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REVIEW

Dielectric Analysis of Microcapsules

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This article describes theoretical and experimental approach to evaluating internal structure of microcapsules, with dielectric analysis. Attention is focused on the microcapsules which have aqueous core and hydrophobic capsule wall, because aqueous suspensions of these microcapsules show dielectric relaxations caused by interfacial polarizaiton mechanism. It is deduced from the theoretical study that the analysis provides us with the information about the electrical conductivity of the core, and the parameter which is a function of the relative permittivity of the capsule wall, its thickness and diameter of the microcapsules. In the light of the results of the theoretical study, the analysis is applied to the mcirocapsules prepared with interfacial polymer deposition thechnique using polystyrene or poly(methyl methacrylate) as the materials of the capsule wall.

KEY WORDS: Dielectric relaxation/ Microcapsule/ Suspension

1. INTRODUCTION

Microcapsules are minute containers made of natural or synthetic polymers, with diameters in a rage from 1 to 500 μm[1]. In various fields, great efforts have been made to prepare microcapsules[2] because of the following remarkable functions of microcapsules: i) changing the properties or nature of materials (e.g., from liquids to powders), and ii) controlling the release of materials.

The microcapsules are regarded as small particles with inhomogeneous internal structure consisting of core and capsule wall. Information about the internal structure is important in the study of the microcapsules. In this article, we show that dielctric analysis is one of effective methods for evaluating the internal structure of the microcapsules.

Suspensions of small particles show dielectric relaxations by various mechanisms[3,4]. Interfacial polarization is one of these mechanisms. In the formulation of the interfacial polarization, the suspensions are regarded as inhomogeneous systems consisting of discrete regions. Each region is considered to be homogeneous, and is specefied by relative permittivity and electrical conductivity. Characteristics of dielectric relaxations, intensities and relaxation frequencies, shown by the suspensions depend on their electrical structure, namely, geometry, and values of the permittivity and the conductivity of the regions. This suggests that the electrical structure of the

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suspensions and suspended particles can be evaluated with the dielectric analysis.

Utility of the dielectric analysis is illustrated by the fact that it played an important role at early stages of cell biology[5]. In the analysis, impedance of biological tissues and aqueous suspensions of biological cells was measured at various frequencies. These specimens showed dielectric relaxations caused by the interfacial polarization. This result shows that biological cells comprise two regions, namely, an outer (cell membrane) and an inner (cytoplasm) regions characterized by low and high electrical conductivities, respectively. This picture is used as a basis of further study in cell biology.

In this study, we choose the microcapsules composed of aqueous core and hydrophobic capsule wall, as the specimen. We study the dielectirc behavior of aqueous suspensions of these microcapsules with an expenctation that the electrical structure of the suspensions of the microcapsules is the same as that of the suspensions of biological cells. Results of theoretical and experimental studies are surveyed in this article.

2. THEORETICAL STUDY

2.1 Model of the Electrical Structure of a Microcapsule

We assume that a microcapsule is represented by a concentric shelled sphere as shown in Fig. 1(B). Inner and outer regions represent aqueous core and capsule wall, respectively. Electrical structure of the microcapsule is represented using the following parameters: outer diameter D, thickness d of capsule wall, the relative permittivities ε_i, ε_s, and the electrical conductivities κ_i, κ_s, where subscripts i and s denote the core and the wall, respectively. The relative complex permittivity ε^* for each region is written by a relation $\varepsilon^* = \varepsilon + \kappa/(j2\pi f\epsilon_v)$ in terms of the relative permittivity ε and the electrical conductivity κ of the region, imaginary unit j, frequency f, and permittivity ϵ_v of vacuum.

