Microencapsulation By Complex Coacervation: Study Of The Emulsification Step

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INTRODUCTION AND OBJECTIVE

Microencapsulation by the complex coacervation process relies on the phase separation of "complex coacervate" particles from association of two hydrocolloids and their subsequent deposition onto particles of an active ingredient or emulsified oil droplets (Gouin, 2004). The complex coacervation phenomenon involves electrostatic interactions between two oppositely charged polymers. Gelatin/acacia gum system is the most widely used complex coacervation system. The process of microencapsulation by complex coacervation consists in five steps when gelatin is used. These steps are presented in Figure 1.

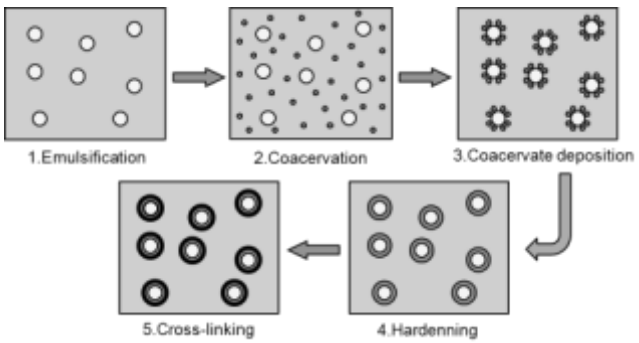


Figure 1: Description of the microencapsulation process by complex coacervation

Microencapsulation by complex coacervation has been extensively investigated and the influence of process parameters on microcapsules size distribution and morphology is well documented. The gelatin-acacia system could not be used to encapsulate large microparticles (above 335 µm average diameter) due to incomplete coverage of the particles by the coacervate droplets (Madan 1972). Also for the whey protein-acacia gum system, small oil droplets (< 50 µm) could be encapsulated into a coacervate matrix more easily than large droplets. Large oil droplets (> 200 µm) were occasionally only partially encapsulated (Weinbreck 2004). It appears that such troubles mainly come from the emulsification process. The emulsification is often performed using classical homogenization processes, so that many reports show that the emulsification step is very similar to that of classical o/w emulsions. As example, it has been reported that the morphology and size distribution of the microcapsules are affected by the rate of homogenization in generating emulsions of the oil-gelatin solution (Yeo 2005). Moreover it has been shown that in case of mononucleated capsules, the particle size of the capsule was mainly determined by size of the parent oil droplet, which was controlled by the settings of the emulsification step (Lemetter 2009). In spite of this large body of experimental evidences, it suggests a similar behaviour to a classical emulsification process, the above mentioned troubles suggest that the emulsification using gelatin (or a protein) as emulsifier makes the emulsification more tricky than usually.

The main objective of this work is to identify the optimum process parameters of the emulsification step in order to control the size distribution of microcapsules prepared by complex coacervation, without adding surfactants.

MATERIALS AND METHODS

Preparation of emulsions

Stock dispersions of gelatin 3% (w/w) were heated at 55°C under moderate stirring rate (300 rpm) to facilitate dissolution of gelatin. Then 10 or 20 g of linseed oil were added into the solution and emulsified for different times (15, 30 and 45 min) at different shearing rates (800, 1,000 and 1,200 rpm).

Preparation of microcapsules

Stock dispersions of gelatin 3% (w/w) and acacia gum 3% (w/w) were prepared at ambient temperature under magnetic stirring. The gelatin solution was heated at 55°C to facilitate dissolution gelatin. Then 10 g of linseed oil were added into the solution of gelatin and emulsified for 15 min at 800 rpm. The acacia gum solution was added into the emulsion at the stirring speed of 300 rpm and pH was adjusted down to around 4.1. After coacervate microcapsules have been observed, the solution was cooled at 5°C. Glutaraldehyde was finally added to the system and the temperature was increased to 25°C. After a cross-linking time of 2h30, stirring was stopped, the microcapsules creamed to the top, they were collected, rinsed with deionised water and kept in aqueous suspension for storage.

