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ORIGINAL CONTRIBUTION

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Dielectric analysis of polystyrene microcapsules using scanning dielectric microscope

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Abstract A dielectric imaging technique with a scanning dielectric microscope was applied to polystyrene microcapsules in an aqueous environment to study the electrical properties of individual ones. The dielectric images obtained over a frequency range from 10 kHz to 10 MHz showed frequency dependence, which indicated dielectric dispersion (or relaxation) due to interfacial polarization or the build up of charge on the boundaries between the microcapsule shell and the aqueous phases. The dielectric dispersion was analyzed based on an equivalent electrical circuit model and a shell-sphere model in which a spherical core is covered with an insulating shell.

Key words Dielectric dispersion – polystyrene microcapsule – scanning dielectric microscope – interfacial polarization – dielectric imaging

Introduction

In the laboratory research and industrial quality control of microcapsules that are widely used in various industrial and medical fields, it is important to elucidate their structural and electrical properties in non-destructive way. Dielectric spectroscopy is well suited for this purpose. Zhang et al. [1, 2] first reported dielectric behavior of polystyrene microcapsules in suspension, which was excellently analyzed by a dielectric theory based on interfacial polarization. This method, termed the "suspension method", was also successfully applied to polymethylmethacrylate microcapsules by Sekine [3, 4]. However, the suspension method is not appropriate for getting information on individual microcapsules because it provides only their average properties. In order to characterize individual microcapsules we developed a method that can measure a single microcapsule with a small three-terminal dielectric chamber [5]. Recently, a scanning dielectric microscope (SDM) which can image the capacitance (or permittivity) and conductance (or conductivity) of fine particles using a fine sensing electrode has been developed [6]. The SDM is also suited for characterizing individual microcapsules in an aqueous environment that show dielectric dispersion in the radio frequency range, which cannot be measured by similar types of instruments so far developed, namely the scanning capacitance microscope working in air at a fixed ultrahigh frequency [7–9] and the scanning ion-conductance microscope [10] applicable to a sample in an electrolyte solution under a dc field. In this paper, I apply the SDM to polystyrene microcapsules and attempt to analyze their dielectric images to estimate the electrical parameters of individual ones.

Materials and methods

Preparation of microcapsules

Polystyrene microcapsules were prepared by an interfacial polymer deposition technique as reported previously [1, 5, 11]. The internal aqueous phase of the microcapsules contained 3 mM KCl and 0.1% (w/v) gelatin. The

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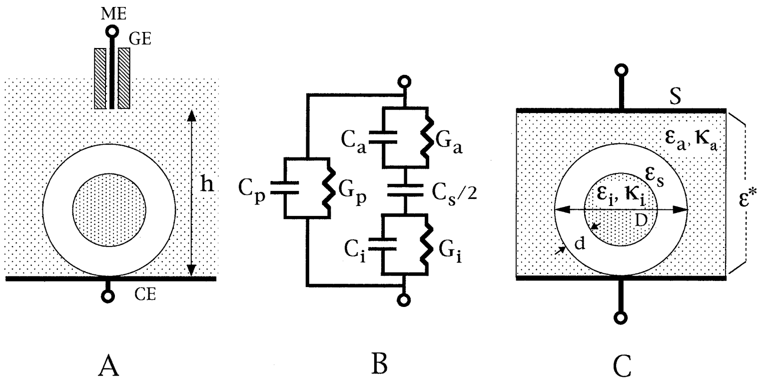

Fig. 1 The electrode configuration of the scanning dielectric microscope and the electrical models used for estimation of the electrical parameters of a polystyrene microcapsule. (A) The scanning dielectric microscope: A coaxial probe consisting of an inner measuring electrode (ME) and an outer guard electrode (GE) is scanned over a microcapsule on a counter electrode (CE) at the constant height *h*. (B) An equivalent circuit model for the spot measurement: C_a and G_a are the capacitance and conductance of the external aqueous phase between the probe end and the top of the microcapsule, C_s is the capacitance of the shell, C_i and G_i are the capacitance and conductance of the internal aqueous phase, and C_p and G_p are the stray capacitance and the leakage conductance. (C) An electrical model for a microcapsule in a cylindrical parallel plate capacitor of surface electrode area *S* and distance *h*: ε and κ are relative permittivity and conductivity, *d* is the shell thickness, *D* is the outer diameter and the subscripts *a*, *s* and *i* refer to the external, shell and core phases, respectively. $\varepsilon^*(= \varepsilon - j\kappa/2\pi f\varepsilon_0)$ is the equivalent complex permittivity of the system

microcapsules were stored in a 3 mM KCl solution at room temperature. For dielectric measurements the microcapsules of 700–850 μm in diameter that were fractionated with mesh screens were used.

