Microencapsulation of Ascorbic Acid as Redox Initiator with Tripalmitin

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Abstract
We have tried to microencapsulate powdery ascorbic acid as a redox initiator for polymerization with tripalmitin of the shell material by the coating method in order to give the core water resisting qualities. Microencapsulation was performed in the mill pot in which the core and the shell were mixed together with the pulverizing solvent.

In the experiment, the added amount of tripalmitin as the shell material and the concentration of ethyl alcohol as the pulverizing solvent were mainly changed stepwise. It was investigated how the operational conditions affected the characteristics of microcapsules such as the water proof degree, the content of core material, the microencapsulation efficiency and the yield.

The water proof degree of microcapsules was increased with the added amount of shell material and the concentration of pulverizing solvent. The microencapsulation efficiency was changed from 70 to 90% according to the operational conditions. The yield and the content were changed from 90 to 100% and from 35 to 46% according to the operational conditions, respectively. It was found that the microcapsules were able to induce polymerization of methyl methacrylate by breaking the microcapsule shell due to heating.

Keywords
Microencapsulation; Dry Coating Method; Ascorbic Acid; Tripalmitin; Redox Initiator

Introduction
Many kinds of microcapsules have been prepared to apply to the various fields such as information recording materials, paintings, cosmetics, food materials, adhesives, medicine and so on (Kondo, 1967; Tanaka, 2008). The main purposes of microencapsulation are to protect the core material from environment, to release the core material according to occasion demands, to handle the gaseous and the liquid core materials as the solid particles (Tanaka, 2008). Moreover, we can prepare the microcapsules with the various functions by how to select the physical properties of the core and the shell materials and how to combine these materials. For examples, there are the combination of the hydrophilic core materials with the hydrophobic and/or the hydrophilic shell materials, and the combination of the inorganic core materials with the organic and/or the inorganic shell materials. Also, we can select the shell materials with the various physical properties such as magnetism, electric conductivity, thermal conductivity, chemical resistance, biodegradability and so on (Tanaka & Hayashi, 1989; Tanaka & Hayashi, 1990; Tanaka, et al., 1992; Tanaka, et al., 1992; Kimura, et al., 1995; Taguchi, et al., 1999; Taguchi, et al., 2001; Taguchi, et al., 2003).

Ascorbic acid is well known as a redox initiator for polymerization of styrene and methyl methacrylate. If the redox initiator could be microencapsulated and added into these monomers beforehand, polymerization may be induced by breaking the microcapsules due to appropriate stimuli. In dental treatment using polymerization stated above, it has been strongly desired to microencapsulate powdery ascorbic acid with the hydrophobic material. Namely, if ascorbic acid as a redox initiator for polymerization could be microencapsulated with the hydrophobic and chemical resistance materials, the microcapsules could be added into monomer such as styrene and methyl methacrylate beforehand and polymerization should be induced by breaking microcapsules due to heating. As a result, it may be expected that dental treatment has to be extremely improved.
In general, it is well known that the preparation method by using the water phase is not suitable to microencapsulation of water soluble core material (Kofuji, et al., 2005; Chen, et al., 2013; Luizildo, et al., 2013; Michael, et al., 2011, 2012). For an example, as the water soluble core materials dissolve in the water phase in the microencapsulation process, the content of core materials may be decreased. Accordingly, it is desirable that the preparation method without the water phase is applied for microencapsulation of the water soluble materials and the hydrophilic materials. So, it is necessary to develop the method without any water for preparing the microcapsules containing the water soluble materials or the hydrophilic materials.

In this study, it is tried to microencapsulate powdery ascorbic acid with tripalmitin as the hydrophobic and thermal responsible shell material by using the dry coating method, in which the core and the shell materials are mixed in the mill pot together with pulverizing solvent and the surface of core material is coated with the shell material.

