Surface Oil Content of Microcapsules Containing Various Oil Fractions and Oil–Droplet Sizes

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Effects of oil fractions and oil–droplet sizes within microcapsules produced by dehydrating oil–in–water (O/W) emulsions on the surface oil content were examined by simulating the two– and three–dimensional models of percolation, depicted by square and cubic models, respectively. The square and cubic models were divided into \( N_s \times N_s \) and \( N_c \times N_c \times N_c \) equal lattices, respectively, where \( N_c \) was the number by which a side of the models was divided. A random number ranging from 0 to 1 was generated for each lattice. When the number was smaller than a volumetric oil fraction, the lattice was considered to be occupied by oil. The oil in the lattices connected with the surface lattice on a side or a plane in the two– and three–dimensional models was assumed to be extractable. In both the models, the surface oil content was lower when the oil content was lower in the solid microcapsules, especially when the \( N_c \) values are larger (smaller oil droplets). The simulation suggested that the smaller droplets were more favorable for the production of microcapsules wherein the oil was hardly oxidized. The effect of the formation of central voids in the microcapsules on the surface oil content was also examined. The formation of larger voids made the content larger, although this effect was not significant.

Key words: surface oil, microencapsulation, oil–droplet size, percolation

1. Introduction

Much attention has been paid to the physiological functions of polyunsaturated fatty acids such as docosahexaenoic and eicosapentaenoic acids, and their healthful benefits [1]. However, they are prone to oxidation because of the high degree of unsaturation. The oxidation causes rancidity, and in certain cases, the oxidation products are harmful to the human health [2]. One of the methods used for suppressing or retarding the oxidation is the microencapsulation of oil within the dehydrated wall materials. Microencapsulation involves two steps: i) emulsification of oil with a dense solution of a wall material to produce oil–in–water (O/W) emulsion; and ii) dehydration of the resultant O/W emulsion to prepare microcapsules. In the latter step, spray drying is commonly used.

The oxidative stability of the microencapsulated oil is affected by several factors, including the type of wall material used [3,4] and drying method [5,6]. The surface oil content, defined as the fraction of oil exposed on the surface of a microcapsule to the entire oil within the microcapsule, is related to the susceptibility of the microencapsulated oil to oxidation [7,8]. We also reported that the oil content was an indication of such susceptibility [9,10]. The surface oil content was lower for microcapsules with smaller oil droplets [11,12]. We examined the effect of the volumetric fraction of oil to wall material on the fraction of easily oxidized oil during the relatively short storage period based on the two– and three–dimensional models of percolation [13].

In this study, the models of percolation theory [14] were adopted to examine the effects of the oil–droplet size and oil fraction within microcapsules on the surface oil content. Depending on the drying conditions, hollow particles with central voids were formed [15]. The effect of the void size on the surface oil content was also examined.
2. Theoretical Considerations

Simple square and cubic models were used as the two- and three-dimensional models of percolation, respectively, for the surface oil content. The square and cube models were divided into \( N_x \times N_y \) and \( N_x \times N_y \times N_z \) equal lattices, where \( N_x \) was the number by which a side of the square and cube was divided. The larger \( N_x \) corresponded to the smaller oil-droplet size in the microcapsule. A random number within the range 0–1 was generated for a lattice. When the number was smaller than the oil fraction in a microcapsule, the lattice was considered to be occupied by the oil.

In the two- and three-dimensional models, the oil was extracted from all the four sides of a square and all the six faces of a cube, respectively. The oil in the lattices, which were connected to the surface lattices on either one side or one plane, was considered to be extractable in the two- and three-dimensional models. Figure 1 shows examples of the two-dimensional model for the oil fraction 0.35. One side of the square was divided into 10 and 50 parts, shown in Figs. 1(a) and 1(b), respectively. The lattices shaded in black and gray were occupied by oil. The oil in the lattices shaded in black was extractable because the lattices were connected to one of the four sides of the square via the lattice side; on the other hand, the oil in the lattices shaded in gray was isolated, i.e., it was not connected to the lattices, and hence, was not extractable. The surface oil content of the microcapsules was defined as the ratio of the number of lattices shaded in black to those shaded in both black and gray.

