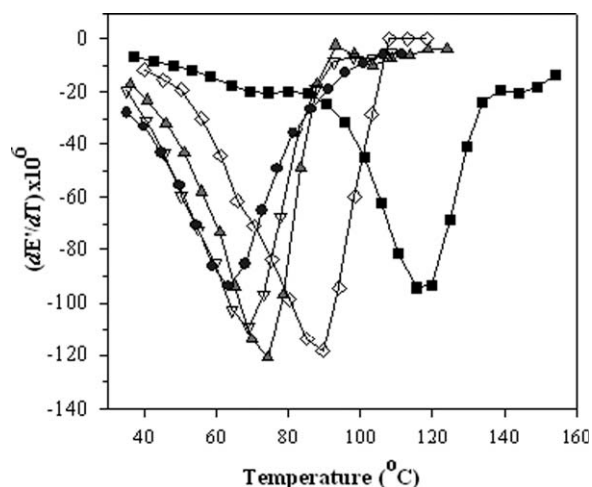


Figure 4 First derivative of the storage modulus as a function of temperature of KL-based materials plasticized with 10% (squares), 20% (diamonds), 30% (triangles), 40% (down triangles), and 50% (rounds) glycerol contents, molded at 80°C.

with the ones in the literatures showing a higher T_g for the protein blend (187°C²⁴ for WG, 160°C,²⁵ or 144°C¹⁹ for KL). In both cases, T_g decreased with increasing glycerol content, which demonstrated the plasticizing effect of glycerol on both polymers. However, glycerol appeared to have a stronger plasticizing effect on WG than on KL as shown in Figure 5.

It has been suggested that WG plasticization occurred by the formation of hydrogen bonds between the plasticizer and glutamines residues located on the protein β -turn structure.³ In KL-based materials, hydrogen-bonding small molecule also plays a role of plasticizer. KL plasticization by water (and other plasticizers) was studied by Bouajila et al. (2006),²⁵ who showed that in the common range of plasticizer content, the plasticization occurred in two steps. In dry conditions (low plasticizer content), plasticizer addition strongly decreased the T_g , whereas in wet conditions, the decrease was less important, and the plasticizer efficiency was linked to the difference in solubility parameters between the polymer and the plasticizer. The same evolution was observed here: from 0 to 20%, the glycerol addition resulted in a strong T_g decrease, whereas it became weaker at higher glycerol content. Moreover, if expressed on a molar basis, the change in plasticization mechanism occurred at the same plasticizer content with water²⁵ or with glycerol (in this study), i.e., at about 11 mol %. This observation can be easily correlated with the molecular origin of the plasticization in biopolymers mixtures, which have been also observed with WG.³ Once the number of plasticized site accessible on the polymer chain are saturated, the plasticization mechanism become nonspe-

cific and less efficient.²⁶ It is clear from Figure 5 that when compared to WG, the plasticization of KL with glycerol is less efficient, both in the first and the second step. In the first step, this might be attributed to a lower number of plasticizing sites in KL, which is a more hydrophobic molecule than WG, as assessed, for example, by the water absorption measurements given later in this article. The fact that the plasticization is also less efficient in the second step suggests that the solubility parameter of WG is closer to the one of glycerol than the one of KL.

Therefore, it can be concluded that while in the native state, KL had a lower T_g than WG, the opposite behavior was observed in the presence of a sufficient amount of plasticizer. In the following part of this study, we will describe materials with plasticizer contents higher than 10%, for which plasticized KL has a higher T_g than plasticized WG.

Effect of lignin on thermomechanical properties

The effect of the KL content on the material thermomechanical properties was studied at a constant overall plasticizer concentration. Therefore, materials in this study consisted of KL/WG/glycerol ranging from 0/70/30 to 40/30/30 (weight basis, samples L₀G₇₀g₃₀ to L₄₀G₃₀g₃₀: L referred to the lignin content, G to the gluten content, and g to the glycerol content). At high KL contents (from 50 to 70%), the behavior of the material became too fluid at high temperature, and measurements were no longer possible at and above glass transition temperature when using the conventional method.

