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Edible wheat gluten (WG) protein films

Preparation, thermal, mechanical and spectral properties

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Abstract Commercial wheat gluten (WG) films, hard wheat gluten films and soft wheat gluten films, plasticized with glycerol have been cast from water–ethanol solutions. The effect of aging on various film properties has been investigated. The films were aged for about 6 months at 50% relative humidity and ~25 °C, and the mechanical (tensile strength and the percentage of elongation at break (E_b)), thermal (TG and DSC) and Attenuated Total Reflectance (ATR)-FTIR spectral properties have been studied. Changes in the protein structure were determined by ATR-FTIR spectroscopy. Films from soft WG exhibited the highest E_b (508%) and the highest TS (6.33 MPa). The TG analysis results show that the moisture content in all three kinds of WG protein films is about 5%. The absence of the glycerol phase transition in DSC curves implies that there is no separate phase containing glycerol in the WG protein-glycerol films with 40% glycerol.

Keywords DSC · TG · FTIR · Tensile strength · Elongation at break · WG protein films

Introduction

Wheat gluten (WG) proteins can be utilized to make films with novel functional properties, such as selective gas barrier properties and rubber-like mechanical properties. WG-based materials are homogeneous, transparent, mechanically strong, and relatively water insoluble. They are biodegradable and a priori biocompatible, apart from some WG specific characteristics such as allergenicity. They are also edible when food-grade additives are used, and the presence of impurities is avoided. Wheat gluten proteins are insoluble in water and require a complex solvent system with basic or acidic conditions in the presence of alcohol. Generally, changing the pH of the medium disrupts hydrogen and ionic interactions, while ethanol disrupts hydrophobic interactions. The isoelectric point for WG is at about 7.5. Wheat gluten films do not form in the protein's isoelectric region (pH 7–8), most likely impeded by intermolecular protein repulsive forces. Also, WG dispersion at pH 5–6 is very poor, resulting in films of uneven thickness and containing big particles of coagulated protein particles, which were unsuitable for property evaluation. However, adjusting the solution to acidic or basic conditions (above and below this pH (7.5)) will favor the protein solubility and the film forming process. It is well-known that heat treatment affects protein conformation and improves some film properties depending on heating conditions. Temperature has an aggregating effect on WG inducing the formation of covalent bonds between proteins. Raising the temperature can denaturate globular proteins. This means that gliadin proteins when denaturated lose the native conformation and they open, exposing previously unexposed intramolecular disulfide bonds which now can be reduced and form other new intermolecular disulfide bonds. The drying step is also a critical part of the film forming process which can affect the final film properties. During drying, all volatile disruptive agents are progressively eliminated. Solvent removal increases the concentration of WG proteins. Consequently, active sites for bond formation become free and close enough to each other to create new interactions. New hydrogen bonds, hydrophobic interactions, and disulfide bonds contribute to the formation of a good oxygen barrier three-dimensional network. There are many parameters which must be controlled when making WG films. Functional properties of

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gluten films are highly dependent on WG concentration in solution, pH, additives, solvent polarity, temperature, and drying rate.

Wheat gluten films have been found to be very effective oxygen barriers. So, packaging applications that utilize the films' oxygen barrier ability are one possible area for WG film application. Several food items susceptible to lipid oxidation could benefit from multilayer packaging materials consisting of protein coatings in combination with an external moisture barrier. Protective protein coatings could also be used on certain food products, such as meat pies and high-moisture low sugar cakes that require films that are highly permeable to water vapor. Employing protein coatings as carriers of antioxidants and other food additives is another envisioned application. Protein films can also have applications in implant medicine, biosensor design, food processing and chromatographic separation. Thermo-physical techniques are valuable tools in the characterization of protein films. This study deals with the preparation and various thermal and mechanical characterization such as TG, DTA, DSC, elongation at break, and tensile strength (TS) of protein films to identify their values and virtues.

Wheat gluten is an interesting alternative to synthetic plastics in food packaging applications due to its combination of attractive mechanical, oxygen barrier, and film-forming properties, and renewability. From an industrial point of view, the advantage of vital WG is that it is readily available at a low price with only a small variation in quality [1]. Several studies have dealt with the film-forming properties of WG proteins, mostly involving water–ethanol dispersions/solutions [2–10].

