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# Formation of heat-resistant nanocapsules of jasmine essential oil via gelatin/gum arabic based complex coacervation

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ABSTRACT

The formation of heat-resistant flavor nanocapsules was achieved by gelatin and gum arabic based complex coacervation. The colloidal behavior of complexes was investigated using turbidity titration (600 nm) with the help of an in situ acidifier – glucono-δ-lactone. The soluble complexes formed at a quite narrow pH range, and pH 4.80 under the mixing ratio of 1:1 (gelatin/gum arabic, w/w) was favorable for the nanoparticles preparation. Subsequently, corresponding nanocapsules with jasmine essential oil entrapped were successfully prepared and cross-linked by transglutaminase. Their heat-resistance capability against 80 °C was evaluated by both structural characteristics (size, polydispersity index and zeta potential) and flavor analysis. The results showed that the nanocapsules cross-linked at alkaline conditions could endure the water bath of 80 °C for 7 h. However, the analysis of volatile compounds by GC–MS revealed that their flavor profiles of jasmine essential oil began to destroy above 5 h.



## 1. Introduction

Protein and polysaccharide are often applied simultaneously to prepare particulate structures of micron size. These fabricated microparticles confer great application in the fields of food (Dong et al., 2011; Weinbreck, Minor, & De Kruif, 2004; Yeo, Bellas, Firestone, Langer, & Kohane, 2005) and pharmaceutical (Huang, Cheng, Yu, Tsai, & Cham, 2007; Lee & Rosenberg, 2000). They could be used to encapsulate bioactive agents or flavor ingredients, with the aim to protect the targeted components from the harsh environmental conditions during the processing or storage. Such spherical particles can also be employed to replace fat in certain food systems, due to the similarity with lipid droplets in rheology, light scattering and mouthfeel (Laneuville, Paquin, & Turgeon, 2005). Furthermore, such protein-polysaccharide assembly has been successfully applied in interface stabilization (Singh, Tamehana, Hemar, & Munro, 2003; Speiciene, Guilmineau, Kulozik, & Leskauskaite, 2007), edible films (Park, Daeschel, & Zhao, 2004) and biomaterials in tissue engineering (Samuel et al., 2002; Taravel & Domard, 1996). Therefore, the investigation and application of such system has attracted increasing interest in recent years.

For the formation of such biopolymer particles, electrostatic force between oppositely charged biopolymers is the major factor behind the phase separation. It is also known as complex coacervation. Depending on the intensity of electrostatic interactions, either soluble complexes or insoluble complexes would exist (de Kruif, Weinbreck, & de Vries, 2004), which in correspondence for the preparation of nanoparticles and microparticles. Compared with the microparticles' fabrication, the conditions for nanoparticles formation are much stricter. If the chosen polysaccharide is strongly negatively charged, only the insoluble complexes or precipitated coacervates would be achieved, which will be unsuitable for the preparation of nanoparticles. Thus, only few combinations of protein and polysaccharide with moderated charge density could be used for the formation of both soluble and insoluble complexes through the adjustment of specific conditions.

Although the microparticles are much easier to be prepared, their application is restricted in many regions. Specifically, they can not be used as additive in transparent beverage or fabrics due to its cloudy appearance or larger size. Among these fields, the nanoparticles could present more desirable effects. Furthermore, due to more extended employment of the nanoparticles in pharmaceutical

*Abbreviations:* GDL, glucono-δ-lactone; TGase, Transglutaminase; TEM, transmission electron microscopy; PDI, polydispersity index; GC–MS, gas chromatography–mass spectrometry; SPME, solid phase micro-extraction.

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or biomaterials, their preparation technology has received more attention.

Recently, the controlled heating process was frequently mentioned for the fabrication of nanoparticles between globular protein and polysaccharide (Hong & McClements, 2007; Jones, Decker, & McClements, 2009). This approach was dependent on the thermal denaturation of globular protein (e.g., β-lactoglobulin), which induced the folding structure exposed, easily to be interacted with anionic polysaccharide chains. Moreover, such additional processing was proved to strengthen the formed complexes against pH variation (Jones, Decker, & McClements, 2010).

As to the present work, a combination of gelatin and gum arabic was chosen as raw materials for self-assembly complexes. As a hydrolyzate of collagen, gelatin loses majority of its secondary and tertiary structure and exhibits polydispersity for fractions with different distance and flexibility. Its molecular conformation is extended, facilitating to reach the targeted anions sites of the polysaccharide molecule (Lv, Zhang, Zhang, Abbas, & Karangwa, 2012b). Thus, the involvement of gelatin in nanoparticles formation does not need the additional heating treatment as most of the globular proteins. Gum arabic is a complex polysaccharide composed of three distinct fractions with variable protein contents as well as molecular weights. This peculiar composition confers to gum arabic an efficient surface property. Besides, it owns a molecular structure with main galactan chain carrying heavily branched galactose/arabinose side-chains, which contributes to a much higher negative charge density compared to a linear polysaccharide having the same composition (Vandevelde & Fenyo, 1987). Moreover, gum arabic has a good cold-solubility due to the presence of residual charged groups and peptide fragments (Phillips, Takigami, & Takigami, 1996). Gelatin and gum arabic are the oldest materials used for complex coacervation since the pioneering work of Bungenberg de Jong and Kruyt (Bungenberg de Jong & Kruyt, 1929, pp. 849–856). However, their further exploitation in mechanism and application are both limited.

