Mechanical Properties of Whey Protein Films

Martin Anker, Mats Stading, and Anne-Marie Hermansson

SIK–The Swedish Institute for Food and Biotechnology,
P.O. Box 5401, S-402 29 Göteborg, Sweden

ABSTRACT

Mechanical properties of whey protein isolate (WPI) films at varying pH were studied using sorbitol (S) as a plasticizer. At pH 9, Young's modulus was not affected when the concentration of WPI or S varied. At pH 7, Young's modulus increased when the concentration of WPI increased, and decreased when the concentration of S increased. This contrast in behavior between the pH values is probably due to a structural difference which occurs above pH 8.

INTRODUCTION

Whey proteins are a byproduct of cheese-making and have generally been disposed of as animal feed or used in infant formulas, sports food, clinical nutrition products, etc. Today, great efforts are being made to find new uses for whey protein, for example, as edible and biodegradable films.

This study on whey protein *films* was promoted by the work previously performed on β-lactoglobulin and whey protein *gels* in our laboratory. The findings from these studies have been used as a basis to produce films and to obtain further data that can be used in future food packaging applications.

β-lactoglobulin is the dominating protein of the whey proteins and tends to influence the behavior of whey protein gels. The microstructure and physical properties of whey protein gels are sensitive to the heating conditions, amount of salt addition, pH, and concentration of whey protein, as well as the concentration of other additives such as plasticizers. The heating rate has therefore been held constant in this investigation, no salt has been added, and the influence of the other factors will be elucidated in this study.

Whey protein forms gels on heating and can form two types of gel network structures: fine-stranded and particulate[1]. The isoelectric point of the whey proteins is around pH 5.2. Between approximately pH 4 and 6, the repulsion in the system is small, and white and opaque gels are formed, with network strand dimensions on the order of micrometers, that is, particulate gels. The particulate gel network is composed of almost spherical aggregates linked together and forming the threads of the network. At high and low pH values, the repulsion in the system is high, leading to the formation of more transparent gels with network strand dimensions in the order of nanometers, that is, fine-stranded gels. Langton and

Hermansson[1] found that the fine-stranded gels formed at low pH (pH <4) were composed of short stiff strands, whereas the fine-stranded structures at high pH (pH >6) had longer, more flexible strands. This is in agreement with results from Stading and Hermansson[2], who found it possible to differentiate between particulate and fine-stranded gels using viscoelastic measure-ments. Large deformation measurements showed that fine-stranded gels at low pH had different properties from thost of the fine-stranded gels formed at high pH: the gels were brittle at low pH and rubber-like at high pH. Hermansson[3] showed that the microstructure of whey protein gels at pH 9 was finer than that of the more aggregated structure at pH 7.

Whey protein films produced at different pH values in a pilot study preceding this present investigation showed behavior that was similar to that of the gels presented above. All films were cast from heated aqueous solutions and dried at room conditions. At pH 4–6 the films were white and opaque, at pH <4 they were transparent and fragile, whereas at pH >6 the films were both transparent and flexible. Hence, a pH range from 7 to 9 was chosen to study how pH affects the mechanical properties of practically usable films.

All whey protein films need to have some kind of plasticizer to induce sufficient flexibility and to avoid cracking of the films during the drying process. The plasticizers often used in edible and biodegradable films are polyols such as glycerol, sorbitol, and propylene glycol. Sorbitol was used in this investigation as it binds less water than glycerol and imparts a better barrier against water vapor at low and intermediate relative humidity (≤60% RH)[4].

The concentrations of whey protein and sorbitol were varied between 10 and 14% (w/w) based on the dry weight to give a multivariate design with reproducible films with enough durability and flexibility in each design point. Higher whey protein concentrations tended to gel during the heating process and made it difficult to cast films.

