PREPARATION OF BIOCOMPOSITES BASED ON GLUTEN RESIN AND UNIDIRECTIONAL FLAX FIBERS

N. Vo Hong[1*], P. Van Puyvelde[2], A. Van Vuure[1], I. Verpoest[1]

[1]*Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44, 3001 Heverlee, Belgium*
[2]*Department of Chemical Engineering, Applied Rheology and Polymer Processing, Katholieke Universiteit Leuven, Willem de Croylaan 46, 3001 Heverlee, Belgium*
[*]*Nhan.vohong@mtm.kuleuven.be*

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Abstract

Recently, wheat gluten has been investigated for potential use in non-food applications such as biopolymers and biocomposites. In order to improve the mechanical properties of gluten composites, two factors are usually considered: use of plasticizers and fiber length. A new method for making gluten composites is presented without the need to (semi) permanently plasticize the gluten and with a good control of fiber alignment. Water was used as processing aid together with the use of unidirectional flax fibers to obtain the strongest properties in the fiber direction. A flexural modulus of 12 GPa, a strength of 117 MPa and a failure strain of 1.3 % at 35 % fiber volume fraction were obtained. The properties are still only about 50% of what is theoretically possible, most likely due to insufficient impregnation, due to too large particle size used and also due to insufficient fiber-matrix adhesion.

1 Introduction

Gluten, a side product of the starch industry, has a long standing track record in food technology. Recently, wheat gluten has also be considered as the starting material for the production of a biobased material, for instance by molding at high temperatures [1-4].

Due to the very difficult melt processing of wheat gluten, many methods have been suggested to produce gluten composites by using a plasticized matrix, such as a combination of gluten with glycerol [5-9]. However, the drawback of this method is that typically low mechanical properties are obtained. Moreover, in these studies, short fibers have most often been used, which does not lead to the best mechanical performance.

Some research groups have shown interest in long fiber reinforced gluten composites. Ye and colleagues [10] studied basalt reinforced wheat gluten which was dissolved in meta-cresol. For the bending modulus of unidirectional composites at 40 % fiber volume fraction, a value of almost 8 GPa was achieved. Reddy and Yang [11] proposed another method by using semi-plasticized wheat gluten with water. They published results on the mechanical properties of unidirectional jute/gluten composites with a modulus of 7.7 GPa, at 40 % fiber volume fraction. Both these results show relatively low properties, much lower than can theoretically be expected based on the fiber properties.

In this research, a new approach has been developed for improving properties of gluten composites. This method is the combination of using water to adhere the gluten onto the fibers and to help control fiber straightness. Afterwards, water evaporates during drying and compression molding, so it does not remain in the final product. Therefore, improved mechanical properties are anticipated.

The interfacial adhesion between the flax fibers and the gluten matrix was studied through scanning electron microscopy in order to explain the properties. In addition, it was shown that the gluten powder particle size affects the properties of gluten composites.

2 Experiments

2.1 Materials

Wheat gluten powder was obtained from Syral (Aalst, Belgium); it contains 77.8 % protein and 11 % starch, and has 5.6 % moisture content on a mass basis.

Scutched flax was delivered by Van De Bilt – Zaden en Vlas (Belgium). This form of flax needed to be combed in order to control fiber alignment. It was then cut into a suitable dimension for preparing the prepregs.

2.2 Methodology

2.2.1 Prepreg processing

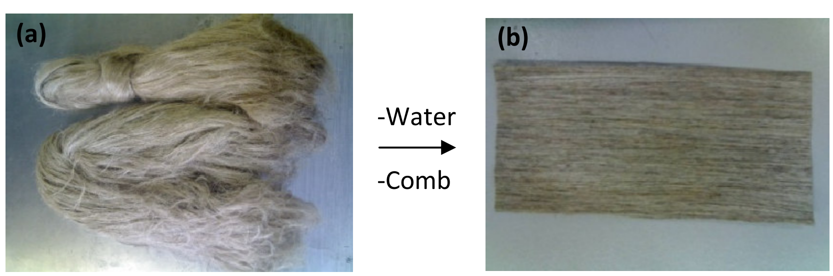

Figure 1. Flax fibers before (a) and after (b) combing with water

Since it is not evident to control the alignment of fibers during the thermo-molding process, a prepreg methodology has been developed. It consists of a dry combing step, followed by a wetting step to increase alignment. After a subsequent drying procedure at 60 °C, to keep the directional configuration, the fibers were wetted again with enough water in order to stick gluten powder on their surface. Finally, the products were dried at 20 °C to avoid any premature cross-linking at higher temperature of the gluten. The final product of this preparation step is hence a prepreg material.