Packaging materials must have time-stable properties in order to protect the foodstuff and give a long shelf life. However, biopolymers, including WG films, suffer from aging. To limit aging, it is important to identify and understand the mechanisms and reasons for the time-dependent physical and chemical changes. Only a limited amount of studies have been reported on this topic despite that it is perhaps the most important problem that has to be solved before WG films can be of commercial interest for the packaging industry. Examples of factors that have an impact on the aging of protein films are phase separation, diffusion/migration, and loss of additives [4, 10, 11] and thiol oxidation [7, 12]. In the case of WG films the migrating species can be water and ethanol, originating from the solvent and added plasticizer (e.g. glycerol). Since these components plasticize the film, migration or phase separation results in a time-induced brittleness [10]. Other time-dependent changes may also possibly occur, including protein aggregation and oxidation that increase the brittleness. Vital WG contains a small amount of starch that inevitably also ages. The film and film-forming properties are strongly dependent on the pH of the dispersion, and they are normally inferior close to the isoelectric point, which for WG is of the order of 7.5 [13]. Gennadios et al. [2] obtained homogeneous WG films at pH 2–4 and pH 9–13, whereas films were of poor quality at pH 5–6 and did not form at pH 7–8. This study aims toward an understanding of the mechanisms responsible for the aging of films of plasticized vital/commercial WG cast from water–ethanol solutions at pH 4 and pH 11. The choice of these pH values was based on the idea of having acidic and basic solutions far from the isoelectric point.

Casting was used since it is closely related to dispersion coating, an interesting potential application technique for vital WG on e.g., paperboard in packaging applications. The films were stored at 50% relative humidity (RH) on a blotting paper. The aim was to reveal if the plasticizer migrates to the paper during aging. This may be a critical issue in case WG is to be laminated with paper in future applications. This is, to our knowledge, the first study on the correlation between protein structure, film "homogeneity", volatile mass loss, plasticizer migration, and mechanical and permeation properties during aging of flexible WG films.

Possible applications of protein films

The goal of protein and other biodegradable films are simple: replace existing synthetic, non-biodegradable products at the lowest cost for uses such as

(a) Reduce oxygen, aroma, oil, and/or moisture migration.
(b) Maintain food product integrity and enhance food product appearance.
(c) Minimize the cost of coating materials and coating process and reduce packaging needs.

However, protein films and coatings are normally not meant to be replacements for existing non-edible films and coatings. They may at least reduce the use of existing synthetic, non-biodegradable products. As edible films, protein films offer an alternative packaging to synthetic packaging materials. Because of their biodegradability properties and renewable natural resources, they can play a very important role in packaging and coating industry.

Protein films can be used as "Frozen and Refrigerated Dough" and can contribute in extended shelf life after baking volume. They can have application as "Frozen Bread Dough" and can contribute in better, softer mouth-feel, fresher tasting, and extended baking. As edible films and coatings, they can be used in "Par-Baked Bread" and can contribute in improved color, crust, and texture. They can also have application as "Par-Baked Pizza Crust Pocket Sandwiches" and can contribute in moisture barrier

coating. Protein films can also be used as "Dry Mixes (breads/cakes)" and can improve moistness of finished products and can give more flavor [9]. Protein films can also have application in implant medicine, biosensor design, food processing, and chromatographic separation [10].

Currently, nondegradable petroleum-based synthetic polymers are used for food preservation and storage. Protein films find strong competition from nonedible synthetic films but have an environmental advantage in that they are renewable and biodegradable. Substituting some of this synthetic packaging with edible packaging could help reduce solid waste. Over 5 billion tons of packing-related solid wastes are discarded every year, and 30% of the wastes are plastics. Plastic biodegradation is a slow process, and the rate is affected by the nature of the material and its form. It takes several hundred years to degrade petroleum-based synthetic plastics, which have caused serious solid waste contamination in the world. Hence, a demand exists for natural biodegradable films from renewable sources as an alternative to synthetic polymers. During the past two decades, the use of increasingly large amounts of synthetic, nonbiodegradable packaging, and wrapping materials has created disposal and environmental problems. This study focuses on the possibility of replacing synthetic polymers with biodegradable polymers derived from renewable agricultural sources. The development of biodegradable packaging films from agricultural polymers would not only ease environmental problems but would also provide new uses for surplus agricultural products. The following methods have been used to assess the biodegradation of plastics: changes of mechanical properties in soil; biological oxygen demand (BOD) changes or CO_2 evolution in slugs molecular changes by enzymatic or microbial treatment, mechanical property changes or CO_2 evolution in soil; gas evolution by anaerobic digestion; and mechanical property changes in several compositing soil conditions. Recently, considerable research has been reported on the preparation and the evaluation of biopolymer films derived from renewable resources to replace petroleum-based packaging materials.