The aim of this paper was to study the mechanical properties in films made of whey protein isolate (WPI) using sorbitol (S) as a plasticizer. The influence of the three variables: concentration of WPI, concentration of S, and pH, were evaluated. Both quantitative and multivariate analyzes were used to evaluate and interpret the results. This paper is a part of a larger investigation in which Anker et al.[5] present more results together with a more thorough discussion.

MATERIALS AND METHODS

Materials

WPI was obtained from MD Foods Ingredients (Videbaek, Denmark). WPI is a functional WPI used for protein fortification of clinical nutrition products, infant formulas and sports foods. Sorbitol (S) was used as a plasticizer and was obtained from Sigma Chemical Co. (St. Louis, MO, USA).

Film Formation

The solutions were mixed and dissolved with distilled deionized water at room temperature for 1 h. Solution pH was adjusted with 1 M sodium hydroxide after the mixing and before the heat treatment. The concentration of the solutions was compensated for the amount of sodium hydroxide added. A vacuum was applied at 10 min. to remove dissolved air. The solutions were heated in an oil bath to 76.5, 70.5, and 68 °C for pH 7, 8, and 9, respectively. The solutions gelled at different temperatures, depending on the concentration and pH, and therefore different maximum temperatures for each pH were used. Hence, the solutions were cast at 10 °C above the denaturation temperature of β-lactoglobulin. The denaturation temperatures were determined, by using differential scanning calorimetry[6], as 66.5, 60.5, and 58 °C for pH 7, 8, and 9, respectively. The cast solutions were allowed to cool and dry at room temperature for ≈4 h and were then dried in a climate chamber at 23 °C and 50% RH for 16 h. Dried films could be peeled intact from the casting surface. Films were preconditioned in the climate chamber at 23 °C and 50% RH for at least 48 h prior to all testing.

Mechanical Properties

A texture analyzer (model TA-XT2, Stable Micro Systems, Godalming, England) was used to determine mechanical properties in tension in accordance with ASTM D882-91. Force and elongation were recorded during extension, and Young's modulus (*E*), stress at maximum force (σ_y), stress at break (σ_b), and strain at break (ε_b) were determined.

A reduced, three-level, factorial design was used to evaluate main effects as well as interaction effects. Four experimental points (X1–X4) and three central points (X5–X7) were measured.

RESULTS AND DISCUSSION

The rheological behavior between the different pH values and concentrations from the quantitative measurements is summarized in Table 1.

Table 1. Stress and strain at break for X1–X7.

Design points	σ_b[a] (MPa)	ε_b[a] (%)
X1	3.5 ± 0.5	22 ± 4
X2	1.9 ± 0.2	71 ± 19
X3	0.3 ± 0.1	36 ± 9
X4	2.1 ± 0.2	68 ± 19
X5–X7	1.5 ± 0.3	45 ± 14

[a] Stress and strain at break data are mean values ± standard deviations.

The films produced at design point X1 are stiff, have a high stress and a low strain at break compared with the other films produced at the other design points. X1 consists of 14% (w/w) WPI and 10% (w/w) S at pH 7. Almost the opposite is true of the films cast at design point X3 which are weak but slightly more stretchable. These films also had some difficulty in sticking together due to their lack of solidity. X3 consists of 10% (w/w) WPI and 14% (w/w) S at pH 7. The films produced at design point X4 and X2 reveal good mechanical properties with a strain at break of ≈70%. X4 consists of 14% (w/w) WPI and 14% (w/w) S at pH 9 and X2 of 10% (w/w) WPI and 10% (w/w) S at pH 9. The variation of the stress and strain curves of the central design point, X5, X6, and X7, were small, which indicates good reproduction of the film-forming process in the experimental domain investigated. X5–X7 consist of 12% (w/w) WPI and 12% (w/w) S at pH 8.

The WPI films show a higher strain at break (ε_b) for design points X4 and X2 at pH 9 than for X3 and X1 at pH 7. The ratio of WPI:S is different between X4 and X2 versus X3 and X1, but the results nevertheless reveal a clear difference between pH 7 and 9.

