



Comparison of Kraft lignin and lignosulfonates addition to wheat gluten-based materials: Mechanical and thermal properties



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ABSTRACT

Two types of industrial lignin, namely Kraft lignin and ammonium lignosulfonates, have been introduced into wheat gluten-based bioplastics. Mechanical, thermomechanical and water vapor sorption properties of the materials have been investigated in detail. The behaviors are clearly distinct depending on the lignin type. The addition of Kraft lignin produces stiffer materials, with increased Young's modulus but almost constant elongation at break. Glass transition temperature is higher and water vapor sensitivity reduced when Kraft lignin is added. Conversely, the incorporation of lignosulfonates leads to materials with higher elongation at break, but almost unchanged water sensitivity and glass transition temperature. Both lignins thus appear as of great interest to tailor the properties of wheat gluten-based materials. Structural differences between Kraft lignin and lignosulfonates are believed to be responsible for the distinct behaviors observed in this study.

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1. Introduction

It is now widely accepted that bio-based polymers can represent an alternative to synthetic polymers for some common applications. The growing interest for biodegradable polymers has led researchers as well as industrials to focus on polymers from agro-resources. Among others, plant proteins have been extensively studied and recently reviewed (Hernandez-Izquierdo and Krochta, 2008; Zhang and Mittal, 2010). The most common are wheat gluten, soy protein isolate and corn zein, but some studies also focus on sunflower (Orliac et al., 2003) or pea proteins (Gueguen et al., 1998). Wheat gluten presents some advantages that make it interesting: it is widely available at a reasonable cost as a by-product of the starch industry, and it can be treated through classic thermoplastic processing (hot mixing and thermo-molding, extrusion (Redl et al., 1999; Hochstetter et al., 2006; Verbeek et al., 2009), injection molding (Cho et al., 2011)), to produce fully biodegradable materials (Domenek et al., 2004b).

Wheat gluten is composed of two types of proteins, gliadins and glutenins, which present similar amino-acids composition. They differ in terms of disulfide bonds stabilizing the proteins: in gliadins, cysteine residues are only engaged in intramolecular

disulfide bonds, whereas in glutenins, they can form both intra- and intermolecular disulfide bridges between glutenin subunits, thus leading to higher molecular weight (Shewry and Tatham, 1997; Wieser, 2007). During the processing of wheat gluten using thermo-mechanical treatments, intramolecular disulfide bonds are broken, and new intermolecular disulfide bonds can thus be formed. This leads to the formation of a cross-linked three-dimensional protein network (Morel et al., 2002). It has later been shown that this phenomenon, called gluten aggregation, induces both radical and nucleophilic reactions (Auvergne et al., 2008). The addition of a plasticizer, usually glycerol, is necessary to reduce non-covalent interactions between polymer chains and thus obtain materials with sufficient processability and deformability. Wheat gluten-based polymer films present good viscoelastic properties, water insolubility and low oxygen permeability (Gällstedt et al., 2004). However, their mechanical properties are still low when compared to synthetic polymers, and their major drawback remains their high sensitivity to moisture (Gontard et al., 1993; Pouplin et al., 1999; Gällstedt et al., 2004).

To improve wheat gluten properties, several strategies can be developed: optimizing the operating conditions, reinforcement with fibers (Kunanopparat et al., 2008; Muenri et al., 2011; Reddy and Yang, 2011) or particles (Zhang et al., 2007; Angellier-Coussy et al., 2008) to produce composites, or blending with another polymer (Mohamed et al., 2010). It is preferable to reinforce wheat gluten with another renewable and biodegradable component to maintain its advantages over synthetic polymers. In this study, another biopolymer, lignin, has been blended together with wheat gluten.

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Lignin is after cellulose the second most abundant renewable forest resource. It is a complex macromolecule, based on the repetition of three different phenylpropane units, linked together by ether or C–C bonds (Gellerstedt and Henriksson, 2008). Lignin is characterized by a wide diversity depending on both the botanical origin and the extraction process: many functional groups (carbonyl, phenolic or aliphatic hydroxyls, carboxyl . . .) can be found in different proportions (Boeriu et al., 2004; Gosselink et al., 2004; El Mansouri and Salvadó, 2007), and the molecular masses can extend from thousand to several tens of thousands of mol⁻¹ (Baumberger et al., 2007).

The interest for lignin has continuously been growing for several years, mainly because the production is supposed to increase dramatically with the development of second generation bioethanol (Doherty et al., 2011). However, the paper pulp industry remains today the most important producer of lignin, with two major processes: Kraft and bisulfite processes.

