THE EFFECT OF MIXING AND SONICATION DURING PROTEIN COAGULATION ON THE PARTICLE SIZE DISTRIBUTION IN THE SUSPENSION CREATED

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Abstract. The microparticulation process in the course of acidic coagulation of milk proteins under mixing conditions has been investigated. Water solutions of milk protein concentrates were acidified by the glucono-delta-lactone (GDL) and stirred with high-shear, inclined toothed-blade impeller. Additionally the system was treated using ultrasound disintegrator to reduce the size of the particles in suspension. The protein suspension obtained consisted of particles with variable particle size distributions dependent on protein and GDL concentration as well as intensity of mechanical treatment during coagulation.

Keywords: protein microparticulation, mixing, sonication, particle size distribution.

1. INTRODUCTION

Recently obtaining proteins in the form of fine, insoluble particles with various functional properties is of great importance in the development of new food products. Microparticles are usually obtained by thermal aggregation of whey proteins under strong shear conditions [1,2]. They are utilized in low-calorie formulations as fat replacements [1,3]. An attempt has been also taken to produce microparticles containing casein as drug delivery system for controlled release of active ingredients [4]. The structure and rheology of the set system consisting both of casein and whey proteins may be strongly dependent on the mixing process applied [5].

The objective of this study was to assess the effect of mixing and strong ultrasound treatment during gelation process of milk proteins on the particle size distribution in the resulting suspensions of microparticles.

2. EXPERIMENTAL

Milk protein ultrafiltrated concentrate (MPC 75) has been used as a source of protein in the water solutions containing 5.0 or 8.0 g of powder per100 g liquid. Experiments were conducted in two series comprising coagulation of hydrated native proteins and heat-treated (95°C/30 min) solutions. Acidic coagulation was performed at 25°C by means of hydrolysis of glucono-delta-lactone (GDL), which has been added in the amount of 2.0-3.0 g/100 g solution. The mechanical treatment including mixing and combined mixing followed by sonication of the system has been applied immediately after the addition of GDL to the solution.

The system has been subjected to mixing for 30 min. using toothed-blade dissolver stirrer (IKA R1300) rotating with n = 10.0 or 12.5 s⁻¹ in the impeller-tank system of dimensions...
D=80 mm, T=H=180 mm. The time course, rotational speed and torque changes during the experiment were recorded by the software of the Eurostar control-visc overhead stirrer (IKA).

For the sonication of the protein solutions the ultrasonic disintegrator type UD 11 (ELPAN) has been used. The samples of 50 cm$^3$ volume were homogenized by ultrasound energy for 30 s with simultaneous chilling to avoid excessive rise in temperature. This process has been applied as additional treatment after mixing.

Table 1. Reagents concentrations and process conditions during the experiments

<table>
<thead>
<tr>
<th></th>
<th>MPC concentration (C)</th>
<th>GDL addition (G)</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/100 g</td>
<td>g/100 g</td>
<td></td>
</tr>
<tr>
<td>Min value (0)</td>
<td>5.0</td>
<td>2.0</td>
<td>no</td>
</tr>
<tr>
<td>Max value (1)</td>
<td>8.0</td>
<td>3.0</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>mixing (M) ultrasound (U) heat (H)</td>
</tr>
<tr>
<td></td>
<td>g/100 g</td>
<td>n, s$^{-1}$</td>
<td>26 kHz/30 s</td>
</tr>
<tr>
<td>Min value (0)</td>
<td>5.0</td>
<td>10.0</td>
<td>no</td>
</tr>
<tr>
<td>Max value (1)</td>
<td>8.0</td>
<td>12.5</td>
<td>yes</td>
</tr>
</tbody>
</table>

