WHEAT GLUTEN CROSS-LINKING AND ITS IMPORTANCE FOR THE MECHANICAL PROPERTIES OF RIGID BIOPLASTICS

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Introduction

Gluten proteins, the storage proteins of wheat, consist of single-chained gliadins and multi-chained glutenins. As a co-product of the industrial gluten-starch separation, gluten is available in large quantities and used both in the food and in the non-food industry [1,2]. It is an interesting biopolymer for producing biobased materials because of its annually renewable, abundant availability, low cost, biodegradability and unique network forming properties [2]. In absence or at low concentrations of plasticizer, high-temperature compression molded wheat gluten vitrifies into a rigid, glassy material upon cooling. Nevertheless, current gluten-based materials are still outperformed by their synthetic counterparts [2]. The objective of this research was to produce rigid gluten-based materials with mechanical properties approaching those of plastics such as *e.g.* polystyrene. Hereto, it is necessary to understand the molecular changes taking place during bioplastic formation and to establish their impact on the mechanical properties of the end product.

Results and discussion

First, the effect of molding temperature (130-170 °C), time (5-25 min) and gluten resin moisture content (5.6-9.1%) on protein cross-linking during high-temperature compression molding and on the mechanical properties of the rigid, glassy end products was investigated [3,4]. Protein cross-linking was affected by all parameters studied. At 130 °C, the cross-linking was predominantly based on disulfide bonds. At higher molding temperatures, also non-disulfide bonds contributed to the gluten network. Under the experimental conditions, the dehydroalanine-derived cross-link lanthionine (LAN) was detected in all gluten samples molded at 150 and 170 °C. Degradation was observed for samples molded at 170 °C.

The flexural modulus of all molded samples was affected neither by any of the processing parameters nor by the resulting altered protein characteristics. In contrast, the strength and failure strain of samples prepared from gluten with the same initial moisture content, increased with the degree of protein cross-linking and were maximal when compression molded for 5 min at 170 °C. The strength and the failure strain decreased when gluten proteins were degraded during molding. These results provide further evidence for the statement by Meijer and Govaert [5] who, in their review on the mechanical performance of polymer systems, postulated that the modulus of non-oriented polymers in the glassy state is determined by the polymer's secondary bonds and free volume kinetics (involving aspects of thermal history and aging), while the network's primary bonds potentially induce delocalization of local strain out

of the area of the largest stress that in turn may bring toughness. Altering primary bonds by introducing cross-links is thus not expected to heavily affect the modulus of glassy materials but may enhance their toughness.

Next, the impact of the gliadin-glutenin ratio was examined. Cross-linking was more extensive for glutenin-rich than for gliadin-rich samples molded under the same conditions. The relative contribution of non-disulfide bonds to the gluten network was higher for glutenin-rich than for gliadin-rich samples. Interestingly, while the modulus of molded samples did not depend on the degree of cross-linking, it increased with gliadin content, possibly pointing to strong secondary interactions between the constituents. Relaxation enthalpies increased with gliadin contents and were correlated with the modulus. The degree of cross-linking tended to increase the strength and failure strain of molded glutenin-rich samples, but not that of molded gliadin-rich samples.

Subsequently, gluten was pretreated with acid or alkali prior to compression molding [6]. Alkaline pretreatment strongly affected gluten cross-linking, while acid pretreatment had little effect on the gluten network. After molding, alkaline treated gluten showed enhanced cross-linking but also degradation when pretreated at high alkali concentrations, while acid pretreatment restricted gluten cross-linking. Under alkaline conditions, formation of the non-disulfide cross-link LAN was enhanced. In contrast, the formation of non-disulfide cross-links during molding was hindered in acid pretreated gluten. The bioplastic strength was higher for alkali pretreated samples than for acid pretreated ones, while the flexural modulus was only slightly affected by either alkaline or acid pretreatment. The ratio of disulfide to non-disulfide bonds did not seem to affect the mechanical properties of rigid gluten materials.

Finally, disulfide cross-linking was specifically targeted with the monothiol 3-mercaptopropionic acid (MPA) [7]. This additive acted as reducing agent during mixing with gluten and, thus, decreased the molecular weight of the gluten aggregates during the mixing stage. The strength and the failure strain of the molded samples with MPA was higher than that of samples without MPA, while the modulus remained unaffected. Interestingly, the strength was independent of the MPA concentration, while the degree of cross-linking decreased with increasing concentration. It is hypothesized that MPA facilitates conformational changes which result in a rearrangement of the secondary interactions between protein chains and/or an increased entanglement degree which could affect the mechanical properties of glassy gluten materials. This view was further supported by preparing a rigid material which only contained a very low level of covalent cross-links, but still showed high strength.

Conclusion

In this work the molecular changes occurring during compression molding of gluten as well as the relationship between network and mechanical properties was investigated. The latter cannot be explained by cross-linking alone. It is hypothesized that also secondary interactions and/or entanglements can yield materials of high strength. This knowledge opens perspectives for the production of gluten-based bioplastics with improved mechanical properties.

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