Formation of Craters in Polymer Capsules

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An emulsion encapsulation method is applied to the fabrication of polymer capsules in inertial confinement fusion (ICF) experiments. Craters on the capsule surfaces make the capsules useless. This paper introduces the origins of the craters and focuses on ways to remove the craters from polymer capsules. Three origins are discussed and their influence can be restrained to reduce the cratering to meet the demand for mass production of targets.

An emulsion microencapsulation method has been employed in the preparation of polymer capsules in the inertial confinement fusion (ICF) experiments. The polymer capsules cover polystyrene (PS) capsules and poly (α-methyl styrene) (PAMS) capsules. The latter is the basis of a degradable mandrel technique for the fabrication of other capsules such as polyimide, GDP and beryllium capsules. Craters on the surface of a polymer capsule, as shown in Fig. 1 (a), will affect its sphericity; such capsules cannot be used in subsequent processes. In the application of inertial fusion energy (IFE), mass production of capsules is required. The existence of craters will dramatically disrupt product-line operation.

From the viewpoint polymer capsule formation, three origins of craters are discussed, and suppression of crater formation to diminish their impact on polymer capsules is described.

The regular process for the preparation of polymer capsules is adopted as follows. First, deionized water is added dropwise into polymer solution to form a water-in-oil (w_1/O) emulsion. The resulting emulsion is transferred into a PVA solution under stirring to form a double emulsion (W_1/O/W_2), as shown in Fig. 1 (b). With the diffusion of organic solvent from the polymer solution layer, a polymer capsule with water inside is obtained.
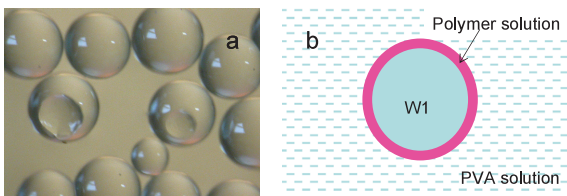

Fig. 1   a) Craters on the surface of polymer capsules; b) Double emulsion system for forming polymer capsules

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Data about the craters is gathered via sampling with the aid of a microscope. Capsules less than 200 μm in diameter are not considered.

Three sources contribute to crater formation on the surface of polymer capsules: collision between colloids, electrolyte-induced water diffusion and depletion induced by water-soluble polymer solution (here, PVA). For convenience, we define the disfigurement rate R_d = (number of cratered capsules)/(total number of capsules). Approximately, we can express R_d as

$$R_d = R_d^c + R_d^d + R_d^e,$$

where R_d^c, R_d^d and R_d^e represent the contribution from collisions, the depletion effect and electrolyte-induced water diffusion, respectively.

The depletion force plays an important role in colloidal stability [1, 2]. The interaction free energy due to depletion can be expressed as [3]

$$A^d(M) \approx 2\pi a \frac{\mu_0 - \mu_0^*}{\upsilon_0} \left(\Delta^{\text{eff}} - \frac{M}{2} \right)^2 \left(\frac{M}{2} \le \Delta^{\text{eff}} \right),$$

