Surface-oil Contents of Microcapsules with Different Oil Droplet-to-Microcapsule Size Ratios

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The surface-oil contents of microcapsules with differing oil droplet-to-microcapsule size ratios were estimated based on a two-dimensional percolation model to examine the effects of differences in the ratio distribution. In the model, squares were divided into equal lattices that were sized to obey a log-normal distribution. The surface-oil contents of microcapsules with various volumetric oil fraction and different variances of the ratio were evaluated. The variance in the distribution of the oil droplet-to-microcapsule size ratio had no significant effect on the surface-oil content at any oil fraction in the microcapsules.

Keywords: surface oil, microcapsule, oil droplet-to-microcapsule size ratio, percolation

1. Introduction

Liquid lipids or lipophilic flavors can be encapsulated by emulsification in a dense solution of wall material and subsequent dehydration of the emulsion. The technical benefits of microencapsulation include the suppression of lipid oxidation [1-3] and the controlled-release of flavor [4-6].

The surface-oil content of a microcapsule is defined as the ratio of the oil exposed on its surface to the entire volume of oil that it contains, and it is an indication of the susceptibility of the microencapsulated lipid to oxidation. Oils in microcapsules with lower surface-oil contents are less easily oxidized [7-9]. Experimentally, lower surface-oil contents have been demonstrated for microcapsules with smaller oil droplets [10], and such results are reasonable as considered by the probabilistic method based on percolation theory [11].

In actual microcapsules, both the particles (microcapsules) and the oil droplets are distributed in size. The particle size is usually tens of micrometers, for example, 50 μm. On the other hand, the oil-droplet size in microcapsules ranges from submicrons to a few micrometers [10]. Therefore, the oil droplet-to-microcapsule size ratio would have a wide distribution. However, the effect of the distribution in the ratio on the surface oil content has not fully been elucidated. In our previous work [11], the effect of the oil-droplet size on the surface-oil content was examined without consideration of this distribution. Because a microcapsule would have variously sized oil droplets, it would be difficult to estimate the surface-oil content based on the model of percolation. In this study, the effect of the distribution in oil droplet-to-microcapsule size ratio on the surface-oil content was, therefore, estimated based on a two-dimensional model of percolation, in which squares were divided into equal lattices whose size distribution obeyed log-normal one.

2. Theoretical Considerations

2.1 Log-normal distribution of the oil droplet-to-microcapsule size ratio

A square was divided into N×N equal lattices, where N was the number by which a side of the square was divided. The 1/N corresponded to the oil droplet-to-microcapsule size ratio. Many squares were divided into lattices by various division numbers. The frequency function of the oil droplet-to-microcapsule size ratio, f(x), is assumed to obey the following log-normal distribution
with parameters $\mu$ (mean) and $\sigma$ (standard deviation):
\[
f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{(x-\mu)^2}{2\sigma^2} \right]
\]
where $x$ is a random variable expressing the oil droplet-to-microcapsule size ratio. The expectation, $E$, and variance, $V$, values for the distribution are given by Eqs. (2) and (3), respectively.
\[
E = \exp(\mu+\sigma^2/2) \tag{2}
\]
\[
V = [\exp(\sigma^2)-1] \exp(2\mu+\sigma^2) \tag{3}
\]

2.2 Estimation of surface-oil content

A set of $\mu$ and $\sigma$ were estimated to give $E$ values of 0.05, 0.02, 0.01, or 0.005; these corresponded to the division of a side of a square by factors of 20, 50, 100, or 200, respectively. An adequate variance $V$ was assumed for a specific expectation $E$, and the $\mu$ and $\sigma$ parameters of the log-normal distribution were evaluated by solving Eqs. (2) and (3) simultaneously. Four adequate $V$ values, which were largely different from each other, were evaluated for a specific $E$ value. The random variable $x$ was converted to another random variable, $y=\ln x$. Using the random variable $y$, the frequency function of the oil droplet-to-microcapsule size ratio is expressed by the Gaussian normal distribution $f(y)$
\[
f(y) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{(y-\mu)^2}{2\sigma^2} \right] \tag{4}
\]
and the expectation and variance are given by $\mu$ and $\sigma^2$, respectively.