In the current study, for the purpose of disclosing the appropriate conditions for nanocapsules preparation, the formation process of soluble complexes by gelatin/gum arabic was first carefully studied, and suitable hardening condition was then selected to make the rise of heat-resistant nanocapsules with jasmine essential oil entrapped.

## 2. Materials and methods

### 2.1. Materials

Gelatin (type B) and gum arabic (from *Acacia senegal trees*) were purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation (Shanghai, China). From the analysis of the raw materials, the results are as follows: gum arabic powder contained 8.10 ± 0.03% moisture, 2.04 ± 0.14% protein (using Kjeldahl analysis with N conversion factor of 6.60 (Blakeney, Harris, Henry, & Stone, 1983)) and 3.50 ± 0.05% ash (mineral content: 0.22% $Mg^{2+}$, 0.98% $Ca^{2+}$, 0.012% $Na^{+}$, 0.73% $K^{+}$); gelatin granules contained 12.20 ± 0.12% moisture, and 81.43 ± 0.77% protein (using Kjeldahl analysis with N conversion factor of 5.4 (Muyonga, Cole, & Duodu, 2004)). Jasmine essential oil was a gift from Shanghai Linbo Fragrance and Flavor Corporation (Shanghai, China). Transglutaminase (TGase) was purchased from the Yiming Fine Chemical Corporation (Taixing, China), with a nominal activity of 100 U/g of powder, as labeled. Glucono-δ-lactone (GDL) was purchased from the Luoluo Food Additives Corporation (Shanghai, China). All other reagents were of analytical grade.

### 2.2. Preparation of stock dispersion

Stock dispersions of individual gelatin, gum arabic or gelatin/gum arabic with the desired ratio were prepared in percentage by weight (wt%) with determined biopolymer concentration by dissolving biopolymer powders in deionized water under gentle stirring at 60 °C for 2 h. Subsequently, the stock dispersions were centrifuged at 3000 g for 30 min at room temperature to remove insoluble matter or air bubbles. The homogeneous mixtures were used for the further tests.

### 2.3. Turbidity titration

Turbidimetric analysis upon acidification was achieved via an in situ acidifier – GDL. GDL powder was used to be a self-adjusted acidifier. The gelatin/gum arabic mixture was prepared at a total biopolymer concentration of 0.5% (w/v). The process was initiated by adding GDL powder (0.2%, w/v) to the pre-prepared mixture. Then, the sample was stirred for 1 min to allow a homogeneous dissolution of the GDL. Subsequently, one sample was used for measurement of turbidity at 600 nm (UV-1600, Shanghai Mapada Instrument Company, China); the other same sample was used for pH measurement. For the same sample, both pH and corresponding turbidities were recorded, simultaneously. The sample without addition of GDL was used as blank. The biopolymer dispersions with gelatin/gum arabic mixing ratios of 2:1, 1:1 and 1:2 were applied to this method. All measurements were made in more than triplicate for accuracy consideration.

### 2.4. Preparation of nanocapsules

The gelatin/gum arabic nanocapsules were obtained using a solution with total concentration of 0.5% (w/v) and biopolymer mixing ratio of 1:1. Jasmine essential oil was initially mixed with the same amount of surfactant, which was composed of 50% of Span 80 and 50% of Tween 80 (w:w), then added into the biopolymer solution with a core/biopolymer ratio of 1:1 (wt%). Subsequently, the whole solution was emulsified with a high-speed dispersing machine (FJ200-S, Shanghai Specimen Company) at the stirring rate of 10,000 rpm for 3 min. The mixture was held at room temperature under moderate stirring rate of ~400 rpm at a desired pH for 30 min. Acetic acid (10%, v/v) was used for acidification. Next, TGase (0.25%, w/v) was added to harden the formed nanocapsules under a stirring rate of 400 rpm at a room temperature for 3 h and pH was adjusted with sodium hydroxide (10%, w/v) and acetic acid (10%, v/v).

### 2.5. Particle size distribution of nanometer dispersion or nanocapsules

Size distributions of nanometer scale were carried out with a dynamic light scattering type Zetasizer Nano (Malvern Instruments, U.K.) apparatus, with a scattering angle of 173°. Vertical cuvette with a path length of 10 mm was used as a scattering cell. The refraction index applied were 1.59 for material and 1.33 for water dispersant. Furthermore, an analysis model called general purpose with normal resolution was chosen, which was appropriate for the majority of dispersions or emulsions. All measurements were performed at room temperature. The gelatin/gum arabic dispersions (0.5%, w/v) with three mixing ratios were measured under variable pH to obtain the specific size distribution pattern in intensity. Also, the fabricated nanocapsules were applied in the same way.

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