Storage modulus (E') and $\tan \delta$ evolutions of the materials containing 0–40% KL content (L₀G₇₀g₃₀–L₄₀G₃₀g₃₀) as a function of temperature are shown in Figure 6. The values of T_g (determined as the maximum of $\tan \delta$ and of E' , in glassy and rubbery

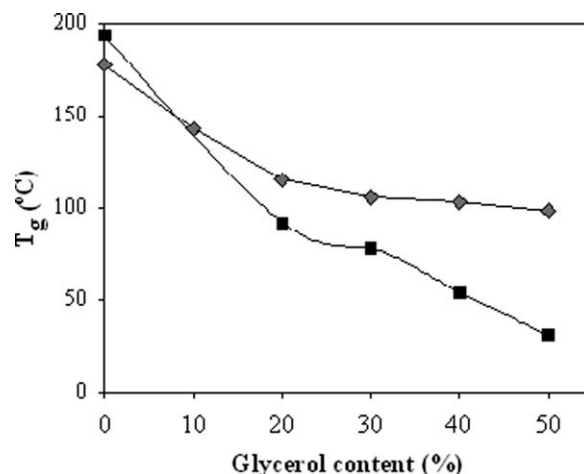


Figure 5 T_g of WG-based (squares) and KL-based (diamonds) materials plasticized with different glycerol contents.

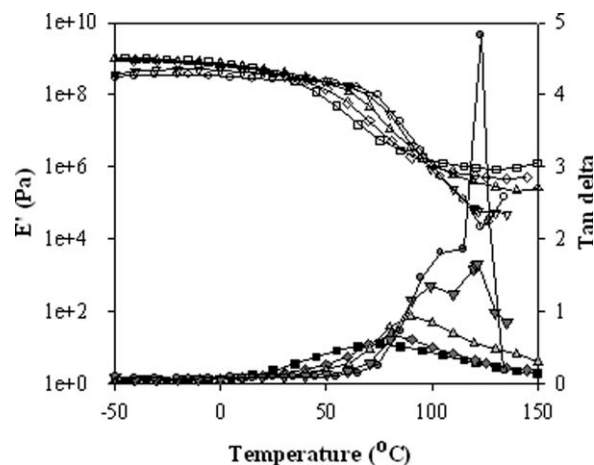


Figure 6 Storage moduli (empty symbols) and $\tan \delta$ (full symbols) of materials containing different KL contents as a function of temperature: $L_0G_{70}g_{30}$ (squares), $L_{10}G_{60}g_{30}$ (diamonds), $L_{20}G_{50}g_{30}$ (triangles), $L_{30}G_{40}g_{30}$ (down triangles), and $L_{40}G_{30}g_{30}$ (rounds).

regions (determined from the plateau curves and at 130°C , respectively) are given in Table I.

The general shape of the curve of a plasticized gluten material showed a clear decrease of E' at the glass transition. In such material, the absolute value of both the vitreous and the rubbery plateau, as well as of the glass transition temperature, are controlled by interaction forces (mainly hydrogen bonds) that exist between proteins^{26,27} and by covalent linkages (disulfide bond). They are thus function of the plasticizer content and of the thermomechanical history of the product: plasticizing molecules interact through hydrogen bonding with the protein, thus reducing the protein–protein interactions, and temperature favors crosslinking.

The addition of KL resulted in an increase of the material T_g , a decreased of E' at the plateau (both rubbery and glassy plateau), and the arising of a double $\tan \delta$ peak at 30–40%KL content. The latter evolution resembles the one previously observed on gluten–glycerol samples. This suggests that above the T_g , where the material elastic modulus decreased to values in the order of 10^5 Pa, the methodology used here was not anymore pertinent for intrinsic material properties determination.