During the Kraft cooking, lignin and hemicelluloses are solubilized into the cooking liquor, called black liquor, which is then burned to produce energy, thus conferring to the pulp mills self-sufficiency in energy consumption. Modern Kraft mills even produce excess energy and could then afford to extract part of the lignin for higher added value applications. Nevertheless, only a minor part of Kraft lignin is currently extracted (around 35 000 t out of 70 Mt produced every year). On the contrary, lignin produced by the bisulfite process is commonly extracted as lignosulfonates and commercialized, with a world production of about 1.5 Mt/yr. Lignosulfonates are of particular interest, because they possess sulfonate groups –SO₃⁻, which are grafted to the aliphatic chain, thus conferring to the macromolecule water solubility, allowing applications as dispersant, emulsifier or additive in concretes (Lora, 2008).

Recently, Kunanopparat et al. (2009) blended Kraft lignin with wheat gluten. They showed that Kraft lignin was able to interact with the gluten aggregation pathway, leading to a reduced cross-linking, probably because of the radical scavenging activity of lignin phenol groups toward thyl radicals (Kaewtatip et al., 2010). They found that the incorporation of Kraft lignin could really improve material properties, such as inducing higher stiffness and strength coupled to reduced water sensitivity (Kunanopparat et al., 2012).

The aim of this study is to compare the influence of both Kraft lignin and lignosulfonates on wheat gluten properties. By using different lignin types, it is expected to better understand the complex interactions between gluten and lignin, and to determine which kind of lignin would be more suitable to enhance wheat gluten properties. It is also a way to investigate new potential applications for industrial lignins.

2. Experimental

Wheat gluten (WG) was supplied by Tereos Syral (Marckolsheim, France). Softwood ammonium lignosulfonates (LS, ARBO T11N5) were supplied by Tembec Avebene (Tartas, France), and softwood Kraft lignin (KL, Indulin® AT) by Mead Westvaco (Richmond, VA). Moisture content of the powders measured after 24 h drying at 105 °C were respectively 12.4% (WG), 7.8% (LS) and 4.8% (KL). The mean particle diameters measured with a laser diffraction particle size analyzer (Mastersizer S, Malvern) were respectively 45 μm for WG and 25 μm for both lignins. Residual sugar content of lignin was measured by gas chromatography after total hydrolysis. LS contains 12.7% sugars whereas KL contains less than 3.0%. Glycerol (reagent grade, ≥99.0%) was purchased from Sigma Aldrich.

Table 1

Composition of the samples. All percentages were calculated on a dry weight basis.

Sample name	Lignin type	Glycerol (%)	Gluten (%)	Lignin (%)
WG	–		65	0
LS5			60	5
LS10	Lignosulfonates		55	10
LS15			50	15
LS20		35	45	20
KL5			60	5
KL10	Kraft Lignin		55	10
KL15			50	15
KL20			45	20

2.1. Preparation of the samples

WG and either LS or KL powders were first hand mixed to the desired proportions (Table 1). Then, the resulting powder was mixed with glycerol (35 wt%, based on total dry weight) in a two-blade counter-rotating batch mixer, turning at 3:2 differential speed (Brabender, Duisburg, Germany). Mixing was performed for 15 min, at a mixing speed of 100 rpm and a temperature of 70 °C. Glycerol was first introduced into the chamber, as it provides more homogeneous blends.

The blends were then thermomoulded in a heated press (Carver laboratory press, Carver Inc, Menomonee Falls, WI) at 120 °C. Approximately 4 g of polymer blends were placed between two aluminum sheets in a rectangular mold (8 cm × 4 cm) for 10 min without pressure, followed by 3 min under 15 MPa of pressure. They were then removed from the mold and cooled at ambient temperature. The resulting films were about 0.5 mm thick. Prior to tensile tests and dynamic mechanical analysis the films were conditioned into a desiccator producing 43% relative humidity at 24 °C for 1 week.

2.2. Scanning electron microscopy

Scanning electron microscopy (SEM) was performed with a JEOL JSM-6100 microscope (Tokyo, Japan). The samples were frozen under liquid nitrogen, then fractured, mounted, coated with gold/palladium on a JEOL JFC-1100E ion sputter coater, and observed. SEM micrographs were obtained using 8 kV secondary electrons.

2.3. Tensile tests

Tensile tests were performed on a universal testing machine (INSTRON 4301). Wheat gluten-based films were cut into dumbbell-shaped samples of 10 mm in effective length and 5 mm in width. The thickness was measured each time with a caliper. The tests were performed at 24 °C, with a crosshead speed of 10 mm min⁻¹ on 8 replicates per sample. Young's modulus, tensile strength and elongation at break were averaged and standard deviations were calculated in order to compare the different samples.

2.4. Dynamic mechanical analysis

Dynamic mechanical analysis was performed on a RSA II testing machine in tensile mode at a frequency of 1 Hz with 0.01% strain amplitude. Analyses were performed on rectangular samples (approximately 20 mm × 10 mm × 0.5 mm) from –90 to 150 °C at a heating rate of 3 °C/min. Storage modulus (*E'*), loss modulus (*E''*) and tan δ (= *E''/E'*) were continuously recorded during the experiment. Each sample was analyzed in triplicate.

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