2.2.2 Compression molding

Compression molding was used to make gluten composites from the prepregs. At first, gluten powder was distributed in the mold with a sieve of mesh-size 1 mm; after this the aligned flax fiber prepregs were put into the mold. Subsequently, another gluten powder layer was passed through the mesh. These steps were repeated till the required fiber volume fraction and composite thickness were obtained. Finally, the materials were thermo-molded at 150 ^{o}C for 5 minutes in a hot press (Pinette Press Zenith 2, Pinette Emidecau Industries, France). A constant pressure of 5 bars was used, like in the experimental work of Woerdeman [3] and of Jansens [12].

2.3 Mechanical characterization

Based on ASTM D790-03, five test bars were cut from the composite sample and stored at 20 °C and a relative humidity of 50 % for 2 days. Afterwards, flexural tests were performed on an Instron 4467 with a 1 kN load cell. The support length of the specimens was at least 16 times the thickness of the plates (± 2 mm), to obtain pure bending.

2.4 Scanning electron microscope (SEM)

Scanning electron microscopy (SEM 30 XL FEG) was used to examine the adhesion between flax fibers and gluten matrix after fracture. The samples were fixed with double-sided carbon adhesive tape mounted on aluminum stubs. The surface was then coated with ionized gold and observed using secondary electrons.

2.5 Particle size analysis

To determine the particle size distribution, a gluten suspension was prepared from gluten powder mixed in a 70 % ethanol solution. The particle size of this powder was determined by light scattering (Mastersizer micro^{+}, Malvern). The temperature during the experiment was maintained at 20 °C.

3 Results and discussion

3.1 Mechanical properties

The longitudinal flexural stiffness, strength, and strain to failure of the flax/gluten composite were respectively 12.0 GPa, 117 MPa, and 1.31 % (see table 1). Better properties were found than the results on gluten composites by Ye [10] and by Reddy and Yang [11], though these authors used other types of fibers. The properties of composites are dominated by fiber orientation; meaning that the strongly aligned fibers used in this study were beneficial for the final properties.

However, the results were not yet at the level of theoretical calculations, using the rule of mixtures. Such values of the flexural Young's modulus and strength can for be calculated using equations (1) and (2):

$$E_C = V_f E_f + (1 - V_f) E_m \tag{1}$$

$$\sigma_C = \sigma_f^* V_f \tag{2}$$

where V_f is the fiber volume fraction, E_C the composite flexural stiffness, σ_C the composite flexural strength, σ_f^* the fracture strength of the fibers.

Regarding the measured stiffness for the composite (12.0 GPa), it only reaches 46.6 % of the theoretical value (25.7 GPa), indicating that the quality (impregnation) of the unidirectional composite was probably not very good. Comparing the value of the longitudinal flexural strength (117 MPa) with the value calculated theoretically (280 MPa), this means that only 42 % of the fiber strength was efficiently transferred into the composite performance. Possible explanations are again lack of impregnation and/or adhesion, or that e.g. the fiber bundles were not well distributed in the prepregs. This was further analyzed by means of scanning electron microscopy and particle size analysis.

	Flexural modulus (GPa)	**Flexural strength (MPa)**	**Strain to failure (%)**
Gluten	4.22 ± 0.08	54.5 ± 3.1	1.33 ± 0.08
Flax/gluten (V_f = 35 %)	11.96 ± 0.85	117 ± 9	1.31 ± 0.06

Table 1. Mechanical properties of gluten biopolymer and flax/gluten composites

3.2 SEM

In order to explain the properties of the flax/gluten composites, SEM was used to examine the interface between fiber and matrix. Figure 2 shows different failure modes of flax fibers after the fracture. There are a few fiber failures as in figure 2a whereas most of the failures are concentrated at the fiber–matrix interface. Visible are either fibers pulled out of the matrix (2b and d) or traces are visible of pulled-out fibers on the matrix surface (2b, 2c). These phenomena point to a relatively low interfacial adhesion, which will contribute to the longitudinal strength not reaching the theoretical value.

