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Wheat gluten/chitosan blends: A new biobased material

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ABSTRACT

Wheat gluten and chitosan are renewable materials that suffer from some poor properties that limit their use as a potential replacement of petroleum-based polymers. However, polymer blends based on wheat gluten and chitosan surprisingly reduced these shortcomings. Films were cast from acidic aqueous or water/ethanol solutions of wheat gluten and chitosan. Wheat gluten was the discontinuous phase in the 30–70 wt.% wheat gluten interval investigated. The most homogeneous films were obtained when reducing agents were used (alone or together with urea or glycerol). They consisted mainly of 1–2 μm wheat gluten particles uniformly distributed in the continuous chitosan phase. Slightly smaller particles were also observed in the water/ethanol solvent system, but together with significantly larger particles (as large as 200 μm). Both small and large particles were observed, albeit in different sizes and contents, when surfactants (both with and without a reducing agent) or urea (without a reducing agent) were used. The particles were often elongated, and preferably along the film, the most extreme case being observed when the glyoxal crosslinker was used together with sodium sulfite (reducing agent), showing particles with an average thickness of 0.6 μm and an aspect ratio of 4.2. This film showed the highest transparency of all the blend films studied. For one of the most promising systems (with sodium sulfite), having good film homogeneity and small particles, the mechanical and moisture solubility/diffusivity properties were studied as a function of chitosan content. The extensibility, toughness and moisture solubility increased with increasing chitosan content, and the moisture diffusivity was highest for the pristine chitosan material. It is noteworthy that the addition of 30 wt.% wheat gluten to chitosan reduced the moisture uptake, while the extensibility/toughness remained unchanged.

1. Introduction

Due to the demand for the use of sustainable materials, there is an increasing interest in using polymers from renewable resources. Most work on renewable polymers considers pristine or plasticised materials, but blends of these polymers has also been studied, see e.g. Refs. [1–5]. Both wheat gluten and chitosan have been extensively studied, but little attention has been given to blends based on these polymers. Park and Bae [6] observed that when only 3 wt.% chitosan was added to wheat gluten, the tensile/puncture strength and elongation at break increased, together with increased water vapour barrier and improved antimicrobial properties, relative to those of the pure wheat gluten material. Fernandez-Saiz et al. [7] showed that blends of wheat gliadin and chitosan had a greater water resistance than pure chitosan. On the other hand, the microbial resistance of the film increased with increasing chitosan content. Li et al. [8] reported that wheat gliadin/chitosan materials showed a two-phase morphology in blends with a chitosan content of

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20–60 wt.%, and that a phase inversion occurred at ca. 40 wt.% chitosan. The stiffness and strength of these blends increased with increasing chitosan content, whereas the strain at break decreased. At the same time, the water vapour permeability and the water uptake increased with increasing chitosan content. To summarize, hitherto reported studies have been concerned with blends with a very low chitosan content ($\leqslant$3 wt.%) and with wheat gliadin/chitosan, which are expected to behave differently from blends with wheat gluten. In addition, making homogeneous blends with wheat gluten, rather than with wheat gliadin, is more challenging due to its higher molar mass, but it is also more interesting from a commercial point of view because of the simplified manufacture eliminating one process step (extraction), and the higher yield since both glutenin and gliadin are present.

Blending wheat gluten with chitosan provides a compromise that reduces the drawbacks associated with each of the two materials. It is shown here that the extensibility and toughness of wheat gluten increase with the addition of chitosan. On the other hand, the moisture sensitivity/moisture uptake decreases with the addition of wheat gluten to chitosan. Another advantage of adding wheat gluten to chitosan is the reduction in price. Chitosan is significantly more expensive than wheat gluten [9–11]. Possible future applications of films of wheat gluten/chitosan blends are in various packaging (e.g. food, edible, medical) or as 3D objects in e.g. hoods in home appliances.