Potential applications of WG films

Although WG films are poor water vapor barriers, they have been found to be very effective oxygen barriers. Consequently, packaging applications that utilize the films' oxygen barrier ability should be primarily sought for WG films. For example, use of such films as oxygen barrier layers in multilayer packaging materials appears to be feasible. This is analogous to the use of moisture-sensitive ethylenevinyl alcohol and polyamide films as oxygen barriers in multilayer packages. Several food items susceptible to lipid oxidation could benefit from application of protein coatings in combination with an external moisture barrier. Protective protein coatings could also be used on certain food products, such as meat pies and high-moisture low sugar cakes that require films highly permeable to water vapor. Employing protein coatings as carriers of antioxidants and other food additives is another envisioned application [2].

Limitations of protein films compared to conventional films and coatings

Despite the benefits that biodegradable films offer, there are still significant obstacles that must be overcome, such as retailer and consumer scepticism, material costs, and the added costs of switching technologies. Moreover, biopolymer film properties still have some restrictions and drawbacks which limit their use in large-scale applications. Apart from not yet competitive mechanical properties, biopolymers films are still difficult to process in comparison with synthetic polymers. Some of the main drawbacks and limitations of biopolymer films are listed below [6].

Water sensitivity

As pointed out earlier, the major challenge for the material manufacturer is the by nature hydrophilic behavior of many biobased polymers, as many food applications demand materials that are resistant to moist conditions. Most of the biobased materials including WG are not soluble or are difficult to dissolve in water but they show large water uptake (swelling) and high water permeability. Moreover, films made by biological materials do change their mechanical and barrier properties in high-moisture conditions, which is also a great disadvantage. This water sensitivity can develop a more spontaneous, rapid, non controllable degradation under the influence of bacteria (the disadvantage of biodegradability).

Aging of biodegradable polymers

One of the challenges for the successful use of biodegradable polymer products is to achieve controlled lifetime. Products must remain stable and function properly during storage and intended use, but after that they should biodegrade efficiently. Only by appropriately controlling water activity, pH, nutrients, temperature, oxygen levels, and time can package integrity and microbial stability be assured. Thus, biodegradable polymer films may be safely stored in dry environments and used with dry food products over a relatively long period of time, whereas acceptable time of storage in moist environments or time of use with moist foods would be limited [12]. Biodegradable polymers suffer

a change in their properties during time, aging, which make them not suitable for commercial applications. The aging of a biodegradable film can be due to physical or chemical reactions in the polymer matrix. The most common aging processes that films use to go through are:

Physical aging: migration of additives from the matrix

This is a physical process that the films suffer when plasticizers migrate to the surface. Generally, migration of these low molecular compounds leads to stiffer and less extendable polymers, which may decrease the protective function of the packaging and consequently reduce the shelf life of the packaged food. Plasticizer molecular Mass, concentration, and the hydrophobic or hydrophilic character influence the migration. Water, as one of the most powerful plasticizer for these types of films, also migrates with time from the matrix to the surface and evaporates leaving more brittle films [13].

Chemical aging: oxidation

Some studies have shown that formation of disulfide bonds by thiol oxidation occurred during WG film storage, even in conditions (temperature and RH) under which the mobility of molecules is reduced. Therefore, mechanical properties of the films might be changed with film aging, depending on the rate of thiol oxidation during film drying and storage [14, 15]. The sulfhydril in the cystein amino acid is responsible for the formation of disulphide cross links during oxidation [16]. This is a process which is accelerated when heating the film solution to make films, and it is of major importance for achieving good mechanical properties of the final product [17]. During time of storage, oxidation of un-reacted thiol groups and a reorganisation of the intramolecular disulfide bonds to intermolecular disulfide bonds via thiol-disulfide exchange reactions can occur. This will induce an increase of protein aggregation and a brittleness of the film structure [18]. Thermal and spectral analyses are very useful methods for materials characterization. Therefore, many authors have used these techniques for various materials characterization [19–39]. In this study, various edible WG protein films have been prepared and their thermal, mechanical, and spectral properties have been investigated.