Equivalent complex permittivity ε_q^* of the microcapsule is given by the following relation:

$$\varepsilon_q^* = \varepsilon_s^* \frac{2(1-v)\varepsilon_s^* + (1+2v)\varepsilon_i^*}{(2+v)\varepsilon_s^* + (1-v)\varepsilon_i^*}, \qquad (1)$$

with

$$v = (1 - 2d/D)^3. \qquad (2)$$

2.2 Formulas for Suspensions of Uniform Microcapsules

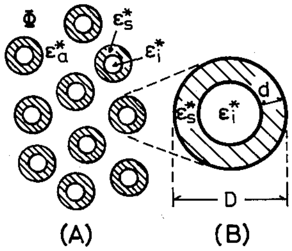

Fig. 1. Schematic diagram for the electrical structure of a microcapsule suspension. (A) A suspension of microcapsules consisting of aqueous core (relative complex permittivity ε_i^*) and capsule wall (ε_s^*) in an aqueous suspending medium (ε_a^*) with a volume fraction Φ. (B) The electrical structure of a microcapsule, which is a concentric shelled sphere in shape, with outer diameter D and thickness d of the capsule wall.

According to the theory of the interfacial polarization, the complex permittivity ε^* of dilute suspensions of uniform microcapules is represented by the following relation[6]:

$$\frac{\varepsilon^*-\varepsilon_a^*}{\varepsilon^*+2\varepsilon_a^*} = \Phi \frac{\varepsilon_q^*-\varepsilon_a^*}{\varepsilon_q^*+2\varepsilon_a^*}, \tag{3}$$

where Φ denotes volume fraction of the microcapsules, and ε_a^* the complex permittivity of aqueous medium characterized by the permittivity ε_a and the conductivity κ_a.

The following relation is effective for concentrated suspensions[7]:

$$\frac{\varepsilon^*-\varepsilon_q^*}{\varepsilon_a^*-\varepsilon_q^*}\left(\frac{\varepsilon_a^*}{\varepsilon^*}\right)^{1/3} = 1-\Phi. \tag{4}$$

2.3 Formulas for Suspensions of Microcapsule Mixture

As described by Kondo[1], a batch of microcapsules is a mixture of capsules which vary in size. Further, thickness of the capsule wall is dependent on the capsule size. These suggest that the theoretical relations should be extended to mixtures of microcapsules which vary in their electrical structure.

Equation (3) can be extended to suspensions of microcapsule mixture. In the formulation, the mcirocapsules are classified into groups according to their electrical structure. The electrical structure of a microcapsule classified into k-th group is specified by the parameters with a subscript k, namely, D_k, d_k, ε_{ik}, κ_{ik}, ε_{sk} and κ_{sk}. The equivalent complex permittivity of the microcapsule is represented by ε_{qk}^* given by Eq. (1). The volume fraction of this group is ϕ_k. Using these parameters, the complex permittivity ε^* of the multicomponent suspensions is given by the following relation[8]:

$$\frac{\varepsilon^*-\varepsilon_a^*}{\varepsilon^*+2\varepsilon_a^*} = \Phi\sum_k\left(h_k\frac{\varepsilon_{qk}^*-\varepsilon_a^*}{\varepsilon_{qk}^*+2\varepsilon_a^*}\right), \tag{5}$$

where Φ denotes the total volume fraction, and h_k the reduced volume fraction for the k-th group. They are given by the following relations:

$$\Phi=\sum_k \phi_k, \quad \text{and} \tag{6}$$

$$h_k=\phi_k/\Phi. \tag{7}$$

Relations for ε^* for concentrated suspensions of microcapsule mixture can be derived from Eq. (5). The relations for twe-component suspensions were derived recently, being found elsewhere[9].

The following relation is derived as an approximate equation derived from Eq. (5) under a condition $\Phi \ll 1$[10]:

$$\varepsilon^*=\varepsilon_a^* + 3\Phi\sum_k\left(h_k\varepsilon_a^*\frac{\varepsilon_{qk}^*-\varepsilon_a^*}{\varepsilon_{qk}^*+2\varepsilon_a^*}\right). \tag{8}$$

2.4 Approximate Formulas for Microcapsule Suspensions

In order to obtain a simplified view of the dielectric behavior of aqueous suspensions of microcapsules used in this study, Eq. (8) is modified under the assumption that the following requisites are satisfied by every microcapsules[10]:

a) Thickness of the capsule wall is much smaller than diameter of the microcapsule.

b) Electrical conductivity of the capsule wall is much lower than those of the core and the suspending medium.

c) Electrical conductivity of the core is much higher than that of the suspending medium.