Protein particle size distribution (PSD) in the solutions prior the coagulation was measured using dynamic light scattering method. Measurements were made on a Zetasizer Nano ZS instrument (Malvern). The results were expressed in terms of the mean hydrodynamic diameter ($Z_{avg}$) and polydispersity index (PDI). PSDs of the microparticles in the suspensions obtained as a result of mixing and sonication during coagulation were analyzed by laser light diffraction method using Mastersizer 2000 system (Malvern). The particle sizes were expressed as $d_{0.1}$, $d_{0.5}$, $d_{0.9}$ and Sauter ($d_{32}$) diameters and the distribution width was characterized by span value defined as follows:

$$Span = \frac{(d_{0.9} - d_{0.1})}{d_{0.5}}$$  \quad (1)

As an additional analysis the protein coagulation was monitored by performing oscillatory test using Haake Rheostress RS1™ rheometer with serrated parallel plates sensor (35 mm diameter, gap 1 mm, deformation $\gamma = 1\%$, oscillation frequency $f = 0.01$ Hz). The process time required to equalization of storage ($G'$) and loss ($G''$) moduli was assumed as the gel point of the system.

3. RESULTS

Prior to coagulation the solutions contained native protein particles of average hydrodynamic size of 184.2 nm. Heat treatment caused formation of casein-whey protein complexes [6] of slightly greater $Z_{avg}$ size 262.5 nm at simultaneously wider particle size distribution PSD (Tab. 2).

Table 2. Basic characteristics of protein particle size distribution in the solutions before the coagulation

<table>
<thead>
<tr>
<th>Magnitude</th>
<th>Protein solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>native proteins</td>
</tr>
<tr>
<td>$Z_{avg}$ nm</td>
<td>184.2±48.3</td>
</tr>
<tr>
<td>PDI</td>
<td>0.151±0.066</td>
</tr>
</tbody>
</table>

As a result of GDL hydrolysis the decrease in pH occurred with time and under the conditions of non-destructive oscillatory test the development of gel structure caused characteristic changes in rheological properties of the system were observed (Fig. 1).
Figure 1. Changes in the rheological properties of gelling protein solution as a result of pH decrease (experiment C1G1H0)

The relatively small differences between viscous and elastic properties of the medium after equalization of moduli $G'$ and $G''$ values indicate that the structure of gel formed is weak, therefore it may be susceptible to easy breakdown by shearing forces when subjected to mixing or other mechanical treatment [7].

Application of mixing and sonication simultaneously with protein coagulation prevented system from gel structure development and as the result suspensions consisting of micro-gelled particles were formed. The particle size distribution in the suspensions was distinctly dependent upon reagents’ concentration and intensity of mechanical treatment (Fig. 2).

Figure 2. Examples of particle size distribution protein suspensions obtained (the codes of the experiments correspond with Table 1)

The most tiny microparticles were obtained from the native protein solution as a result of mixing at lower rotational speed, but in this case a considerable portion of whey proteins was not included into structure of the particles and PSD was multimodal. Heat treatment preceding coagulation process led to total precipitation of the proteins in the form of rigid slightly greater particles ($d_{32}$ up to 56 μm) with more uniform particle size distribution (Fig. 3). Sonication following mixing process did not give significant diminishing of the particles, neither produced narrow PSD.
Figure 3. Mean Sauter diameter and span values as affected by various mechanical treatment of the suspensions in the course of protein coagulation

4. CONCLUSIONS

The experiments performed revealed possibility to create microparticulated milk proteins by application of extensive mixing when acidic gel was formed as a result of GDL hydrolysis. These particles either in the form of liquid suspension or as dried material can be used as ingredients for formulated foods or as a carrier of active ingredients which might be entrapped in the gel structure. However, obtaining particles of pre-defined particle size requires experimental optimization of both process variables and mixer design.

5. NOMENCLATURE

- $d_{0.5}$: volume median diameter, μm
- $d_{0.9}$: 90% of the volume distribution is below this diameter, μm
- $d_{0.1}$: 10% of the volume distribution is below this value, μm
- $G'$: storage modulus, Pa
- $G''$: loss modulus, Pa
- $\eta^*$: complex viscosity, Pa s
- PDI: polydispersity index
- Span: width of the distribution based on the 10%, 50% and 90% quantile
- $Z_{avg}$: hydrodynamic particle diameter, nm

6. REFERENCES


