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Developing rigid gliadin based biocomposites with high mechanical performance

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ABSTRACT

We aim to produce unidirectional fiber composites with high mechanical performance based on flax fibers and a rigid gliadin matrix. As a fraction from wheat gluten, gliadin is soluble in alcohol containing media. The fabrication process did not involve any further solvents or plasticizers. Finally, samples were cooled at different rates. Overall, the cooling rate does not strongly affect the mechanical properties although slowly cooled materials contain a higher amount of non-disulfide cross-links, next to disulfide bonds within the gliadin matrix. At 40% fiber volume fraction, flax/gliadin composites with a flexural modulus and strength of respectively 21.5 GPa and 240 MPa were obtained when loaded in the longitudinal direction. These high values demonstrate that in this composite fabrication process, a good impregnation of the polymer matrix in between the fiber bundles has been achieved. However, the fiber–matrix adhesion, as measured by transverse flexural and tensile tests, was still relatively modest.

1. Introduction

Since most synthetic polymers cannot be degraded by natural organisms, their disposal in nature has resulted in several environmental problems. Therefore, considerable research effort is devoted to the development of fully biodegradable materials, especially from renewable resources such as agricultural byproducts. Wheat gluten, a co-product from the starch and bioethanol industry, is an interesting candidate because it is a low-cost raw material, annually renewable and readily available.

Wheat gluten contains two main fractions: monomeric gliadins and polymeric glutenins. The gliadins have a molecular weight of 30–60 kDa, can be dissolved in aqueous alcohol and only contain intra-molecular disulfide bonds. The glutenins contain both intra- and intermolecular disulfide bonds and has a low level of free sulfhydryl groups. They have molecular weights ranging from 80 kDa to several million. They are composed of glutenin subunits with a high molecular weight and glutenin subunits with a low molecular weight, which are connected by disulfide bonds [1].

Thermo-molding or, more specifically high-temperature compression molding or injection molding, is an interesting way of producing gluten based materials as it is fast and requires no solvent. Moreover, during the high temperature treatments, a gluten molecular network is formed by spontaneous crosslinking. Depending on the type and amount of plasticizer, gluten based materials obtained via such processes can either be in the glassy state or in the rubbery state at room temperature.

A rubbery state at room temperature is obtained when the amount of plasticizer exceeds 15% [2]. Plasticizers are frequently used in the fabrication process to reduce strong inter- and intramolecular interactions and to increase mobility of the protein chains [3,4]. The addition of plasticizers leads to an increase of the failure strain of the materials, whereas both modulus and strength are strongly decreased [4]. The mechanical properties of such rubbery gluten polymer materials also depend on the molding conditions. With increasing molding temperature above 100 °C, the tensile modulus and strength increase while the elongation at break decreases. These effects have been associated with an increase of the cross-linking density [5,6].

In the absence or at low concentrations of plasticizer, high temperature compression molding of wheat gluten results in rigid, glassy materials with high stiffness and strength [7,8]. Their

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mechanical properties approach those of synthetic resins such as epoxy. However, the main drawback for these types of materials lies in their brittleness. These materials are characterized by a failure strain typically below 2% [8]. The molding conditions also affect the mechanical properties of such rigid gluten polymers. Ye et al. [9] reported that the flexural strength slightly increased with increasing molding temperature from 110 to 150 °C while the modulus remained unaffected. The same trends were observed by Jansens and colleagues [8] who studied the gluten molecular structure and mechanical properties after compression molding in the range 130–170 °C. They found that the modulus was not heavily affected by cross-linking degree. However, the strength and failure strength increased with increasing molding temperature, which corresponds to an increase in the degree of cross-linking. In addition, the type of protein cross-links in rigid gluten polymer materials depends on the molding conditions and the initial gluten powder moisture content. Disulfide bonds are the main dominating gluten cross-links, but at molding temperature exceeding 130 °C, other non-disulfide bonds were formed such as dehydroalanine and/or lanthionin [10].

In order to improve toughness, natural fibers can be incorporated into gluten polymers. Natural fibers have an advantage over synthetic fibers since they are intrinsically biodegradable, available in large amounts, can have low cost and have low energy utilization. Two types of gluten composites reinforced with natural fibers have been studied so far: random short fiber gluten composites and aligned continuous fiber gluten composites.

For short fiber gluten composites, a plasticizer like glycerol is most often used to facilitate processing. Just as for rubbery gluten polymers, the failure strain in these composites increases at the expense of both modulus and strength with increasing levels of plasticizer. Kunanopparat and colleagues [11,12] found that the molding conditions and fiber contents also affected the mechanical properties of such rubbery gluten composite materials. When increasing the molding temperatures from 100 to 130 °C, the modulus and strength increased due to an increase in degree of matrix cross-linking. At higher fiber contents, the modulus and strength increased. However, no significant effect was observed on the degree of cross-linking with increasing fiber contents, suggesting that fiber addition had no influence on the gluten cross-linking.