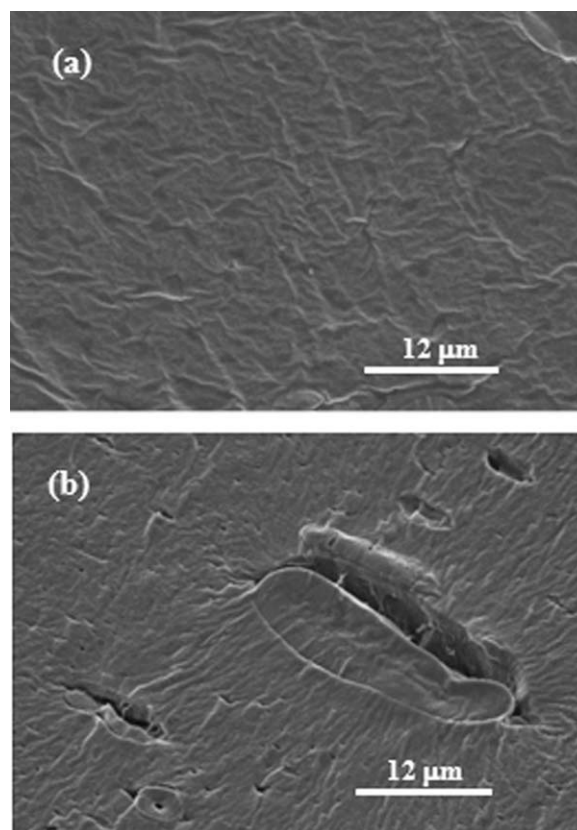


Figure 7 Materials with 0% (a) and 10% (b) KL observed by SEM.

However, it was possible to study the evolution of the sample internal structure with the KL content increase by SEM. Figure 7(a) shows that the WG-based material without KL was homogenous. When KL was added at 10–20%, the appearance of a KL phase dispersed in the matrix was observed [Fig. 7(b)]. This was characteristic of the presence of a compatibility limit between KL and WG as it was already shown for WG and fatty acids.²⁸

The significant increase of the $\tan \delta$ peak temperature with KL content was coherent with the delayed E' drop, both indicating an increase of the materials T_g . The mixture T_g is in between the one of the plasticized WG and the one of the plasticized KL. A theoretical T_g was calculated, for each KL content, by a simple summation of the T_g of plasticized KL and

TABLE I
Characteristics of E' and $\tan \delta$ Curves of WG Materials Containing 0–40% KL Contents

Sample	1st peak		2nd peak		Glassy storage modulus at the plateau (Pa)	Rubbery storage modulus at 130°C (Pa)
	T_g ($^\circ\text{C}$)	$\tan \delta$ peak height	T_g ($^\circ\text{C}$)	$\tan \delta$ peak height		
$L_0G_{70}g_{30}$	77.7 ± 2.4	0.58 ± 0.02	–	–	$9.9 \pm 0.2 \times 10^8$	$7.5 \pm 1.7 \times 10^5$
$L_{10}G_{60}g_{30}$	84.6 ± 3.5	0.73 ± 0.04	–	–	$7.4 \pm 1.5 \times 10^8$	$5.2 \pm 0.6 \times 10^5$
$L_{20}G_{50}g_{30}$	91.7 ± 0.8	0.95 ± 0.01	–	–	$7.4 \pm 2.2 \times 10^8$	$2.2 \pm 0.8 \times 10^5$
$L_{30}G_{40}g_{30}$	98.6 ± 0.7	1.35 ± 0.01	118.5 ± 0.7	1.71 ± 0.05	$4.8 \pm 0.2 \times 10^8$	$5.4 \pm 0.1 \times 10^4$
$L_{40}G_{30}g_{30}$	107.3 ± 3.2	1.86 ± 0.04	123.9 ± 0.9	4.83 ± 0.07	$3.2 \pm 0.3 \times 10^8$	$3.8 \pm 0.4 \times 10^4$

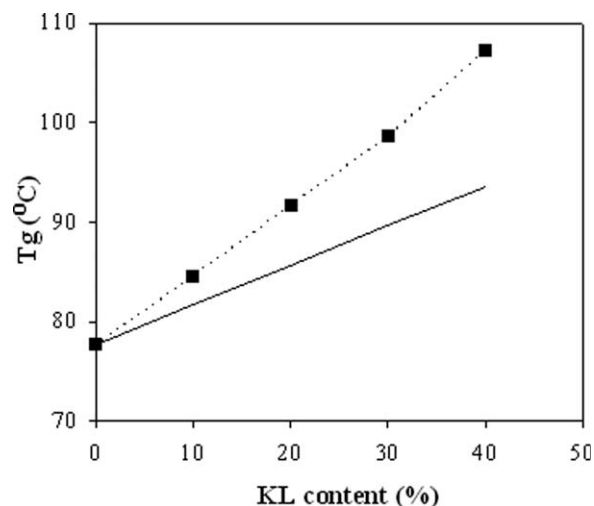


Figure 8 Comparison between the T_g s determined assuming a simple mixing rule (solid line) and experimental results (squares) for WG/KL materials plasticized with 30% glycerol content.