Experimental

Experimental protocol for the preparation of WG films

Wheat gluten (~5% w/w) was dispersed through a sieve with stirring at low speed in water–ethanol containing

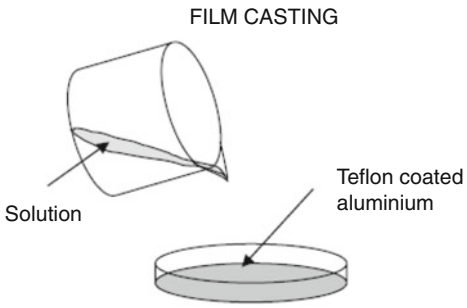

Fig. 1 Film casting procedure

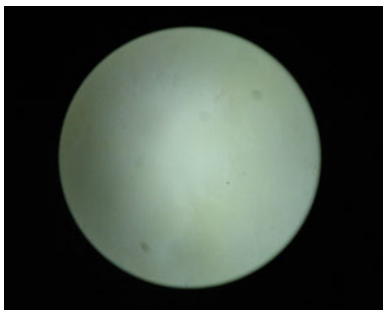

Fig. 2 Picture of a CWG nanobiofilm

(~3% w/w) glycerol. The pH was controlled during stirring and adjusted ~10 with NaOH. After ~3/4 h of stirring, the solution was put into a water bath at 70 °C for ~15 min. Then ~20 mL of the resulting dispersion was poured into a Petri dish. The cast films were placed in a box. The film casting procedure is presented in Fig. 1. The boxes were covered with cheesecloth and put in a temperature and RH semi-controlled environmental chamber (globe box). To investigate the effect of temperature and RH on film properties, 25–75 °C and 35–55% RH was used. Drying was performed until films could be easily removed. Films were stored at 20 °C and 50–60% RH before determining mechanical and physical properties [1–6]. A synthesized film has been presented in Fig. 2 as an example.

Tensile property test

The WG films were tensile tested using a MiniMat 2000 miniature materials tester, Rheometric Scientific, Inc., USA (Fig. 3). The films specimens were punched out from the films with a length and width of the narrow section of 12 and 5.0 mm, respectively. The thickness of each specimen was taken as the average of five readings.

The measurements were performed as described in ASTM 882 with a crosshead speed of 20 mm/min. 5 replicates of each sample were measured. The TS and the percentage of the elongation at break were determined.

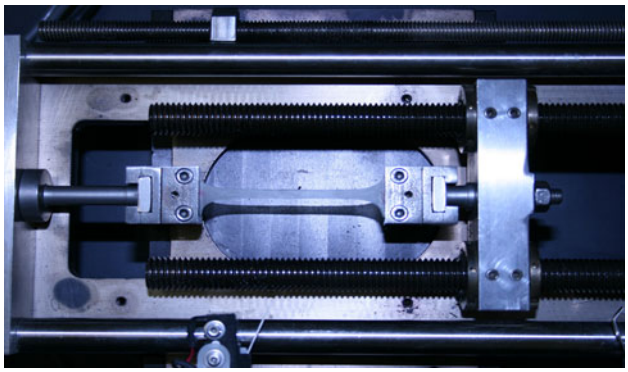

Fig. 3 Mechanical testing of WG nanobiofilm

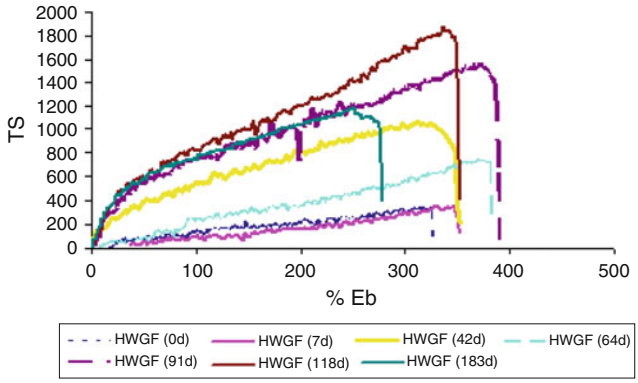

Fig. 4 Stress-strain curves of hard WG films

TG analysis

TG analysis of thin film samples (10–20 mg) were carried out using a SDT 2960 T.A. instrument at 10 °C/min from room temperature (rT) to 500 °C under helium atmosphere using a flowing rate of 120 mL/min. The WG films were cut into small strips and the TA instrument was calibrated for temperature before the measurement.