The multivariate analysis of the mechanical properties is shown in Fig. 1.

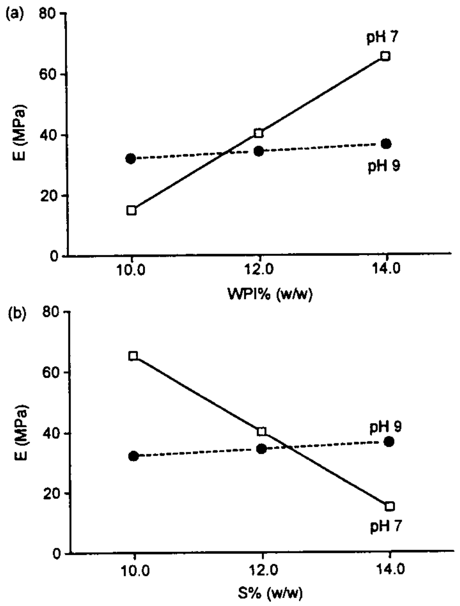

Figure 1. Interaction effect on Young's modulus (*E*) of WPI films as a function of (a) WPI concentration and pH [fixed variable: 12% (w/w) S] and (b) S concentration and pH [fixed variable: 12% (w/w) WPI].

The interaction effect plots on E show two different types of behavior at pH 7 and 9. At pH 9, E is not affected when the concentration of WPI or S varies. However, at pH 7, E increases when the concentration of WPI increases, and E decreases when the concentration of S increases. The behavior for σ_y and σ_b follows the behavior for E presented above. Hence, this difference in performance is probably due to a structural difference at the different pH values, which need to be further studied.

CONCLUSIONS

The mechanical properties are greatly influenced by the ratio of the WPI concentration and the S concentration. pH exerts a strong effect on the mechanical properties, and a structural difference in the polymer matrix occurs probably above pH 8. The multivariate analysis has proved to be a valuable tool for evaluating and quantifying the influences of the separate variables, as well as the interaction effects between the variables, in a specified experimental domain.

Further research should be carried out with WPI films to fully understand the changes in structural behavior at the different pH values. Microscopic tech-niques could be used to further study the structural behavior as well as dynamic mechanical analyses and differential scanning calorimetry for the thermal behavior.

ACKNOWLEDGMENT

This work has been supported by the Swedish Board for Technical Development (NUTEK), as well as Arla FoU, Stora Corporate Research AB, and Tetra Pak R&D. Oleinitec (Stable Micro System, Goldaming, England) is thanked for the loan of the TA-XT2 texture analyzer.

REFERENCES

1. Langton, M. and Hermansson, A.-M. (1992), "Fine-stranded and particulate gels of β-lactoglobulin and whey protein at varying pH", *Food Hydrocoll.*, **5**, 523–539.

2. Stading, M. and Hermansson, A.-M. (1991), "Large deformation properties of β-lactoglobulin gel structures", *Food Hydrocoll.*, **5**, 339–352.

3. Hermansson, A.-M. (1986), "Water- and fatholding", In *Functional Properties of Food Macromolecules*, Michell, J.R. and Leward, D.A. Eds, Elsevier Applied Science, London, pp. 273–314.

4. McHugh, T.H., Aujard, J.-F., and Krochta, J.M. (1994), "Plasticized Whey Protein Edible Films: Water Vapor Permeability Properties", *J. Food Sci.,* **59**, 416–419, 423.

5. Anker, M., Stading, M. and Hermansson, A.-M. (1998), "Mechanical Properties, Water Vapor Permeability, and Moisture Contents of β-Lactoglobulin and Whey Protein Films Using Multivariate Analysis", *J. Agric. Food Chem.,* In press.

6. Hegg, P.-O. (1980), "Thermal Stability of β-Lactoglobulin as a Function of pH and the Relative Concentration of Sodium Dodecylsulphate", *Acta Agric. Scand,* **30**, 401–404.