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# Processing rigid wheat gluten biocomposites for high mechanical performance

Nhan Vo Hong [a,*], Grzegorz Pyka [a], Martine Wevers [a], Bart Goderis [b], Peter Van Puyvelde [c], Ignaas Verpoest [a], Aart Willem Van Vuure [a]

[a] KU Leuven Department of Materials Engineering, Kasteelpark Arenberg 44, 3001 Leuven, Belgium
[b] KU Leuven Chemistry Department, Polymer Chemistry and Materials Division, Celestijnenlaan 200F, 3001 Leuven, Belgium
[c] KU Leuven Department of Chemical Engineering, Soft Matter: Applied Rheology and Technology, Willem de Croylaan 46, 3001 Leuven, Belgium

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ABSTRACT

Recently, unidirectional rigid gluten biocomposites have received attention because the glassy gluten matrix has comparable properties as an epoxy resin. This research proposes some possibilities to facilitate such biocomposites. The dry method is modified by using water exposed fibers rather than dry ones. The wet method uses an ethanol solution to suspend and partly dissolve original or milled gluten particles, in which the fibers are subsequently immersed. Drying impregnated fiber mats obtained via either the modified dry or wet method leads to prepregs of which stacks were compression molded into composites without the need for any further solvents or plasticizers. Gluten composites made by the wet method give much higher moduli and strengths compared to when using either of the dry methods. Using aqueous ethanol helps to dissolve part of the gluten (the gliadin fraction) and is believed to lead to a good wetting of the matrix between the fibers.



## 1. Introduction

Wheat gluten, a co-product from the starch and bioethanol industry, is used as an ingredient in many food applications. Besides, wheat gluten has also been considered for use as raw material for non-food applications, such as for biopolymers and biocomposites [1–5]. Due to increasing environmental awareness, biodegradable materials such as wheat gluten, have received attention because it is a low-cost raw material, annually renewable, and readily available.

Wheat gluten contains two main fractions i.e. gliadins and glutenins. The gliadin fraction has a molecular weight of 30–60 kDa, can be dissolved in aqueous alcohol and only contains intra-molecular disulfide bonds. In contrast, the glutenin fraction has a molecular weight up to several million Da and is not soluble in alcohol. The glutenin fraction contains both intra- and inter-molecular disulfide bonds and has a low level of free sulfhydryl groups [6].

From economical and environmental viewpoints, thermal processing is an efficient method to produce gluten polymer materials. To reduce the strong inter- and intramolecular interactions and to increase the mobility of the protein chains, large amounts of plasticizers are usually required in this process [7,8]. However, such plasticization significantly reduces the strength and stiffness of the material [8]. In the absence or at low concentrations of plasticizer, high temperature compression molding of wheat gluten results in rigid, glassy materials with stiffness and strength of about 3.8 GPa and 47 MPa, respectively [3,5]. The mechanical properties approach those of synthetic resins such as epoxy. However, the main drawback for of gluten materials lies in their brittleness. Overcoming this issue is an important factor in extending the applications of gluten polymers.

The same issue has been observed for gluten composites. A lot of studies have focused on a plasticized gluten matrix, such as a combination of wheat gluten with glycerol to produce rubbery gluten composites [9–11]. The purpose of adding plasticizers is to increase the mobility of the polymer chains, to improve the flow characteristics and hence the impregnation. However, the drawback of this method is that composites are obtained with typically low modulus and strength. Moreover, in these studies, mostly short fibers have been used, which does not lead to the best mechanical performance.

Alternatively, long and unidirectional fiber reinforced gluten composites have received attention because they can obtain high stiffness and strength – the case of interest to the present paper.

* Corresponding author. Tel.: +32 16373462; fax: +32 16321990.
*E-mail address:* nhan.vohong@mtm.kuleuven.be (N. Vo Hong).

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Ye and colleagues [12] studied basalt reinforced wheat gluten which was dissolved in meta-cresol during processing. A benefit of using solvent was achieved, showing that the bending modulus of unidirectional composites at 40% fiber volume fraction was improved from 4.40 GPa to 8.56 GPa. Reddy and Yang [13] proposed another method by using wheat gluten semi-plasticized with water. They published results on the mechanical properties of unidirectional jute/gluten composites with a modulus of 7.7 GPa, at 40% fiber mass fraction. Nevertheless, their moduli when loaded in the fiber direction (particularly basalt/gluten composites) are far below the values theoretically possible which can be calculated by the simple Rule of Mixtures [14]. Assuming the moduli of basalt fiber and jute fiber are respectively about 90 GPa [12] and 27 GPa [15], the theoretical achievable modulus of unidirectional composites would be around 38 GPa and 12 GPa, respectively.

Hemsri and colleagues [16] obtained mechanical properties close to theoretical predictions for their gluten composites, but they used a low fiber content (matrix/fiber ratio of 85/15 by mass). At low fiber content, impregnation is much easier, but mechanical properties will be modest. They toughened gluten with coconut fiber (by using alkali and silane treatment), with the advantage of high elongation at break of fiber.