DSC analysis

The WG films were cut into small strips, and the samples (5-10 mg) were weighed into aluminum pans in a dry cabinet, sealed, and scanned together with an empty reference pan using a DSC 2920 T.A.I. instrument fitted with a liquid nitrogen-controlled cooling accessory. Samples were scanned at 5 °C/min from −100 to 100 °C under helium atmosphere using a flowing rate of 26 mL/min. The DSC instrument was calibrated for temperature before the measurement.

Results and discussions

Mechanical properties of films

Films from three types of WG (commercial, hard and soft) have been prepared and their thermal, mechanical, and spectral properties have been tested and compared. Stress–strain curves of hard WG films are given in Fig. 4 as an example. The films from all three kinds of WG have shown very good mechanical properties (Tables 1, 2, 3) mainly the percentage of elongation at break (E_b). However, the films from soft WG exhibited the highest E_b (508%) and the highest TS (6.33 MPa). The E_b of soft WG films (SWGF) has decreased a little bit after 57 days but TS increased significantly. The E_b of the films from commercial WG is between 400 and 500% till the fifth month but its E_b has dropt at sixth month. The E_b of hard WG films is between 300 and 400%. The E_b for low-density polyethylene (LDPE) and high-density polyethylene (HDPE) is 500 and 300%, respectively. The published E_b of protein films ranges widely from 1 to 260%. Compared

Table 1 Mechanical properties (TS and E_b) of CWGF

Time/days	E_b/%	TS/MPa
0	448–501	0.29–0.57
8	455–495	0.38–0.66
30	404–445	0.61–0.77
64	446–452	0.57–0.63
94	411–467	0.64–0.84
130	402–471	0.57–0.67
153	482–497	0.75–0.9
180	350–389	0.80–0.95

Table 2 Mechanical properties (TS and E_b) of HWGF

Time/day	E_b/%	TS/MPa
0	310–331	0.24–0.34
7	310–354	0.26–0.35
42	310–354	0.5–0.63
64	360–385	0.59–0.74
91	371–392	0.84–0.96
118	353–358	1.8–1.89
183	228–278	1.17–1.18

Table 3 Mechanical properties (TS and E_b) of SWGF

Time/days	E_b/%	TS/MPa
0	397–437	1.2–1.57
7	484–508	1.66–1.89
28	410–453	3.55–3.91
57	400–424	5.06–6.33
96	397–418	3.91–4.91
120	370–405	4.35–5.39

to the literature value, the films from all (commercial, soft and hard) WG have exhibited very high E_b. Though the TS is not very high, it is in the acceptable range for the protein films. In general, if the films' E_b is higher, the TS is usually lower. Another good property of the commercial WG films (CWGF) (stored at ~30 °C and 50% RH) is that the mechanical properties remain intact till (approx. 5 months) the 153rd day though its E_b has dropt at the sixth month.

Attenuated total reflectance (ATR)-FTIR spectroscopy of WG films

Spectral properties of CWGF, hard WG films (HWGF), and SWGF are investigated using ATR-FTIR spectroscopy. Attenuated total reflectance (ATR)-FTIR is a very useful technique to study the protein conformation in protein films. The ATR-FTIR spectra of CWGF, HWGF and SWGF contain a characteristic set of bands at the range 1653–1655 cm^{-1}. These are one of the most important bands in all WG films spectra and can be assigned to amide-I region (in the vicinity of 1650 cm^{-1}). Another very important set of FTIR bands at the range 1541–1543, present in WG films, are assigned to the amide-II region. The OH stretching bands of WG films at the range 3200–3800 cm^{-1} can be attributed to water, glycerol, and/or EtOH molecules. The peaks, present at the range 855-856 cm^{-1}, are associated with the C–C–O stretch or CH_2 twist of glycerol.

TG analysis

The TG curves of the CWG, HWG, and SWG are given in Figs. 5, 6, and 7, respectively and the TG curves of the CWGF, HWGF, and SWGF are given in Figs. 8, 9, and 10, respectively. The TG analysis results show that the moisture content in WG protein films is about 5%. The TG curves of WG exhibited two decomposition steps corresponding to the elimination of moisture and decomposition of WG. However, the TG curves of WG protein films exhibited four decomposition steps corresponding to the elimination of atmospheric moisture, glycerol, water, and decomposition of WG protein films.

