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Effect of magnesium salt concentration in water-in-oil emulsions on the physical properties and microstructure of tofu

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ABSTRACT

The aim of this research was to prepare water-in-oil (W/O) emulsions encapsulating different concentrations of magnesium chloride ($MgCl_2$) and to investigate the effect of W/O emulsions on the physical properties and microstructure of tofu. The results showed that the stability of W/O emulsions improved as the concentrations of polyglycerol polyricinoleate (PGPR) and $MgCl_2$ increased. Dynamic viscoelastic measurements indicated that gelation time decreased with increasing $MgCl_2$ concentration in W/O emulsions, suggesting a more rapid reaction between magnesium ions and protein molecules. As the concentration of $MgCl_2$ in W/O emulsions increased, the yield and water content of tofu decreased, while the protein and crude fat contents and hardness values increased. At a concentration of 2.0 M $MgCl_2$ in W/O emulsion, the WHC and microstructure of the tofu samples were optimal. The variations in the physical properties of tofu were attributed to the concentration of magnesium ions and the coagulation rate.

1. Introduction

Tofu, originating in China 2000 years ago, is one of the most important traditional soybean foods. Tofu is now increasing in popularity all over the world as it is cholesterol free and contains many nutrients, such as minerals, vitamins, omega-3 fatty acids and isoflavone (Hou, Chang, & Shih, 1997). The main processes of tofu manufacturing are heat treatment, coagulation, molding and pressing. Of these, the coagulation process, which is affected by coagulant type and coagulant concentration, is the key step in determining the yield and quality of tofu (Prabhakaran, Perera, & Valiyaveettil, 2006).

Various coagulants have been used in tofu manufacture with each coagulant resulting in tofu with different textural properties, varying from soft to firm (Karim, Sulebele, Azhar, & Ping, 1999). The major coagulants used in tofu production are calcium sulfate, magnesium chloride ($MgCl_2$), and glucono-δ-lactone. Of these coagulants, tofu coagulated with $MgCl_2$ is preferred by consumers because $MgCl_2$ creates a more natural flavor and preserves the sweet taste of the original soybean. However, the ability of magnesium ions to quickly dissolve in soymilk results in a rapid solidification of the gel and therefore produces tofu with a low yield, a low water-holding capacity (WHC), and a coarse structure (Watanabe, 2000). Several recent studies have focused on exploring methods that may improve the yield and texture of tofu. Li et al. (2015) used a mixture of polysaccharide and $MgCl_2$ as coagulant to improve the yield and texture of tofu. They suggested that adding polysaccharide to heated soymilk could reduce the coagulation rate of $MgCl_2$ as it increased the viscosity of soymilk, thus improving the yield and textural characteristics of tofu. In addition, the segregating interaction between polysaccharides and protein molecules might also contribute to a reduction in the coagulation rate. Previously, our laboratory has developed water-in-oil (W/O) emulsions specifically designed to encapsulate bittern solution (mainly containing $MgCl_2$) and to control the release of magnesium ions from the water phase by optimizing the preparation conditions (Li, Cheng, Tatsumi, Saito, & Yin, 2014; Zhu et al., 2015). Compared with traditional $MgCl_2$ coagulant, the use of a W/O emulsion could significantly slow down the gelation rate of tofu and thereby increase its yield and improve its texture. The release rate of magnesium ions from W/O emulsions could be regulated by the emulsifier type, emulsifier concentration, phase ratio, and homogenization conditions. In addition, compared to W/O emulsion with no added salt, magnesium salt added to the aqueous phase of such emulsions was found to be beneficial for its stability (Zhu, Han, Li, & Yin, 2015). Therefore, it can be expected that the concentration of $MgCl_2$ in the aqueous phase affects the stability of W/O emulsions and the subsequent quality of tofu. However, little information is

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available on modifying the yield and textural characteristics of tofu by adjusting the concentration of magnesium in W/O emulsions.

Several studies have investigated the effect of inorganic salts on the stability of W/O emulsions. Increasing the calcium chloride concentration enhanced the stability of W/O emulsion against coalescence because of the reduction in water droplet size and the increased adsorption rate of surfactant at the oil–water interface (Kent & Saunders, 2001; Márquez, Medrano, Panizzolo, & Wagner, 2010). Koroleva and Yurtov (2003) found that adding inorganic salts to the dispersed phase could reduce the Ostwald ripening rate of W/O emulsions. Nadin, Rousseau, and Ghosh (2014) found that the salt concentration-dependent osmotic pressure gradients also influenced the stability of the emulsion and the release rate of ions in the internal aqueous phase. Melnik, Spyropoulos, and Norton (2010) suggested that a large osmotic pressure gradient, caused by the variation in salt concentrations between the two aqueous phases, could promote the rapid release of encapsulated solutes in primary W/O emulsion to the outer aqueous solution. In addition, coagulant concentration also affects the yield, textural properties, and microstructure of tofu. Saio (1979) found that with an increasing concentration of coagulant, the bulk yield of tofu decreased and the firmness increased. The optimal coagulant concentration for obtaining a finer tofu network is important for tofu preparation. Arii and Takenaka (2013) claimed that a high concentration of magnesium salt induced tofu-like precipitates with a rough surface, while a low concentration produced a smooth surface. Based on these research reports, the quality of tofu might be adjusted to meet different consumers' preferences in the final products by controlling the concentration of magnesium salt in W/O emulsions.