Particle size distribution analysis

The size of either the oil droplets or microcapsules in aqueous suspension was measured by small-angle light scattering using a Beckman Coulter LS 13 320 granulometer.

Microscopic observations

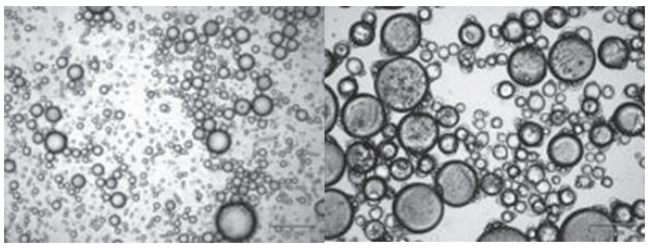
The oil droplets and microcapsules suspended in water morphologies were observed by optical microscopy (LEICA DMLM). Photographs were

taken with the camera ColorView I and analyzed using the software analySIS (Olympus).

RESULTS AND DISCUSSION

Evidence of formation of small oil droplets and their fate during the encapsulation process

The optical microscopy picture of Figure 2A shows that the emulsion contain a lot of small oil droplets. But the small droplets do not appear as individual microcapsules in Figure 2B. These small droplets seem to be encapsulated together with larger oil droplets or they were encapsulated as individual droplets that have been eliminated during the washing step at the end of the process. Indeed the small microparticles containing a single small oil droplet are poor in oil and rich in coacervate; their density is higher than water density, so they settle down to the bottom of the vessel. On the contrary droplets richer in oil undergo creaming and they are collected on top of the liquid medium after the creaming process is completed. So the loss of small microcapsules reduces the encapsulation yield.



A B

Figure 2: Morphology of emulsion oil droplets (A) and corresponding microcapsules (B).

Influence of stirrer type on emulsion droplet size distribution

The use of a propeller and a Rushton mixer were compared in experiments at the same rotation rate of 1000 rpm and for emulsification times in the range from 15 min to 45 min. The Rushton mixer creates more small droplets than the propeller after 30 or 45 min duration On this basis, the propeller was chosen for the rest of the study.

Influence of shear rate on emulsion droplet size distribution

For these experiments emulsification time was fixed at 15 min and the shearing rate was varied from 800 rpm to 1,200 rpm. The fraction of small droplets in the emulsions increases as a function of the shearing rate, from 1.2% at 800 rpm to 4% at 1,200 rpm. The opposite trend is observed for the mean diameter that decreases from 99 µm, to 81 µm, to 68 µm and for the d90 (156 µm, to 135 µm, to 125 µm) at 800, 1,000 and 1,200 rpm respectively. At the end, the preparation of droplets of small diameters always comes along with the fragmentation into very small droplets. If droplet sizes significantly smaller than 100 µm are aimed at, a compromise between a low mean diameter and a low fraction of small droplets have to be found.

Influence of emulsification time on emulsion droplet size distribution

The rotation rate was fixed at 1,000 rpm and the emulsification duration was varied from 15 min to 45 min. The fraction of small droplets (≈2%) does not seem affected by the emulsification time. But mean diameters varied with the emulsification time from 81 µm at 30 min to 74 µm at 45 min. In the same way the d90 decreased from 135 µm at 15 min to 126 µm at 45 min. Since the emulsification time influences the droplet size distribution but not the fraction of small droplets, this parameter can be used to optimize the emulsification process.

CONCLUSION

In this study, we have demonstrated the need to control the emulsification step of the encapsulation process by complex coacervation in order to control the morphology and size of the microcapsules. We have also identified the emulsion parameters which permit to control the size distribution of oil droplets and especially the fraction of small droplets that cause low encapsulation yields. In this study, the main parameter which controls the emulsion oil droplet size distribution is the shear rate. The stirrer type and the emulsification time seem to have secondary roles.

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