where Δ^{eff} is the effective depletion layer thickness and M is the separation distance between two particles. μ_0 and μ_0^* represent the chemical potential of solvent in pure solvent regions and bulk solution, respectively. υ_0 is the solvent molecular volume and a is the radius of colloidal particles. The osmotic pressure difference $(\mu_0^* - \mu_0)/\upsilon_0$ between the bulk solution and the gap forces the particles together, resulting in craters. With increasing concentration of polymer solution, the osmotic pressure increases. At the same time, Δ^{eff} decreases because the osmotic pressure pushes the chains toward the surface. As a consequence of these two opposing effects, the interaction free energy $A^d(M)$ reaches a maximum at a certain concentration of polymer solution. Figure 2 shows the experimental results that offer evidence that R_d reaches a maximum and capsules with larger size possess higher R_d.
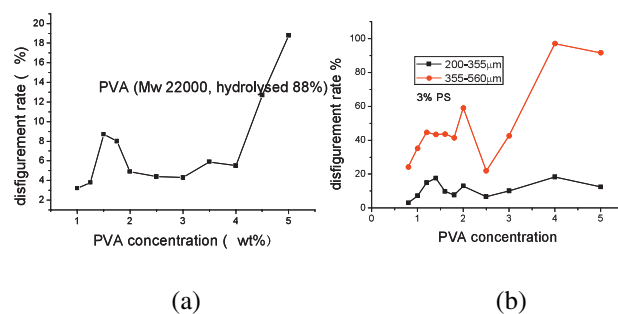
Fig. 2   Dependence of R_d on PVA concentration. a) For capsules larger than 200 μm at 5% PS, b) For capsules of different size at 3% PS
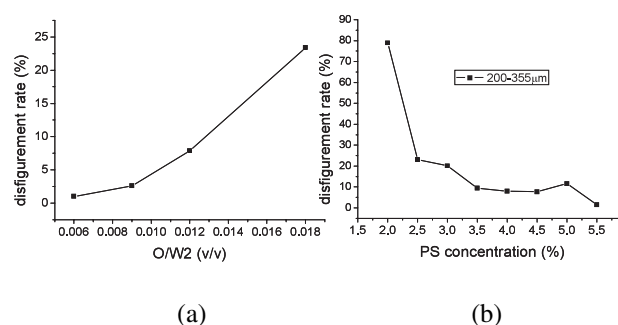

Fig. 3   a) Variation of R_d with phase ratio O/W_2, b) Variation of R_d with organic phase concentration

Fig. 4   Picture of capsules at different CaCl$_2$ concentrations (a: 0%, b: 0.5%, c: 1.5%, d: 2.0%)

Under certain conditions, the possibility of collision between two colloidal particles depends on the particle size and number. We assume that the colloidal particle number is approximately proportional to the phase ratio O/W_2. Experimental results reveal that R_d increases with phase ratio O/W_2, as shown in Fig. 3 (a).

To eliminate the vacuoles in the capsule wall, salts such as CaCl$_2$ and NH$_4$Cl are added to the PVA solution [4]. With the addition of salts, the water activity of W_2 decreases, and the tendency for water to diffuse from W_1 to W_2 is enhanced, which leads to creation of a cavity inside of the oil layer. With cavity growth, at a constant difference pressure between inside and outside of the oil layer, when the oil layer can not maintain the pressure dif-
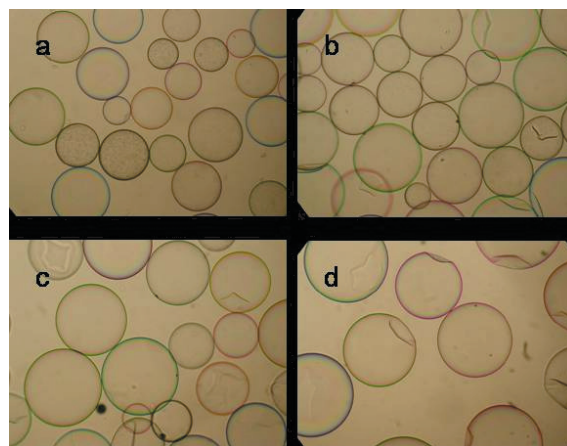
ference, collapse happens and a crater appears.

The thickness and concentration of the oil layer play an important role in offering mechanical strength and preventing water from diffusing across the oil layer, so fewer craters are observed in capsules with thicker walls, and R_d decreases rapidly with increasing oil concentration, as shown in Fig. 3 (b).

More evidence is given in Fig. 4, in which the effect of salt on R_d is clearly visible.

According to our study, the contribution of the depletion effect can be suppressed by adjusting the concentration of PVA solution, while the influence of the other two factors can be inhibited by decreasing the O/W_2 phase ratio and changing the salt addition sequence, respectively.

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