These requisites are expressed in the following way:

$$d_k/D_k \ll 1, \quad \text{and} \tag{9}$$

$$D_k\varkappa_{sk}/d_k \ll \varkappa_a \ll \varkappa_{ik}. \tag{10}$$

Since the permittivity of most hydrophobic materials is not much less than that of aqueous solutions, the following relation holds:

$$D_k\varepsilon_{sk}/d_k \gg \varepsilon_a = \varepsilon_{ik} = \varepsilon_w, \tag{11}$$

where ε_w denotes the permittivity of water. Rearrangement of Eq. (8) by taking account of Eqs. (9)-(11) leads to the following expression for ε^*:

$$\varepsilon^* = \varepsilon_h + \varepsilon_P^* + \varepsilon_Q^* + \varkappa_l/(j2\pi f\epsilon_v), \tag{12}$$

where ε_h denotes the permittivity at high frequencies and $\varkappa_l$ the conductivity at low frequencies. These parameters are given by the following relations:

$$\varepsilon_h = \varepsilon_w, \quad \text{and} \tag{13}$$

$$\varkappa_l = (1 - 3\Phi/2)\varkappa_a. \tag{14}$$

The terms ε_P^* and ε_Q^* in Eq. (12) represent the contribution of dielectric relaxations named P- and Q-relaxation, respectively. Both ε_P^* and ε_Q^* are represented as the sum of the Debye-type dielectric relaxations in the following way:

$$\varepsilon^* = \Delta\varepsilon \sum_k \frac{g_k}{1+j\,f/f_k}, \tag{15}$$

where $\Delta\varepsilon$ denotes the total intensity of the relaxation, g_k and f_k the relative intensity and the relaxation frequency of a constituent Debye-type relaxation, respectively.

The parameters $\Delta\varepsilon$, g_k and f_k for the P- and the Q- relaxation are represented with subscripts P and Q, respectively, being given by the following relations:

$$\Delta\varepsilon_P = \frac{9\Phi}{8} \sum_k (h_k W_k), \tag{16}$$

$$g_{Pk} = h_k W_k / \sum_k (h_k W_k), \tag{17}$$

$$f_{Pk} = \frac{1}{2\pi\epsilon_v} \frac{4\kappa_a}{W_k}, \tag{18}$$

$$W_k = D_k \varepsilon_{sk} / d_k, \tag{19}$$

$$\Delta\varepsilon_Q = 3\Phi\varepsilon_w, \tag{20}$$

$$g_{Qk} = h_k, \quad \text{and} \tag{21}$$

$$f_{Qk} = \frac{1}{2\pi\epsilon_v} \frac{\kappa_{ik}}{3\varepsilon_w}. \tag{22}$$

2.5 Information Obtained from Dielectric Analysis

Volume fraction Φ

Equation (14) suggests that the value of Φ can be evaluated using the value of κ_l obtained from dielectric measurements and that of κ_a obtained separately.

Diameter D of microcapsules, and thickness d and relative permittivity ε_s of capsule wall

Equaitons (16)-(19) show that the characteristics of the P-relaxation are the function of W, which is a function of D, ε_s and d. This means that the information about W is obtained from the characteristics of the P-relaxation, and that the values of D, ε_s and d cannot be estimated separately with the dielectric analysis.

Equation (16) suggests that a mean value of W, which is given by a relation

$$\sum_k (h_k W_k) = \sum_k (\phi_k W_k) / \sum_k \phi_k, \tag{23}$$

can be evaluated from $\Delta\varepsilon_P$.