The purposes of this study are to establish the preparation method of microcapsules containing the water soluble ascorbic acid, to investigate how the operational conditions such as the added amount of shell material and the concentration of ethyl alcohol of pulverizing solvent affect the characteristics of microcapsules and to apply the microcapsule to polymerization of methyl methacrylate.

**Experimental**

**Materials**

Water soluble core material was L-\((+)-\)ascorbic acid (LAA) with the mean diameter of 20 μm (Wako Pure Chemical Industries, Ltd.). Tripalmitin (TP) with the melting point of 80°C was used as the hydrophobic shell material, which was purchased from Kanto Chemical Co., Inc. Ethyl alcohol (EtOH) (Kanto Chemical Co., Inc.) was used as the pulverizing solvent for the shell material. Methyl methacrylate monomer (Kanto Chemical Co., Inc.) was used to investigate whether the microcapsules are able to induce polymerization or not.

**Preparation of Microcapsules**

Fig. 1 shows the purpose of microencapsulation and the microencapsulation mechanism.

In general, it is well known that the naked active materials are easily deactivated by oxygen or humidity. If the active materials are microencapsulated by the shell materials with the barrier ability to oxygen or humidity, the activity of core materials has to be kept for long time. In microencapsulation of the core materials deactivated easily by oxygen or humidity, it is necessary to develop the microencapsulation method without air and humidity. Taking these things into consideration, we have adopted the dry coating method which is performed under nitrogen atmosphere using only the pulverizing solvent.

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revolution speed of 60 rpm. In the mill pot, the three semi mill pots were set to increase the production amount of microcapsules. Microencapsulation may progress in turn such as partial solution of TP with EtOH, adhesion of TP and film formation on the surface of LAA powder. In the preparation method of microcapsules presented here, the concentration of EtOH (CE: wt% to TP) and the added amount of TP to change the feed ratio (R) of TP to LAA were mainly changed. Table 1 shows the experimental conditions adopted in this study.

![FIG. 3 FLOW CHART FOR PREPARING MICROCAPSULES](image)

**TABLE 1 EXPERIMENTAL CONDITIONS**

<table>
<thead>
<tr>
<th></th>
<th>Value(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-(-)+ Ascorbic acid (d=20μm)</td>
<td>2.5g</td>
</tr>
<tr>
<td>Tripalmitin (d=21.5μm)</td>
<td>1.1~3.0g</td>
</tr>
<tr>
<td>Feed ratio of TP to LAA</td>
<td>R=7/3, 6/4, 5/5, 4/6, 3/7</td>
</tr>
<tr>
<td>Pulverizing Medium</td>
<td>Ten nylon balls</td>
</tr>
<tr>
<td>Premixing Time (Semi mill pot)</td>
<td>10min</td>
</tr>
<tr>
<td>Rotational velocity (Semi mill pot)</td>
<td>60rpm</td>
</tr>
<tr>
<td>Mixing Time</td>
<td>6h</td>
</tr>
<tr>
<td>Rotation velocity</td>
<td>60rpm</td>
</tr>
<tr>
<td>Concentration of EtOH(Ce)</td>
<td>0wt%, 0.629wt%, 1.26wt%, 1.89wt%</td>
</tr>
</tbody>
</table>

**Characterization of Microcapsules**

Microcapsules prepared thus were characterized about the following things:

1) **Observation of Microcapsules**

The surface and morphology of a microcapsule were observed by scanning electron microscope (SEM) (VE-9800, Keyence Corp., Osaka, Japan).