For a hollow microcapsule, a small square or cube was considered to lie inside the square or cube. Figure 2 illustrates an example of the two-dimensional model for the hollow microcapsule. One side of the inner square or cube was divided into \( N_w \) parts. The number of lattices in the hollow microcapsule was the same as that in the solid microcapsule when the \( N_w \) value was increased. In other words, the number of lattices was the same for both solid and hollow microcapsules. The oil was assumed to be extracted from both the outer and inner sides or faces in the two- and three-dimensional models.

The surface oil content was calculated at least 50 times with a specific condition of the oil fraction and \( N_w \) value. The averaged values were shown through symbols together with the standard deviation using bars.

3. Results and Discussion

3.1 Surface oil content of solid microcapsules

Figure 3 shows the effect of the oil fraction in a solid microcapsule on the surface oil content. One side of the
square was divided into \( N_o = 25, 250, \) and 2500 parts, corresponding to 625, \( 6.25 \times 10^4 \), and \( 6.25 \times 10^6 \) lattices in the two-dimensional model. In the three-dimensional model, one side of the cube was divided into 25, 250, and 1000 parts. When one side of the cube was divided into 2500 parts, the number of lattices became so huge that the memory of a personal computer was inadequate. Irrespective of the number of lattices, the surface oil content was higher in the three-dimensional model than in the two-dimensional one at any oil fraction. Both in the two- and three-dimensional models, the surface oil content increased markedly at higher oil fractions. This tendency was remarkable for the larger \( N_o \), i.e., for the smaller oil droplet. The large standard deviation of the surface oil content for the middle content indicated that the oil content had uneven value in every experiment, even in the absence of any technical error.

The surface oil content was estimated at different \( N_o \) values for the oil fractions 0.10, 0.35, and 0.60 (Fig. 4). The content largely depended on the \( N_o \) value, and was significantly lower at the smaller \( 1/N_o \). This indicated that the decreasing the oil-droplet size in the O/W emulsion was effective in decreasing the surface oil content of the microcapsule. However, undue downsizing of the oil droplet was unnecessary because the content hardly changed when the \( 1/N_o \) values were sufficiently small.

### 3.2 Surface oil content of hollow microcapsules

The hollow microcapsules are commonly prepared by spray drying. The oil in the lattices connected with the inner surface of the microcapsules was assumed to be extractable. Figure 5 shows the surface oil content of hollow microcapsules at various oil fractions. The \( N_o/n_o \) ratios were 0, 0.4, and 0.8, and the numbers of lattices were \( 1000 \times 1000 \) and \( 250 \times 250 \times 250 \) for the two- and three-dimensional models, respectively. The microcapsule with \( N_o/n_o = 0 \) had no voids. Although the surface oil content was higher for the microcapsules with larger voids, this tendency was not remarkable. This indicated that the formation of the central voids was not a crucial factor in increasing the surface oil content.

The effect of the size of the central voids on the surface oil content was examined in detail with the oil fractions 0.3, 0.5, and 0.7 for the two-dimensional model and with the fractions 0.3, 0.4, and 0.6 for the three-dimensional model (Fig. 6). The numbers of lattices were \( 250 \times 250 \) and \( 250 \times 250 \times 250 \) for the two- and three-dimensional models, respectively, at any \( N_o/n_o \). As mentioned above, it was confirmed that the \( N_o/n_o \) ratio did not largely affect the content, except at extremely large ratios.

![Fig. 5](image1.png) \( \text{Surface oil content of hollow microcapsules at various oil fractions. } N_o \) and \( n_o \) indicate the divisor of outer and inner sides, respectively, of square and cube in two- and three-dimensional models. Symbols are the same as in Fig. 3.

![Fig. 4](image2.png) \( \text{Effect of oil-droplet size, expressed by } 1/N_o, \text{ on the surface oil content of solid microcapsule. } V_{oil} \) indicates the oil fraction in microcapsule. Symbols are the same as in Fig. 3.

![Fig. 6](image3.png) \( \text{Effect of the size of central voids on the surface oil content of microcapsules with various oil fractions (} V_{oil} \).}
The effect of the oil–droplet size, which reflected in the $1/N_o$ value, on the surface oil content was examined with the $N_r/N_o$ ratios 0, 0.4, and 0.8, and with the oil fraction 0.3 for both the two- and three-dimensional models (Fig. 7). The number of lattices was the same as that in Fig. 6. The content was lower for the smaller $1/N_o$ values of the hollow microcapsules, indicating the effectiveness of downsizing the oil droplet for fabricating microcapsules with low surface oil content.