Equation (18) shows that the relaxation frequencies f_P of the P-relaxation are the function of W. This means that, if the microcapsules are uniform in W, the P-relaxation is represented as a Debye-type relaxation. If the microcapsules vary in W, the P-relaxation is represented as a relaxation with distributed relaxation frequencies. In this case, the characteristics of the distribution of W can be evaluated from those of f_P.

Electrical conductivity κ_i of aqueous core

Equation (22) shows that the relaxation frequencies f_Q of the Q-relaxation are the function of κ_i. Hence the distribution characteristics of κ_i can be evaluated from those of f_Q.

3. EXPERIMENTAL STUDY

3.1 Experimental Procedure

In experimental studies[11-15], we used the microcapsules prepared with interfacial polymer deposition technique, using polystylene (PS) or poly(methyl methacrylate) (PMMA) as the materials of capsule wall. The microcapsules prepared were fractionated according to their outer diameter using mesh screens. The microcapsules

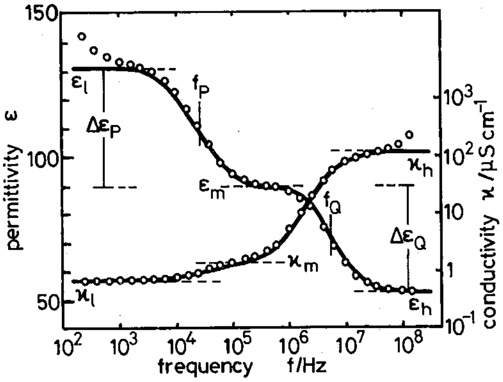

Fig. 2. Dielectric observations on a suspension of polystyrene microcapsules containing a 2% gelatin solution[11].

of sucrose or Ficoll 400 (Pharmacia Fine Chemicals). Microcapsules which had large diameter and low density were used in the experiments. Optical microscopic observations showed that the structure of these microcapsules were very close to the model shown in Fig. 1.

In the dielectric measurement, we used a TR-1C Ratio Arm Transformer Bridge (Ando Electric Co., Ltd.), 4192A LF Impedance Analyzer (Hewlett-Packard) and a 4191A RF Impedance Analyzer (Hewlett-Packeard) for the measurement in the frequency ranges from 20 Hz to 3 MHz, from 5 Hz to 13 MHz and from 1 to 200 MHz, respectively.

3.2 Dielectric Behavior of Microcapsule Suspensions

Figure 2 shows the dielectric observations on a suspension of PS microcapsules containing a 2% gelatin solution[11]. The microcapsules were washed with distilled water repeatedly, and were suspended in distilled water before the dielectric measurement. As seen from Fig. 2, the microcapsule suspension shows two dielectric relaxations, which are expected from Eq.(12). The relaxations located at low and high frequencies are assigned to the P- and the Q-relaxation, respectively.

Dependence of the relaxation frequencies f_P and f_Q on the conductivities κ_a and κ_i was examined using a series of sepcimens containing aqueous solutions of poly(diallyl dimethyl ammonium chloride)(PDDAC)[11]. In the examination, f_P and f_Q were defined as the frequencies at which the value of ε reached $(\varepsilon_l+\varepsilon_m)/2$ and $(\varepsilon_m+\varepsilon_h)/2$, resepctively, where $\varepsilon_l, \varepsilon_m$ and ε_h denote the values of ε at low, intermediate and high frequencies, respectively.

Table 1 shows the values of f_P and f_Q. As seen from Table 1, f_P decreases as the result of repeated washing of the microcapsules with distilled water. The decrease in f_P is attributed to that in κ_a caused by this treatment. This result is consistent with Eq. (18). The value of f_Q does not change by this treatment. However, as shown in Table 1, it decreases with the decrease in the concentration of PDDAC in the core [PDDAC]. The decrease in f_Q is attributed to that in κ_i caused by that in [PDDAC]. This result is explicable from Eq. (22). It is ascertained from these observations and

Table 1. Change in relaxation frequencies f_P and f_Q of P- and Q-relaxation[11].