2) **Mean Diameter of Microcapsules**

The diameters (d) of about 200 (n) microcapsules were directly measured from SEM photographs of them. From these diameters, the mean Sauter diameter (d) was calculated by the following equation.

\[
d_p = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}
\]

3) **Water Proof Degree**

LAA of given weight was dissolved into distilled water of 40 cm³ and then, the concentration of NaOH to neutralize the LAA aqueous solution was measured by titrating with 0.02mol/L NaOH aqueous solution. From these results, the correlating curve between the concentration of LAA and that of NaOH was obtained beforehand. Then, the microcapsules of 0.5 g were added into distilled water of 40 cm³ to be dispersed for 30 min by mixing gently with the magnetic stirrer, under which conditions any microcapsules were not broken mechanically. After this operation, the given volume (10 cm³) of aqueous solution, in which the microcapsules were dispersed, was sampled out and then, the concentration of NaOH to neutralize this solution was measured. By comparing the measured concentration of NaOH with the correlating curve, the concentration of LAA leaking from the microcapsules was estimated. Moreover, the remaining microcapsules were redispersed in distilled water of 40 cm³ and broken by heating up to 80°C (> melting point of TP) to completely dissolve LAA microencapsulated. Thus, the weight of LAA not leaking from the microcapsules was estimated in the same manner as these stated above. From these values, the water proof degree (A) was calculated by using the following equation.

\[
A = \frac{\text{weight of LAA remaining in microcapsules}}{\text{initial weight of LAA in microcapsules}}
\]

4) **Content, Microencapsulation Efficiency, Yield**

The content (Wc) of core material, the microencapsulation efficiency (Fc), the yield (Y) were calculated by using the following equations from the measured values.

\[
W_c = \frac{\text{total weight of LAA microencapsulated}}{\text{weight of microcapsules}}
\]

\[
F_c = \frac{\text{total weight of LAA microencapsulated}}{\text{weight of LAA in feed}}
\]

\[
Y = \frac{\text{weight of microcapsules}}{\text{weight of TP and LAA in feed}}
\]

5) **Application of Microcapsules to Polymerization of MMA**
The microcapsules (0.5 g) were added into a beaker, in which 10 cm³ of MMA monomer dissolving potassium persulfate (KPS) was poured beforehand. It was observed whether polymerization was induced by heating the beaker at 130°C and breaking the microcapsules or not. For comparison, the same experiments as stated just above were conducted by adding only LAA with heating at 50°C and by adding the microcapsules with heating at 50°C, respectively. The microcapsules were not broken at 50°C.

Results and Discussion

Fig. 4 shows the SEM photographs of LAA powder (Fig. 4a) and microcapsule (Fig. 4b) which was prepared under the conditions of $R = 5/5$ and $C_e = 1.26$ wt%. From these photographs, it is found that LAA is irregular granule with the mean diameter of ca. 20 μm and is coated well with TP. Furthermore, a few LAA granules are agglomerated each other at the microencapsulation process to form larger microcapsules.

FIG. 4 SEM PHOTOGRAPHS OF LAA AND MICROCAPSULE

Fig. 5 shows the effect of feed ratio ($R$) of TP to LAA on the microencapsulation efficiency ($F_c$), the content ($W_c$) of core material, the water proof degree ($A$), the yield of microcapsules ($Y$) and the mean diameter ($d_p$). From this figure, the following interesting results are obtained. The yield of microcapsules is almost above 96% and the microencapsulation efficiency above 82% can be obtained. From these results, the microencapsulation process is found to progress satisfactory. However, on changing the feed ratio from 7/3 to 3/7, the water proof degree is decreased from 100% to 45% and the content of core material is increased from 30% to 65%. It is considered that the water proof degree may decrease by decrease in the shell thickness. The shell thickness is able to be estimated to decrease to ca. 28% of the shell thickness (Ca. 9.3 μm) at $R = 7/3$. In this estimation, it is supposed that LAA is spherical and all TP added is adhered on the surface of LAA. The contents of core material measured are smaller than those (40 to 70) calculated on the basis of the feed ratio. This may be considered to be due to adhesion of the shell and the core materials on the mill pot wall or the pulverizing medium. The mean diameter of microcapsules is ca. 42 μm at $R = 7/3$ and increased with $R$, but becomes the constant value of ca. 62 μm at $R = 5/5, 4/6$ and 3/7.