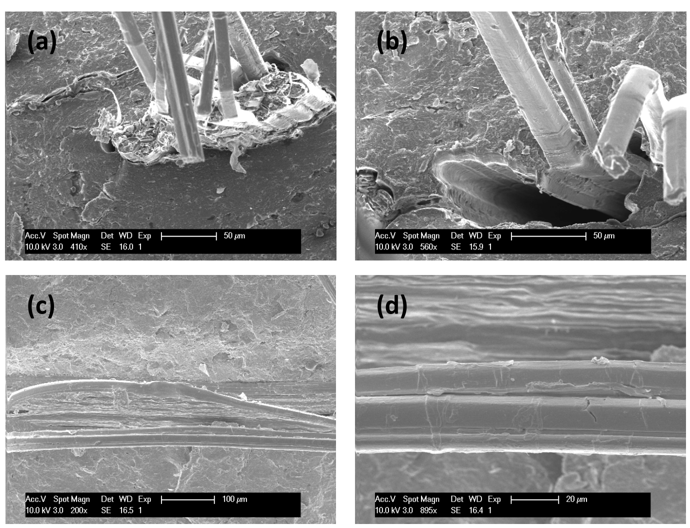

Figure 2. SEM images of the failure modes of flax fiber gluten composites after flexural loading, with some evidence of fiber failure (a), but in most cases evidence of low interfacial adhesion with associated fiber pull-out (b, c) and ‘clean’ pulled-out fibers (d)

3.3 Particle size analysis
It was hypothesized that the particle size of gluten powder may have a profound effect on the mechanical properties of gluten flax fiber composites. Fig. 3a shows the particle size distribution of the used gluten powder which shows a high percentage of sizes around 50-250 µm. These gluten particles are much larger than the fiber diameter of flax which is around 20-30 µm, showing that a large fraction of the powder cannot penetrate the fiber bundles (as illustrated schematically in Fig. 3b). This will likely lead to a low level of impregnation because of the very high 'melt' viscosity of the gluten, even when stuck with water to the fibers, and this will be an important additional reason that the practical flexural modulus (and strength) results were significantly lower than expected.

(a) (b)

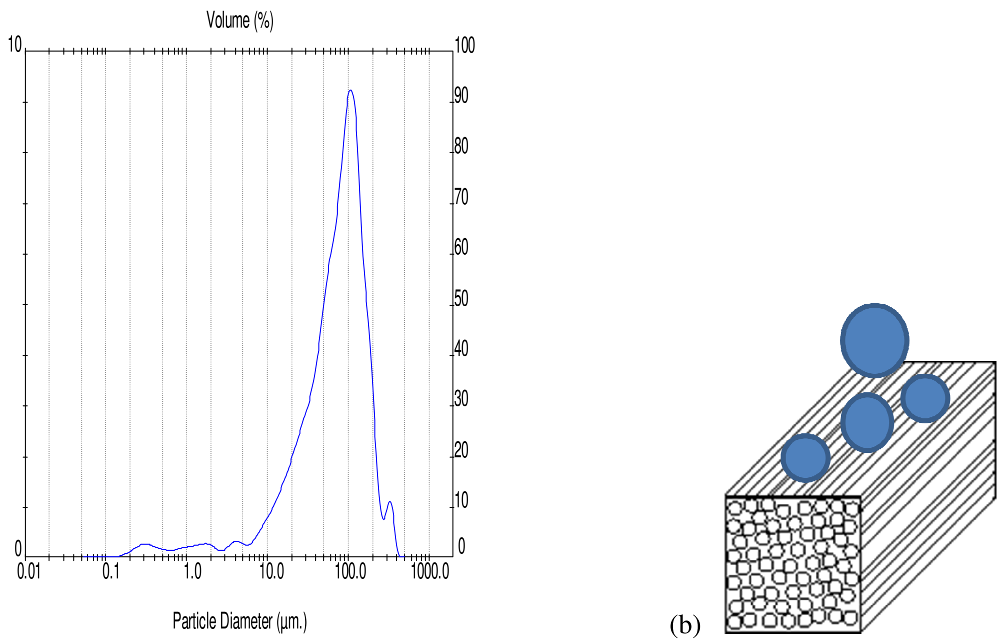

Figure 3. Particle size distribution of gluten powder (a) and an illustration of powder particles on unidirectional fiber yarn (b)

4 Conclusions

Gluten composites were prepared by using aligned unidirectional flax fibers, stabilized in a prepreg, as reinforcement and gluten as the matrix. The mechanical properties were higher than in some studies found in literature. However, the flexural modulus and strength were still only around 50% of what could be expected theoretically. One of the reasons is that the interfacial adhesion between fiber and matrix is not yet optimized. Solutions for this could be realized by either treating the fiber or modifying the gluten formulation, in first instance by using additives. More importantly, it seems the impregnation in the prepared composites must have been incomplete, due to the large average particle size of the gluten powder and the very high melt viscosity of the gluten. This was reflected in the much lower than expected flexural modulus.

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