Aligned continuous fiber rigid gluten composites – the case of interest for the present paper – can potentially maintain a high stiffness and strength, and at the same time, display a reduced brittleness compared to rigid gluten materials when loaded in the longitudinal direction. However, developing a fabrication process for such composites is quite challenging due to the powder form of gluten, the high protein viscosity and the thermoset character of gluten. Indeed, the gluten cross-links formed at high temperatures increase the protein viscosity during compression molding.

Only few strategies to address this challenge have been reported in literature. Ye and colleagues [9] dissolved gluten in meta-cresol and then immersed basalt fibers in the solution. The solvent route clearly is beneficial to material properties as the bending modulus of unidirectional composites at 40% fiber volume fraction increased from 4.40 GPa to 8.56 GPa. Reddy and Yang [13] sprayed both wheat gluten and water on a jute fiber mat and ultimately produced composites with a modulus of about 7.7 GPa at a 40% fiber mass fraction. However, both composites show relatively low moduli as compared to the theoretical predictions 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 [9] and 27 GPa [15], the theoretically achievable modulus of unidirectional composites would be around 38 GPa and 12 GPa, respectively.

Hemsri and colleagues [16] toughened gluten with coconut fiber (treated by alkali and silane) aiming at exploiting the high elongation at break of these fibers. They obtained mechanical properties close to theoretical predictions for their gluten composites but only considered a low fiber content (a matrix/fiber ratio of 85/15 by mass). At low fiber content, impregnation is rather easy but the attainable mechanical properties are only modest. In the previous study of Vo Hong et al. [17], a suspension-solution method was used to facilitate the production of flax fiber/gluten composites. However, the obtained mechanical properties were still below the theoretical values, indicating that further improvements in impregnation and adhesion should be made.

In summary, the mechanical properties of current gluten composites are far below the values that are theoretically possible. These properties are also not good enough for industrial applications. Therefore, the aim of this work is to design a fabrication method to obtain unidirectional fiber composites with superior mechanical performance at medium to high fiber content (at least $V_f = 20\%$). To obtain composites with good mechanical properties, good contact between fiber and gluten molecules is of key importance. To achieve such good contact, immersing fibers in a gluten containing solution could be a good approach. As mentioned above, Ye and colleagues [9] dissolved gluten in the toxic and corrosive solvent meta-cresol. From environmental and safety viewpoints, it would be better to apply another solvent. Gluten consists of monomeric gliadins which are soluble in alcoholic media (e.g. 60–70% ethanol) and polymeric glutenins which are insoluble in alcoholic media [1]. Therefore, in this research, composites were made based on the gliadin fraction. Recently, gliadin based materials have been studied by casting films, in binding particle based composites, or in producing short fiber composites [18–20]. The production of high mechanical performance composites based on long and unidirectional fibers and gliadin polymers as matrix has, to the best of our knowledge, not been investigated.

In this study, the gliadins were dissolved in 70% ethanol and this solution was used to impregnate the fibers. The dry prepregs were stacked and compression molded into composites without the need for any further solvents or plasticizers. In order to investigate the success of our fabrication process, the mechanical properties of gliadin-fiber composites were compared to gliadin polymers without fibers which were subjected to the same compression molding conditions.

According to Jansens et al. [8], compression molding at 150 °C is well suited to maximize the degree of cross-linking, while avoiding excessive gluten degradation. Therefore, in the present case molding at 150 °C was chosen for making gliadin composites. The cooling rate after compression molding was systematically varied and its effect on the mechanical properties was addressed. The cooling rate determines the time spent at high temperatures, which may affect the degree of cross-linking and hence also the material properties. Besides affecting the degree of crosslinking, varying the cooling rate may also affect the material density [21]. In general, the density of an amorphous polymer glass is higher when the glass transition temperature is crossed at a slower cooling rate [21]. Vice versa, rapid cooling may result in vitrified matrices with a higher free volume, which tends to facilitate plastic deformation [22]. It is relevant to explore whether or not such effects have an impact on the composite mechanical properties. Besides the mechanical properties also the degree of protein cross-linking and the material glass transition temperature were characterized and discussed.

2. Experimental

2.1. Materials

Wheat gluten powder with a protein content of 77.8% on a dry matter basis and moisture content of 5.6% was obtained from Tereos Syral (Aalst, Belgium). Remaining fractions mainly include starch and lipids.