FIG. 5 EFFECT OF FEED RATIO ON CHARACTERISTICS OF MICROCAPSULES

Fig. 6 shows the SEM photographs of microcapsules prepared by changing $R$. The shell of microcapsule at $R = 7/3$ is found to be denser (closely packed) and thicker than that at $R = 3/7$ because of more TP. The characteristics of microcapsules are strongly affected by the concentration of pulverizing solvent, because adhesion and shell formation of TP are affected by the concentration of pulverizing solvent.

FIG. 6 SEM PHOTOGRAPHS OF MICROCAPSULES PREPARED BY CHANGING R

Fig. 7 shows the dependencies of the microencapsulation efficiency ($F_c$), the content of core material ($W_c$), water proof degree ($A$), the yield ($Y$) and the mean diameter ($d_p$) on the concentration of EtOH. From this figure, the following results are
obtained. The content of core material is almost kept constant \( (W_C = 40\%) \) over the region of the concentration of EtOH from 0 to 0.63 wt% and then, slightly decreases with the concentration of EtOH. The mean diameters of microcapsules decrease from 200 μm to 120 μm with the concentration of EtOH. The microencapsulation efficiency decreases from 80% to 65% with the concentration of EtOH. The water proof degree increases from 50% \((C_E = 0)\) to 75% \((C_E = 1.26 \text{ wt%})\) and then, decreases at \(C_E = 1.89 \text{ wt%}\). The yield slightly decreases from 100 to 90% with the concentration of EtOH.

From these results, the following microencapsulation mechanism may be presented as shown in Fig. 8. At the lower concentration of EtOH, TP may partially dissolve and adhere on the part of the surface of LAA. In this case, the dense shell may not be formed. On increasing the concentration of EtOH, the more the partial soluble TP becomes, the more the adhered TP becomes. As a result, the complete dense shell may be formed. According to this phenomena, the water proof degree has to be increased. However, at the higher concentration of EtOH, a portion of the complete shell formed already may be re-dissolved and removed from the surface of LAA. Furthermore, a portion of microcapsules may adhere on the mill pot wall. Accordingly, the yield at \(C_E = 1.89 \text{ wt%}\) may become smaller than that at \(R = 5/5\) and \(C_E = 1.26 \text{ wt%}\) in Fig. 5 and the content and the microencapsulation efficiency have to be decreased.

Fig. 9 shows the SEM photographs of microcapsules prepared by changing the concentration of EtOH. It is found that the shell becomes denser by adding EtOH.

Fig. 10 shows the result of application of microcapsules to polymerization of methyl methacrylate. In the case of addition of only LAA into MMA monomer at 50°C, polymerization is induced and polymethyl methacrylate is formed at elapsing time of 15 min. In the case of addition of microcapsules at 50°C, polymerization is found to be not induced even at elapsing time of 15 min. On the other hand, in the case of addition of microcapsules at 130°C, it is found that polymerization is induced and polymethyl acrylate is formed at elapsing time of 15 min. From these results, LAA of core material is microencapsulated well with TP and the microcapsules with responsibility to temperature of 80°C are able to be prepared.

**Conclusion**

We have tried to microencapsulate ascorbic acid with
tripalmitin to give the microcapsules both the water proof and the thermal responsibility and to apply the microcapsules to polymerization of methyl methacrylate.

The following results were obtained.

1. The water proof was able to be increased by increasing the added amount of shell material and the concentration of EtOH, but decreased by the excess concentration of EtOH.

2. The yield, the microencapsulation efficiency and the content of core material were decreased with the concentration of EtOH.

3. The water proof degree of ca. 100% can be obtained at $C_e = 1.26 \text{ wt}\%$ and $R = 7/3$.

4. Polymerization of methyl methacrylate can be induced by breaking the microcapsules with heating.

REFERENCES