plasticized WG, weighted by their respective weight fraction. The difference between the experimental result and this simple prediction (shown in Fig. 8) clearly shows that the materials did not follow a simple mixing rule. More likely, this deviation can be considered as the signature of specific interactions between KL and WG. Upon WG mixing, the combined effect of mechanical and thermal energy results in the formation of covalent crosslinks through a mechanism which involves radical species.²⁹ However, in presence of KL, an opposite effect, i.e., a WG depolymerization has been observed: KL impairs the gluten crosslinking during processing,¹³ a behavior which can be attributed to the presence of phenolic groups with radical scavenging properties in its structure.¹⁴ Additionally, strong specific interactions between polyphenol and proteins,³⁰ might play a significant role.

Another effect of the KL addition was a decrease in the values of the elastic moduli, both in the glassy and rubbery plateaus, i.e., at temperatures far lower or far higher than the T_g . The most important evolution was observed in the rubbery state, in which E' was reduced by one to two decades. Again, this evolution demonstrated the effect of the gluten depolymerization which resulted from the addition of KL. However, a physical effect of KL cannot be excluded: in comparison to WG, KL has a low molecular weight, and number of hydroxyl groups. Those groups are well known for their plasticizing properties,³ so that it can be supposed that at a temperature higher than the KL T_g , the mobility increase of the macromolecules allows the WG plasticization by KL.

WG biomaterials production at an industrial scale is nowadays limited by the high protein sensitivity

against thermomechanical stress,^{1,31} which results in their crosslinking and complicates their processing. Injection molding is generally difficult to achieve due to the high viscosity of crosslinked plasticized WG. Since the KL addition reduces crosslinking and the rubbery modulus at processing temperature, it therefore appears as a convenient and promising additive to facilitate protein-based bioplastics production.

Effect of lignin on materials final properties

The tensile strength properties of materials with 0–30% KL content were measured after a preconditioning of the sample at 53% RH, which ensured reproducible results in conditions close to ambient ones. KL addition dramatically modified the materials properties. As the KL content increased, the tensile strength increased and the elongation at break decreased (Fig. 9). The elongation at break systematically decreased with the KL content, and strongly fell down when the KL content reached 30%, which was associated with the disappearance of the plastic plateau. Materials without KL exhibited a classical viscoelastic behavior. At 20% KL, they became viscoplastic, and fully vitreous at 30% KL. This is consistent with the effect of KL on the materials T_g , from values below ambient temperature (at low KL content), to values above this temperature (at high KL content). In the test conditions of 53% RH, the plasticizing effect of water shifted the T_g values previously determined by DMTA (in dry condition) to lower values. Materials properties are thus probed at a temperature very close to the T_g : the plateau value of E' , determined by DMTA far from the T_g , is not a

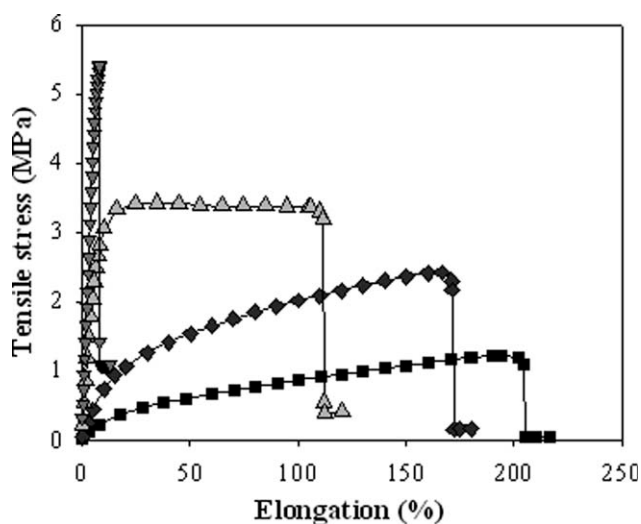


Figure 9 Mechanical properties of samples with different KL contents, molded at 80°C: $L_0G_{70}g_{30}$ (squares), $L_{10}G_{70}g_{30}$ (diamonds), $L_{20}G_{70}g_{30}$ (triangles), and $L_{30}G_{70}g_{30}$ (down triangles).

pertinent parameter to describe the Young's modulus (Table II), which is in fact more dependent on the temperature distance to the T_g , or $T - T_g$. As a result, tensile strength and Young's modulus increased with KL content, at least until KL became the main agropolymer in the sample. It can be noticed that the Young's modulus of samples with 40–60% KL content was still higher than that of the material without KL. Therefore, these glassy materials were very hard and rigid (high Young's modulus) but very brittle and fragile (low tensile strength). Pure KL/glycerol blends ($L_{70}G_{0}g_{30}$) were so brittle that their mechanical properties cannot be measured.

