



Removal of disulfide cross-links from wheat gluten and the effect thereof on the mechanical properties of rigid gluten bioplastic



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ABSTRACT

High-temperature compression molding of wheat gluten at low moisture content yields a rigid, glassy material. Thiol functionalized additives improve the toughness of this material but the underlying mechanism is not yet fully clear. In order to elucidate the relative importance of other factors besides cross-linking, wheat gluten was modified by removing all (disulfide) cross-links in the protein network prior to compression molding. In contrast with what was the case for molded unmodified gluten, covalent cross-linking in molded modified gluten (MG) was minimal to non-existent after molding at 130 °C. However, the flexural strength of modified samples was significantly better than that of unmodified samples. Increasing the molding temperature and thereby altering the degree of cross-linking in the molded MG network did not have any effect on mechanical properties determined by both flexural and compression tests. With increasing levels of glycerol, the decrease in flexural strength and increase in flexural strain was less pronounced for molded MG than for molded unmodified gluten. We postulate that exposing gluten to disulfide reducing agents (such as thiol functionalized additives) enhances intermolecular secondary interactions and increases the number of molecular entanglements, which in turn contribute to improving the mechanical properties of rigid gluten materials. These effects are at least as important as chemical (disulfide) cross-links, which some multifunctional thiol additives may introduce.

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Abbreviations: DHA, dehydroalanine; DTNB, 5,5'-dithio-bis(2-nitrobenzoic acid); DTT, dithiotreitol; LAL, lysinoalanine; LAN, lanthionine; MG, modified gluten; MW, molecular weight; SDS, sodium dodecyl sulfate; SDSEP, extractable protein with SDS containing medium; SDSEPred, SDSEP under reducing conditions; SE-HPLC, size-exclusion high-performance liquid chromatography; SH, sulfhydryl; TCEP-HCl, tris(2-carboxyethyl)phosphine hydrochloride; Tg, glass transition temperature; WAXS, Wide-Angle X-ray Scattering.

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1. Introduction

In recent years, the increased usage of oil-based non-biodegradable plastics and the accompanied accumulation of waste has raised many ecological concerns. In this context, biodegradable material from renewable resources has attracted much attention. Wheat gluten protein, which exhibits unique visco-elastic properties and cross-links when heated, is an interesting candidate for the

manufacturing of biobased materials [1]. Solution casting is arguably the most well studied method to obtain such gluten bioplastics [2]. However, this kind of processing is rather slow and unpractical from an industrial point of view. In this regard, dry processing techniques such as high temperature compression molding are industrially more attractive.

Amorphous high molecular weight polymers inherently display a transition from glass to rubber at a specific temperature, the glass transition temperature (T_g) [3]. At high concentrations (>15%) of plasticizer, gluten materials are rubbery at room temperature whereas at low concentrations of plasticizer they are glassy, stiff and brittle. It is this kind of less-well studied glassy material, with properties highly different from its rubbery counterparts, which is the subject of the present study.

During the compression molding process, a protein melt is formed which at sufficiently high temperatures is susceptible to reactive cross-linking. The cross-linking of gluten protein entails a wide array of possible reactions that can be divided into two main groups: disulfide reactions (with oxidation and interchange mechanisms) and non-disulfide reactions. During molding at 130 °C, disulfide reactions are the most dominant cross-linking reactions in gluten. At higher temperatures, other non-disulfide cross-linking mechanisms (e.g. cross-linking initiated by β -elimination) become increasingly apparent [4]. Higher molding temperatures and longer molding times increase the cross-linking degree in gluten and result in gluten material with better toughness, until a certain point where protein degradation sets in [5]. In their review on the mechanical performance of polymer systems, Meijer and Govaert [6] stated that the modulus of non-oriented polymers in the glassy state is determined by the polymer's secondary interactions (including e.g. hydrogen bonds) and free volume kinetics (involving aspects of thermal history and ageing) while the primary bonds (including disulfide bonds and other cross-links) in the network potentially induce delocalization of local strain out of the area of the largest stress.

The use of additives for improving the mechanical properties of glassy gluten material has been the subject of some study. Alkaline pretreatment of gluten samples increases the degree of cross-linking and alters the type of cross-linking in the resulting end product. The bioplastic strength was higher with alkaline pretreatment whereas the type of cross-linking did not seem to influence the mechanical properties [7]. Thiol (sulfhydryl, SH) terminated additives can be used to influence disulfide cross-linking reactions in gluten. Woerdeman et al. [8] studied the influence of a tri-thiol functionalized molecule on the gluten network. Flexural strain and strength of the samples with the additive were better and the decreased water absorption of the gluten plates was an indication for increased cross-linking in the material. Dicharry et al. [9] thiolated various poly(vinylalcohol)s and used these as additives to obtain rigid gluten materials with improved mechanical properties. For this particular system, no increase in cross-linking was noted and it was postulated that a complex blend morphology was the origin of the improved properties. More recently, Jansens et al. [10,11]

conducted an extensive study on the influence of the chemical structure and the degree of functionalization of different SH functionalized additives on wheat gluten during mixing and after compression molding. Overall, smaller molecules and molecules with a lower amount of SH groups on a single molecule proved to be most effective at improving mechanical properties. Furthermore, it was argued that the improvement of the gluten material could not solely be attributed to increased protein cross-linking. This statement was reinforced by the outcome of an experiment in which a simple monothiol was used, which had no inherent cross-linking abilities but still improved the mechanical properties of the glassy gluten plates to the same extent as those previously obtained by Woerdeman et al. [8] and Dicharry et al. [9]. It was stated that aside from the cross-linking aspect, other factors could also be of significant importance.

Despite the ongoing research in this field, the mechanical properties of current gluten bioplastic are still not up to par with those of petroleum based alternatives. Recent publications have shed more light on the actual role of SH functionalized additives in glassy gluten material [8–11]. However, the exact mechanisms behind these consistent improvements remain unclear. Against this background, the aim of the present study is to obtain a deeper insight into the mechanisms responsible for said improvement. To achieve this goal, wheat gluten was modified via a new procedure which eliminates all cross-links in the gluten sample via disulfide reduction. The obtained modified gluten (MG) could easily be molded into MG based bioplastic. Hence, it is excellent material to investigate the importance of factors other than cross-linking for the mechanical properties of rigid gluten materials. MG was successfully subjected to different molding conditions and the resulting mechanical properties, as determined with three point flexural and uniaxial compression tests, were analyzed and compared with those of unmodified gluten. The gluten network was evaluated indirectly via assessment of the protein extractability in sodium dodecyl sulfate (SDS) containing medium using size-exclusion high performance liquid chromatography (SE-HPLC), water absorption measurements, amino acid analysis, dehydroalanine (DHA) determination and free SH determination. Wide Angle X-ray Scattering (WAXS) was used to probe protein conformational changes. Subsequently, the gluten network characteristics were linked with the mechanical properties. Furthermore, the effect of limited concentrations of plasticizer to alleviate the inherent brittleness of this glassy material was studied on both molded gluten and molded MG samples.

2. Experimental

2.1. Materials

Wheat gluten with a protein content of 77.8% (dry basis) and a moisture content of 5.6% was obtained from Tereos Syral (Aalst, Belgium). The moisture content was determined according to the AACC Approved Method 44-19 [12]. Protein content ($N \times 5.7$) was determined

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