Coumans et al. [16] proposed a simpler model to estimate the effects of the oil fraction and oil–droplet size on the surface oil content by assuming the homogeneous distribution of oil droplets in the shell of a hollow particle. They considered a thin layer on the outer surface and assumed that the fat located in the layer was extractable. Our abovementioned results, obtained under a random distribution of oil droplets, were identical to those obtained by Coumans et al.

Two- and three-dimensional models of the percolation were used for examining the effects of the oil fraction and oil–droplet size on the surface oil content. It was reported previously that the relationship between the fraction of unoxidizable oil within 15 days and the oil fraction could be better expressed by two-dimensional model than by three-dimensional one [13], although microcapsules are three-dimensional materials. However, it is difficult to conclude whether is more adequate to estimate the effects on the surface oil content, two- and three-dimensional models because experimental results are still insufficient.

4. Conclusions

The simulation on the surface oil content of solid and hollow microcapsules, based on the percolation theory, indicated that the downsizing of oil droplets in an O/W emulsion was effective in decreasing the content of both the solid and hollow microcapsules. The oil fraction was also an important factor that affected the surface oil content; the content was lower at lower fractions. The formation of central voids hardly influenced the surface oil content.

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含油率および油滴径の異なる粉末化脂質の表面油率

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魚油や植物油などの液状脂肪を食品高分子（包括剤または賦形剤）の濃厚水溶液とともに乳化し、
得られた O/W エマルジョンを喷霧乾燥などにより急速
に脱水して、微小な油滴を包括剤の乾燥層で被覆する
技術を脂質の粉末化という。液状脂肪を粉末化すると、
脂質の酸化が抑制され、油相に含まれる芳香成分
の放散速度が制御できるなどの利点がある。脂質を粉
末化した際に、表面に露出した油の割合（表面油率）は、
酸化や放散のさびやすさの指標となり、一般的には、
この値が低いほど良好な粉末化物といえる。粉末化物
中の脂質の割合（含油率）が少ないほど、脂質の酸化
が実質的に停止する未酸化率が高く[9]。また油滴が微
細なほど表面油率が低いことが報告されている[12]。
前者の現象に対して、浸透理論[14]を適用した解析が
試みられている[9]。近年、油滴の微細化技術が進展し
てきた。そこで、粉末化する際の油滴径が表面油率に
及ぼす影響を傾向的に知るため、2次元または3次元
の浸透理論を適用して検討した。また、乾燥条件により
粉末化脂質は内部に空隙ができることがある。そのよ
うな中空粒子の表面油率についても検討した。
2次元および3次元モデルでは、正方形または立方体
の一辺をそれぞれNv0分割し、Nv02またはNv03個の格子
を考え、乱数を発生させることにより、粉末中の脂質
の体積分率に対応するように脂質が存在する格子を決
定した。2次元および3次元モデルではそれぞれ、表面
に接する格子の脂質と辺または面で接する格子の脂質
は抽出されると考え、脂質が存在する全格子に対する
表面から連結している格子の割合を表面油率と定義し
た。中空粒子では、正方形または立方体の内部に一辺
の分割数がNvの正方形または立方体を考え、その比
Nv/Neをパラメータとして、中空の大きさが表面油率に
及ぼす影響を検討した。

中実および中空粒子ともに、表面油率が急激に増加
する粉末中の脂質の体積分率の関値が存在し、2次元モ
デルおよび3次元モデルの方がその値は小さかった。また、
中空粒子では、Nv/Neが大きい（中空が大きい）ほど、
表面油率が大きくなった。外辺の分割数Nvの逆数（1/
Nv）は、油滴の大きさに対応する。2次元および3次
元モデルともに、Nvが大きいほど、すなわち油滴が小
さいほど、表面油率が低く、粉末化する際油滴を微
細化することは、脂質の酸化の抑制に有効であること
が示唆された。また、Nv/Neが大きいほど表面油率が
高くなることにより、中空粒子では脂質が酸化されやすいと
の経験則に合致したが、その影響は顕著ではなかった。