For most of the biomaterials made from natural polymers, one main drawback consists in the material sensitivity to water, usually quantified by the water absorption test. During immersion in water, the glycerol contained in the material diffuses in the water bath, while being replaced by water.²³ The water absorption is therefore a measure of the total amount of water absorbed by the material, whatever its degree of interaction with the agropolymers chain. It is a key parameter for any commercialization of the product. Figure 10 shows that the KL addition significantly reduced the water absorption of the sample. The water absorption of materials containing 0–30% KL gradually decreased. A drastic drop of water absorption was observed at 40% KL content. This may be associated with a change of the material structure when KL becomes the major solid component in the sample, in coherence with the mechanical properties evolution previously observed.

Finally, all the materials have a water absorption intermediary between that of the WG/glycerol (high water sensitivity) and KL/glycerol samples (low water sensitivity). KL appeared to be an interesting additive to reduce the water absorption of WG-based materials. This observation confirmed the evolution previously observed by Huang et al. (2003)¹⁰ on soy protein plastics prepared with increasing KL content. It can be attributed to the stronger hydrophobic character of KL,³² when compared to the one of WG.

TABLE II
Mechanical Properties of Materials with 0–60% KL Contents

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
$L_0G_{70}g_{30}$	1.7 ± 0.4	227 ± 51	2.6 ± 0.4
$L_{10}G_{60}g_{30}$	2.6 ± 0.6	219 ± 50	10.4 ± 2.4
$L_{20}G_{50}g_{30}$	3.8 ± 0.7	91 ± 12	45.7 ± 14.3
$L_{30}G_{40}g_{30}$	5.1 ± 0.6	7.1 ± 1.2	93.1 ± 8.1
$L_{40}G_{30}g_{30}$	2.5 ± 0.1	2.6 ± 0.5	105.3 ± 4.7
$L_{50}G_{20}g_{30}$	0.7 ± 0.1	0.7 ± 0.4	54.8 ± 23.6
$L_{60}G_{10}g_{30}$	0.4 ± 0.9	0.2 ± 0.1	32.5 ± 9.5

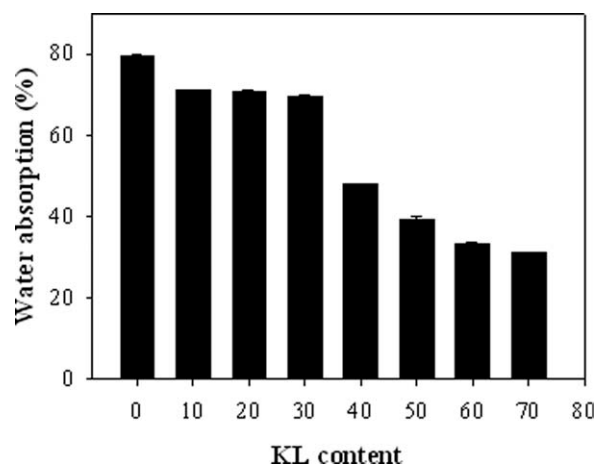


Figure 10 Material swelling after 1 week immersion of WG-based materials containing different KL contents plasticized with 30% glycerol, molded at 80°C.

CONCLUSIONS

This study showed that KL addition is an efficient and simple way to significantly improve WG-based materials properties. Due to its relatively high hydrophobicity when compared to WG, KL reduced the materials water sensitivity, which constitutes one of their main drawbacks. Moreover, its addition increased both tensile strength and Young's modulus. These improvements were attributed to the T_g increase which was shown to result from the lower KL plasticization efficiency by glycerol, in comparison with WG. At temperatures relevant for processing, a strong decrease of few decades of the materials rubbery modulus was observed. The protein depolymerization observed in a previous study,¹³ during WG processing in presence of KL, is probably responsible for this evolution, which might significantly simplified gluten-based materials processing, for example in view of injection-molding operations. In the future, material microstructure should be investigated more deeply to give a complete description of those materials properties.

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