The properties of an immiscible blend such as wheat gluten/chitosan depend on the microstructure of the blend: the type of morphology (discrete/continuous); which of the polymers is the continuous phase and the size of the discrete phase. The focus in the first part of the study was to explore, at a constant wheat gluten/chitosan ratio, how different film preparation conditions (drying, solvent type/heating/ultrasonication) and additives (surfactants/reducing agents/plasticisers/denaturing agents/cross-linker) affect the final blend structure and optical properties, with the specific goal of finding the most promising conditions/blend(s) with respect to blend homogeneity, particle size and transparency. In the second part, for one of the most promising blends, the mechanical and optical properties and the moisture uptake/diffusivity were evaluated as a function of the wheat gluten/chitosan ratio. For comparison, the mechanical properties of a heterogeneous blend were also determined.

2. Experimental section

2.1. Materials

Commercial wheat gluten powder was kindly supplied by Reppe AB, Lidköping, Sweden. According to the supplier, the gluten protein content (according to Mod NMKL nr 6, Kjeltec, Nx5.7) was 77.7% and the starch content was 5.8% (Ewers, polarimetric method). The chitosan provided by Sigma Aldrich had a molar mass of $\overline{M}_n$ = 210 kDa and $\overline{M}_w$ = 790 kDa. The degree of deacetylation was $\geqslant$75%. Anhydrous acetic acid (purity 98%), polyethylene glycol sorbitan monolaurate (Tween 20), 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol (Triton-X), hexadecyltrimethyl ammonium bromide (HTLB), glyoxal (40 wt.% in H_2O), sodium sulfite (98%), DL-dithiothreitol (DTT, >98%), 2-mercaptoethanol ($\geqslant$99%) and sodium dodecyl sulphate (SDS, 20% in H_2O, analytical) were obtained from Sigma Aldrich. Ethanol (96%) and glycerol (ultrapure, HPLC grade) were supplied by, respectively, VWR and Alfa Aesar. Urea ($\geqslant$99.5%) was purchased from Merck. Deionized water was used in all the experiments.

2.2. Preparation of blends

The blend films were prepared according to different methods, as shown in Fig. 1, from separate solutions of chitosan and wheat gluten. Chitosan was dissolved in aqueous acetic acid (acetic acid content: 0.05 mol/L) to a concentration of 1% w/v. The solution was stirred overnight and the pH of the solution was ca. 4. The concentration of wheat gluten in the wheat gluten solution (based on water or water/ethanol) was 5 or 12 wt.%. This solution was prepared in various ways, as shown in Table 1. One of the blends was prepared using ultrasonication (750 Watt Ultrasonic Processors – VCX Series). The treatment lasted for 5 min at a frequency of 20 kHz and an amplitude of 21% of the total power that the machine could supply.

2.2.1. Films produced using the water/ethanol solvent

Wheat gluten/chitosan blend films were made from a wheat gluten solution that was prepared with water and ethanol as solvent (2/1 by mass), according to Olabarrieta et al. [12] (systems 1 and 2 in Table 1). The wheat gluten powder was added to the water/ethanol solution and the mixture was stirred for 20–40 min. The pH of the mixture was lowered to 4 by the addition of acetic acid, after which it was stirred for 20–40 min. In one case, the mixture was heated for 20 min to 70 °C and left at this temperature for 10 min (system 1, Table 1). Subsequently, with or without the heating step, the wheat gluten solution was poured into the chitosan solution and the mixture was stirred for 20–40 min. The solution was then filtered using a TexWipe TX309 cloth (118 * 60 threads per inch, pore size 100–200 μm) and then poured into petri dishes. The films were obtained by drying the solution in an oven at 26 ± 1 °C at ca. 40% relative humidity (RH) (method O) or in a climate room at 23 ± 1 °C, 50 ± 2% RH (method C). In the oven, the air (256 l) was exchanged 40 times per h. The films kept in the oven dried overnight whereas the films in the climate room required approximately one more day to dry.

2.2.2. Films produced with a reducing agent

The wheat gluten solution was prepared using water and a reducing agent and the procedure was partly adopted from Refs. [13,14]. The water and reducing agent were mixed together and stirred for 15–20 min and the wheat gluten powder was then carefully added to the solution. After 30 min stirring, the pH was lowered to 4 by the addition of acetic acid. This solution was subsequently stirred for 20–40 min and then poured into the chitosan