Specimen	[PDDAC][a)] %	f_P kHz	f_Q MHz
Effect of repeated washing with distilled water (The number of the treatments increases from PS1-1 to PS1-3)			
PS1-1	5	2300	74
PS1-2	5	160	74
PS1-3	5	65	74
Effect of the change in [PDDAD]			
PS2	2	40	48
PS3	1	16	25
PS4	0.5	10	14
PS5	0	8	0.22

a) concentration of poly(diallyl dimethyl ammonium cholride) in the core of microcapsules.

Table 2. Results of theretical analysis with a uniform model[11] for the specimens shown in Fig. 2 and Table 1. The analysis was carried out by assuming that $\varepsilon_s=2.65$ and $\kappa_s=0$.

Specimen	Parameters observed		Parameters evaluated				
	D μm	ε_a	Φ	κ_a μS cm^{-1}	ε_i	κ_i mS cm^{-1}	d μm
PS microcapsules containing a 2% gelatin solution (Fig. 2)							
	210	78	0.67	3.8	79	0.55	2.8
PS microcapsules containing PDDAC solutions (Table 1)							
PS1-3 ([PDDAC]=5%)	250	80	0.55	6.8	81	12	1.4
PS2 (2%)	300	81	0.47	4.0	52	5.1	1.1
PS3 (1%)	300	79	0.44	1.5	64	2.8	1.3
PS4 (0.5%)	300	80	0.47	1.9	63	1.9	1.1
PS5 (0%)	300	80	0.54	1.4	73	0.034	1.8

discussion that the P- and the Q-relaxation are caused by the interfacial polarization.

3.3 Analysis with a Uniform Model

The electrical structure of the suspensions of the PS microcapsules was evaluated from Eq. (4)[11] under the assumption that $\kappa_s << \kappa_a < \kappa_i$, using the values of D and ε_a obtained from optical microscopic observations and dielectric measurements of the suspending media, respectively. The value of ε_s was assumed to be 2.65 in the analysis, on the basis of dielectric observations on PS films immersed in aqueous solutions. Values of Φ, κ_a, ε_i, κ_i and d were evaluated from the analysis. The use of the values of D and ε_s obtained separately enabled us to evaluate the values of d.

Table 2 shows the values of the parameters evaluated for the specimens shown in Fig. 2 and Table 1. Despite of the simplicity of the model, these values are reasonable for the specimens, as discussed in the original paper[11]. This suggests that the distribution of W and that of κ_i are not serious in these specimens. Solid lines in Fig. 2 show the frequency dependence of ε and κ evaluated from Eq. (4) using the values of the parameters listed in Table 2. As seen from Fig. 2, the theoretical curves reconstitute the profiles of frequency depencdece observed. Deviation of the observations from the theoretical curves is attributable to the distribution of W and that of κ_i, which act as minor effects in this analysis.

3.4 Dielectric Study of Release of KCl from Microcapsules

Release of KCl from the microcapsules was studied[15] using the PMMA microcapsules containing an aqueous KCl solution. The measuring cell was designed so that the KCl released outside was washed away with distilled water. Results of the measurements were analyzed in the light of Eq. (22).

The dielectric analysis revealed that the values of κ_i decreased, and were distributed in wider ranges as time passed. The decrease in κ_i was attributed to that in KCl concentration in the core caused by the release of KCl. From the increase in the width of the distribution ranges of κ_i, we presumed that the microcapsules varied in their release rate of KCl.

4. CONCLUSION

As descrebed in this paper, the dieletric analysis provides us with information about the internal structure of microcapsules, such as the conductivity of the core, and the parameter which is the function of the permittivity of the capsule wall, its thickness and outer diameter of the microcapsules. Such information is important in the study of microcapsules. Moreover, the merit of the dielectric analysis is that such information can be obtained without breaking the microcapsules. These suggest that the dielectric analysis is one of effective methods in the study of microcapsules.

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