DSC study

Thermal transitions of the plasticized WG films were studied also by DSC. Free glycerol exhibits a glass transition at −77 °C on DSC curve. If all glycerol is not participated to the film forming process, a proportion of the glycerol behaves as a separate phase to the protein with respect to the glass transition and the glycerol glass transition will be observed also in protein films at −77 °C. The absence of the glycerol phase transition (Figs. 11, 12, 13) implies that there is no separate phase containing

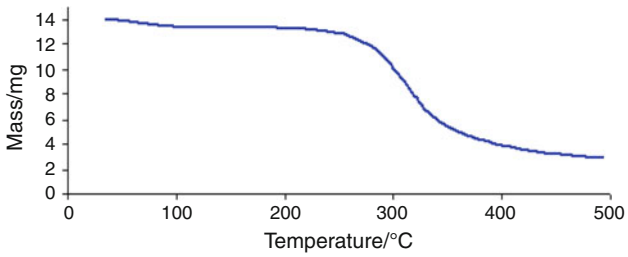

Fig. 5 TG curve of CWG

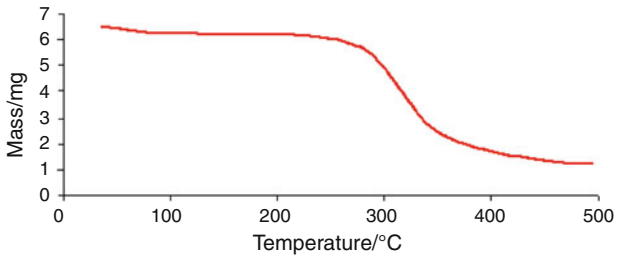

Fig. 6 TG curve of HWG

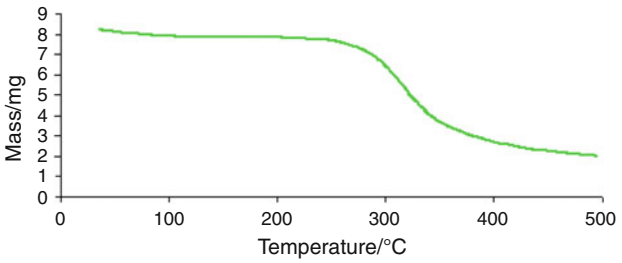

Fig. 7 TG curve of SWG

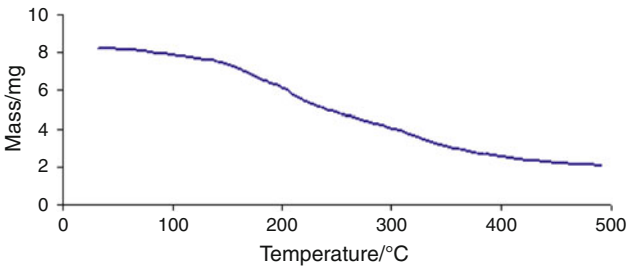

Fig. 8 TG curve of CWGF

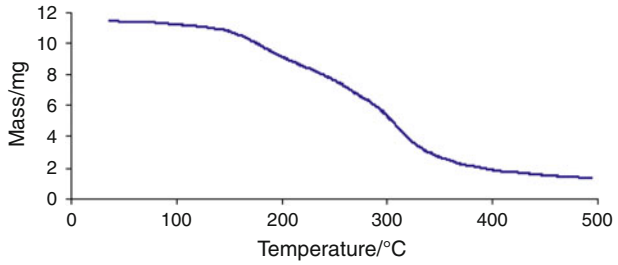

Fig. 9 TG curve of HWGF

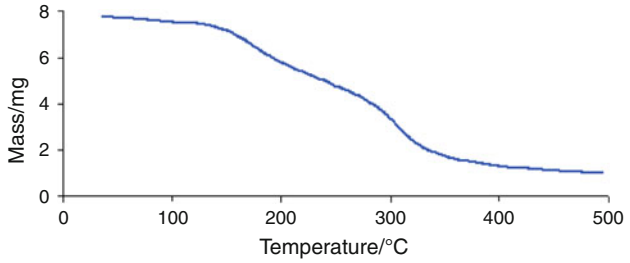

Fig. 10 TG curve of SWGF

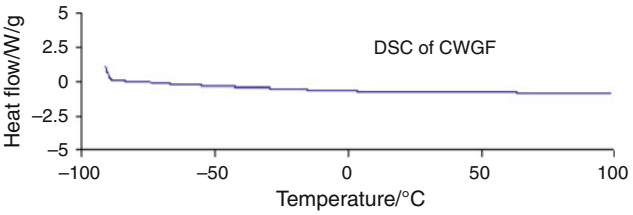

Fig. 11 DSC curve of CWGF

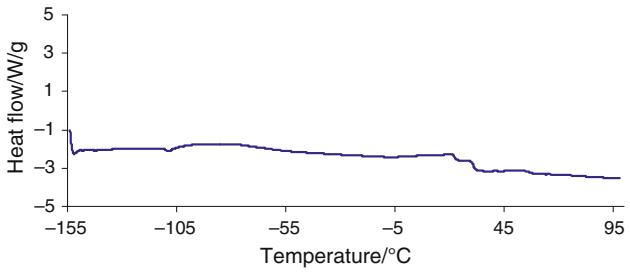

Fig. 12 DSC curve of HWGF

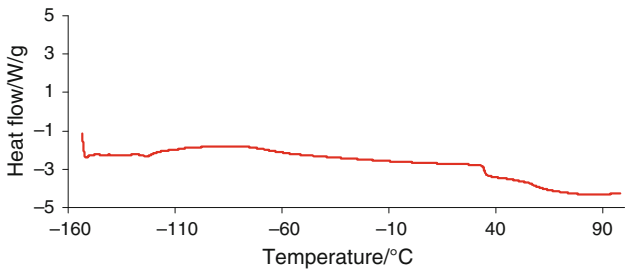

Fig. 13 DSC curve of SWGF

glycerol in the WG protein-glycerol films with 40% glycerol. The implications of this observation are discussed below.

In higher concentration of glycerol in protein-glycerol films, there is a tendency for glycerol to leach out supporting the notion that a separate glycerol phase is formed. A possible explanation of these results lies in the consideration of the processes that are occurring at the molecular level. At low glycerol levels, the glycerol is absorbed onto and possibly into the protein in a manner analogous to the way individual water molecules may bind to specific parts of a protein's structure and can even be termed "structural water". This increases motion and affects the protein conformation allowing the adoption of a secondary structure associated with the solvated protein. At low levels of glycerol, most of the interactions that are occurring between molecules are either protein–protein interactions or protein-glycerol interactions. There are relatively few glycerol–glycerol interactions. As the amount of glycerol increases, the number of glycerol–glycerol interactions increases. At higher concentration (depending on proteins) of glycerol, the number of these interactions is sufficient that at least some of the