Therefore, the objective of the present study was to determine the effect of varying the concentrations of $MgCl_2$ and polyglycerol polyricinoleate (PGPR) on the stability of W/O emulsions to obtain suitable emulsion coagulants. Additionally, rheological measurements and scanning electron microscopy (SEM) were used to study the gelation process and microstructure of tofu gel to clarify the effect of W/O emulsions on the physical and textural properties of tofu.

2. Materials and methods

2.1. Materials

PGPR (818SK) was supplied by Taiyo Kagaku Co., Ltd (Tokyo, Japan). Soybean oil was purchased from a local supermarket and used without further purification. Commercial soybeans (ZhongHuang 13, approval No. 2001009) were purchased from the Chinese Academy of Agricultural Sciences (Beijing, China). Magnesium chloride ($MgCl_2{\cdot}6H_2O$) was obtained from Lanyi Co., Ltd. (Beijing, China). All other reagents were of analytical grade.

2.2. Emulsion preparation

W/O emulsions were prepared as in previous methods with some modifications (Zhu et al., 2015).The oil phase was prepared by mixing 0.6 or 1.0 g PGPR with 60% (w/w) soy oil for 100 g of emulsion. The aqueous phase, with concentrations of $MgCl_2$ varying from 0.2 to 2.6 M, was dispersed in the PGPR-soy oil blend and the mixture stirred for 15 min at 65 °C. A coarse emulsion was made using a high-speed shear machine (Ultra Turrax, model T25 basic, IKA Labortechnik, Staufen, Germany) at 13,000 rpm for 2 min at room temperature. The second step of emulsification used a high-pressure homogenizer (NS1001L Panda2K, GEA Niro Soavi, Parma, Italy) at 60 MPa to obtain the final emulsions.

2.3. Evaluation of W/O emulsions stability

2.3.1. Particle size measurement

The mean particle sizes of the W/O emulsions were determined as described by Choi, Decker, and McClements (2009) with small modifications. All measurements were performed in triplicate by dynamic light scattering using a Zetasizer Nano ZS90 particle size analyzer (Malvern Instruments, Worcestershire, UK) at a fixed angle of 90 °. The emulsions were appropriately diluted with dodecane (refractive index = 1.422, viscosity = 1.34 mPa s at 25 °C), measured by transferring the diluted emulsions into 3 ml plastic cuvettes. Particle size was reported as the *z*-average and the polydispersity index (PDI).

2.3.2. Emulsion stability measurement

The stability of the emulsions was studied by multiple light scattering using a Turbiscan Lab Exper Stability Analyzer (Formulaction, L'Union, France). The transmittance detector received the light that passed through the dispersion at an angle of 180° with respect to the source, while the back scattering detector received the light scattered backwards by the dispersion at an angle of 45°. The analysis of stability was performed as a variation of backscattering (BS) profiles and then exported as ΔBS profiles by the Turbiscan EasySoft Converter software. Then 20-ml W/O emulsion samples were put into glass tubes and loaded into the Turbiscan Lab Expert Stability Analyzer. Two detectors scanned the entire height of the emulsions at 65 °C for 24 h.

The stability of emulsions can be evaluated using the TSI (Turbiscan Stability Index) parameter. The following formulae were applied:

$$BS \approx = \frac{1}{\sqrt{\lambda^*}} \tag{1}$$

$$\lambda^*(\varphi, d) = \frac{2d}{3\varphi(1-g)Q_s} \tag{2}$$

$$TSI = \sqrt{\frac{\sum_{i=1}^{n}(\chi_i - \chi_{BS})^2}{n-1}} \tag{3}$$

where λ^* is the photon transport mean free path in the analyzed dispersion, φ is the volume fraction of particles, d is the mean diameter of particles, g and Q_s are the optical parameters given by the Mie theory. χ_i is the average backscattering for each minute of measurement, χ_{BS} is the average χ_i, and n is the number of scans.

2.3.3. Oil–water interfacial tension measurement

The interfacial tension at the soy oil–water interface was determined using a spinning drop video tensiometer (SVT 20N, Data Physics, Filderstadt, Germany) at 25 °C. A tube was filled with the aqueous phase containing the different concentrations of $MgCl_2$ and closed using a Teflon cap with a rubber septum. The oil phase was then injected into the tube using a syringe after which the capped tube was inserted into the tensiometer slot. A suitable rotation speed was selected to elongate the oil droplet and the final interfacial tension was calculated by the built-in software. The measurements were performed three times for each sample.

2.4. Tofu preparation

The tofu was prepared as in previous methods with some modifications (Zhu et al., 2015). The soybeans were soaked in distilled water at room temperature for at least 10 h. The soaked beans were washed, then ground to produce soymilk. The soymilk was heated to 95 °C and boiled for 10 min using an electromagnetic