The interval $[\mu-1.96\sigma$ to $\mu+1.96\sigma]=[\mu-k$ to $\mu+k]$, which contains 95% of the values in the distribution, was divided into 12 equally spaced subintervals $[\mu-k$ to $\mu-(5/6)k]$, $[\mu-(5/6)k$ to $\mu-(1/6)k]$, $[\mu-(1/6)k$ to $\mu-(3/6)k]$, $[\mu-(3/6)k$ to $\mu-(4/6)k]$, $[\mu-(4/6)k$ to $\mu-(5/6)k]$, $[\mu-(5/6)k$ to $\mu-(1/6)k]$, $[\mu-(1/6)k$ to $\mu-(3/6)k]$, $[\mu-(3/6)k$ to $\mu-(2/6)k]$, $[\mu-(2/6)k$ to $\mu-(1/6)k]$, $[\mu-(1/6)k$ to $\mu-(3/6)k]$, and $[\mu-(1/6)k$ to $\mu+(1/6)k]$. For these subintervals, the fractions of the oil droplet-to-microcapsule size ratios were assumed to be given by the fractions at the medians of the subintervals, $\mu=(11/12)k$, $\mu=(7/12)k$, $\mu=(5/12)k$, $\mu=(3/12)k$, and $\mu=(1/12)k$, having values of 0.0262, 0.0445, 0.0679, 0.0932, 0.1152, and 0.1280, respectively.

For the subintervals $[\mu-k$ to $\mu-(5/6)k]$ and $[\mu+(5/6)k$ to $\mu+k]$, the division number was estimated by rounding the reciprocal of $\mu=(11/12)k$ to an integer $N$. A square was divided into $N^2$ equal lattices. The surface-oil contents for the subintervals were estimated 262 times using the manner reported previously [11]. Briefly, a random number within the range 0–1 was generated for a lattice. When the number was smaller than the volumetric oil fraction in a microcapsule, the lattice was considered to be occupied by the oil. The oil in the lattices, which were connected to the surface lattices on a side, was regarded as the surface one.

Similarly, the surface-oil contents for the subintervals $[\mu-(5/6)k$ to $\mu-(4/6)k]$ and $\mu+(4/6)k$ to $\mu+(5/6)k]$, $[\mu-(4/6)k$ to $\mu-(3/6)k]$, $[\mu-(3/6)k$ to $\mu-(2/6)k]$, $[\mu-(2/6)k$ to $\mu+(3/6)k]$, $[\mu-(1/6)k$ to $\mu-(1/6)k]$, $[\mu-(1/6)k$ to $\mu-(3/6)k]$, $[\mu-(3/6)k$ to $\mu-(2/6)k]$, and $[\mu-(5/6)k$ to $\mu-(5/6)k]$, were estimated 445, 679, 932, 1152, and 1280 times, respectively, and the mean values and standard deviations of the surface-oil contents were then calculated for the set of $\mu$ and $\sigma$, that is, for the specific set of $E$ and $V$.

3. Results and Discussion

The surface-oil contents were estimated at microencapsulated oil fractions of 0.1, 0.35, 0.5, and 0.6. Figures 1(a–d) show the effects of $V$ on the surface-oil content at $E=0.05, 0.02, 0.01$, and 0.005, respectively. A variance of zero indicates no distribution of the oil droplet-to-microcapsule size ratio.

The surface-oil content tended to be lower at large variance in any case, but the effect of the variance on the surface-oil content was not significant due to the larger standard deviation at the larger variance. Although the log-normal distribution is bilaterally symmetric on the semi-logarithmic scale, it is asymmetric and tails at large random variables on the normal scale. The asymmetry is more pronounced for larger $V$. This would explain the tendency toward the lower surface-oil content at larger variance. The results shown in Fig. 1 indicated that the expectation of the ratio largely affected the surface-oil content, but that the variance had no significant effect on the content. Because it would be practically very difficult or impossible to prepare the microcapsules with no distribution of the oil droplet-to-microcapsule size ratio, the simulated results suggested that only the expectation or the mean value of the ratio should be noted to produce the microcapsules of low surface-oil content. The large standard deviation of the surface-oil content also indicated that the oil content had uneven value in every experiment for the microcapsules having a wide distribution in oil droplet size.

The surface-oil content was larger for a microcapsule with a higher oil fraction at any variance. This tendency...
was also true at $V=0$. Thus, heterogeneity in the oil droplet-to-microcapsule size ratio had no significant effect on the surface-oil content of microcapsules.

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