glycerol has properties similar to that in a bulk phase, and this can undergo a glass transition. Because the proteins are still diluted by the glycerol, at this point, there are continuing reductions in protein–protein interactions. However, the nature of the plasticization has changed from a situation in which plasticization behavior is dominated by glycerol-protein interactions to one in which glycerol–glycerol interactions play a significant role. Thus, there is a change in the trend of mechanical behavior.

Conclusions

Wheat gluten films are poor water vapor barriers but they are very effective oxygen barriers. Therefore, packaging applications that utilize the films' oxygen barrier ability should be primarily sought for WG films. For example, use of such films as oxygen barrier layers in multilayer packaging materials appears to be feasible. Several food items susceptible to lipid oxidation could benefit from application of protein coatings in combination with an external moisture barrier. Protective protein coatings could also be used on certain food products, such as meat pies and high-moisture low sugar cakes that require films highly permeable to water vapor. Employing protein coatings as carriers of antioxidants and other food additives is another envisioned application. Films from CWG, HWG, and SWG, plasticized with glycerol have been prepared from water–ethanol solutions. The effect of aging on various film properties has been studied. The films were aged for about 6 months at 50% RH and ~25 °C. TS, E_b, TG, DSC, and PTR-FTIR spectral properties have been investigated. Protein structures were studied using ATR-FTIR spectroscopy. Films from SWG exhibited best mechanical properties. The TG curves of WG exhibited two mass loss steps corresponding to the elimination of moisture and decomposition of WG. However, the TG curves of WG protein films exhibited four mass loss steps corresponding to the elimination of atmospheric moisture, glycerol, water, and decomposition of WG protein films. The process of plasticization of WG films by glycerol may be a model for the behavior of this plasticizer in many other systems. The

combination of spectroscopic, mechanical, and thermal and calorimetric studies on the same system offers a route to understanding of plasticized protein films.

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