The aim of our work is obtaining superior mechanical properties of rigid gluten composites at medium to high fiber content (at least $V_f = 20\%$). Since the modulus is strongly affected by the fiber direction, aligning the fibers within the preforms by wetting and combing is essential. Secondly, a good contact between fiber and gluten polymers is a key to obtaining high mechanical performance composites. Some ways are proposed to process rigid gluten composites reinforced with unidirectional flax fiber. The classical dry method is to distribute gluten powder on dry fiber preforms without using water as processing aid. The modified dry method is to distribute dry gluten powder on water wetted fiber preforms. In the wet method, gluten powder is suspended in an ethanol solution in which the fibers are immersed ("suspension-solution" impregnation). As mentioned above, gluten consists of soluble gliadins and insoluble glutenin in alcoholic media. The use of an ethanol solution is expected to bring the gliadins in between the fibers. The wet method is also applied starting from finely milled gluten powder hoping that smaller, non-dissolved glutenin particles can also go in between the fibers. To figure out whether or not this actually can happen, composites were also manufactured via the wet method but starting from a suspension of the glutenin fraction ("suspension" impregnation).

## 2. Experimental

### 2.1. Materials

Commercial wheat gluten was obtained from Tereos Syral (Aalst, Belgium). According to the manufacturer, its protein and moisture content were 77.8% (dry mass) and 5.6% respectively. Remaining fractions mainly include starch and lipids.

Hackled flax was delivered by Terre de Lin (France). This form of flax is a continuous ribbon, in which the fibers are aligned together (Fig. 1). The linear density of the material is 30,000 tex, and the preform has a width of about 25 cm.

### 2.2. Composite fabrication

#### 2.2.1. Fiber preform handling

The first step in composite manufacturing aims at controlling the fiber straightness. Fiber preforms were wetted and combed to increase the alignment (Fig. 1). After a subsequent drying procedure at 60 °C for 24 h, fibers were weighed immediately in order to know the fiber mass for calculating the fiber volume fraction.

The fiber volume fraction of the prepregs was determined through weight measurement, assuming a fiber density of 1.45 g/cm$^3$ [17] and a measured matrix density of 1.3 g/cm$^3$. The density of the matrix was calculated by the ratio of its weight over its volume which was measured by a gas pycnometer (Model 930, Beckman Instruments, Fullerton, CA 92634, USA). Triplicate measurements were done and the average value was given.

The fiber volume fraction of the prepregs was determined as the value that would be obtained in a composite, assuming no loss of material during manufacture and assuming zero porosity.

#### 2.2.2. Prepreg processing

*2.2.2.1. Dry method.*

*2.2.2.1.1. Dry powder distribution on dry fibers.* For this method, samples were directly prepared inside the mold. Gluten powder was first distributed in the mold with a sieve of mesh-size 1 mm. Next, the dry fiber preforms were inserted into the mold. Subsequently, another gluten powder layer was passed through the sieve. These steps were repeated with 8 layers of fiber preforms in total. The total amount of gluten powder was used according to the total amount of flax fiber for 35% fiber volume fraction of the final composites.

*2.2.2.1.2. Dry powder distribution on wet fibers.* A prepreg methodology has been introduced based on water as processing aid. Flax fiber performs were wetted again (after combing and drying) with enough water for gluten powder to stick on their surface. Powder was distributed with a sieve of mesh-size 1 mm. The amount of gluten powder was used based on the amount of dry flax fiber preform till 35% in fiber volume fraction was obtained. The products were dried overnight under vacuum at 20 °C.

*2.2.2.2. Wet method.*

*2.2.2.2.1. Wet method with original gluten powder.* A gluten suspension-solution was prepared by stirring gluten powder in an ethanol solution (10% weight/volume in 70% ethanol). Flax fibers were immersed in gluten suspension-solution several times

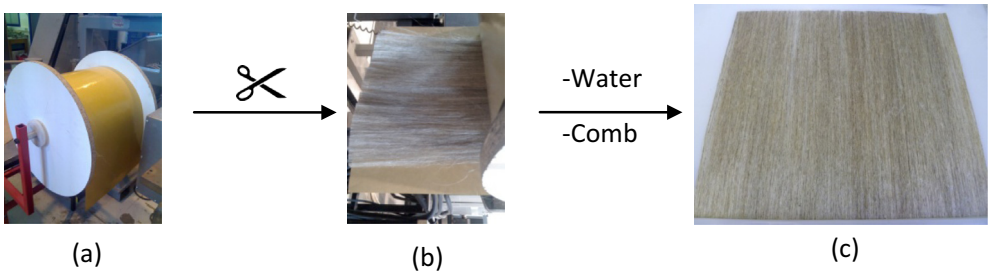


**Fig. 1.** Flax fiber from (a and b) continuous ribbon to (c) unidirectional preform after combing with water and then drying. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)