Scanning dielectric microscopy

A schematic view of the SDM is shown in Fig. 1A. A fine coaxial probe is laterally scanned over a microcapsule on a plate electrode (CE) at a constant height using an x–y stage driven by two dc surbo-motors with a M9103 DC Motor Controller (Chuo Seiki Co., Ltd., Tokyo). The probe consists of a 76 μm diameter platinum wire coated with 10 μm thick Teflon layer as the inner measuring electrode (ME) and a stainless steel tube of 130 μm inner diameter and 330 μm outer diameter, which was fixed in a 90°-cut hypodermic needle. The stainless steel tube and the hypodermic needle, which are electrically connected, work as the outer guard electrode (GE). The gap between the ME and GE was filled with epoxy resin. Dielectric measurement has been based on the three-terminal method, in which both the ME and GE are held at the same potential against the CE, thereby yielding a parallel field between the ME and CE. The effectiveness of the three-terminal method was discussed in a previous paper [6]. Capacitance and conductance were measured over a frequency range of 1 kHz to 10 MHz with a HP-4192A Impedance Analyzer (Hewlett-Packard Co., Palo Alto).

Microcapsules were glued on a stainless steel foil with neoprene (Nisshin EM Co., Ltd., Tokyo). In the manipulation of the microcapsules, care was taken to prevent their deformation and fracture. The foil was fixed on the CE in a chamber on the x-y stage and the chamber was filled with distilled water.

Measurements are performed in three modes: (1) the "spot" mode in which capacitance *C* and conductance *G* are measured at a fixed probe position, (2) the "single-line scan" mode in which a probe is line-scanned over a microcapsule and frequency dependence of *C* and *G* is obtained, (3) the "rasta-scan" mode that yields a two-dimensional image of the *C* and *G* from the data measured at a fixed frequency by rasta-scanning a probe.

Estimation of effective probe area

The effective area S_p of a probe electrode was determined from the relationship between the measured capacitance *C* and the distance *h* between the probe end and the counter electrode. The capacitance measured in water was found to be proportional to the reciprocal of the electrode distance (Fig. 2), indicating that a parallel plate capacitor can be assumed for this system, i.e., the relationship is represented by $C = C_{st} + \varepsilon_w \varepsilon_0 S_p/h$, where C_{st} is the stray capacitance, ε_w is the relative permittivity of water and ε_0 is the permittivity of vacuum. Thus, the value of S_p $(= 4.78 \times 10^{-2}\ \mathrm{mm}^2$, in this case) was obtained from the slope $(= 3.375 \times 10^{-2}$ pFmm) and ε_w (= 79.8 at 20.8 °C). The dielectric cell constant C_c $(= \varepsilon_0 S_p/h)$ can be calculated when the distance *h* is measured. Using the values of

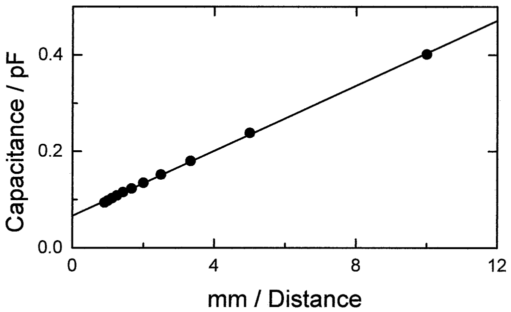

Fig. 2 Estimation of the effective probe diameter. The capacitance C measured in water is plotted against the reciprocal of the probe height (or the electrode distance) h. The solid line is the linear regression line expressed by $C(\mathrm{pF}) = 0.0663 + 0.0338/(h/\mathrm{mm})$

C_c and C_{st} ($= 6.63 \times 10^{-2}$ pF), the measured capacitance and conductance can be converted into the equivalent relative permittivity and conductivity, respectively.

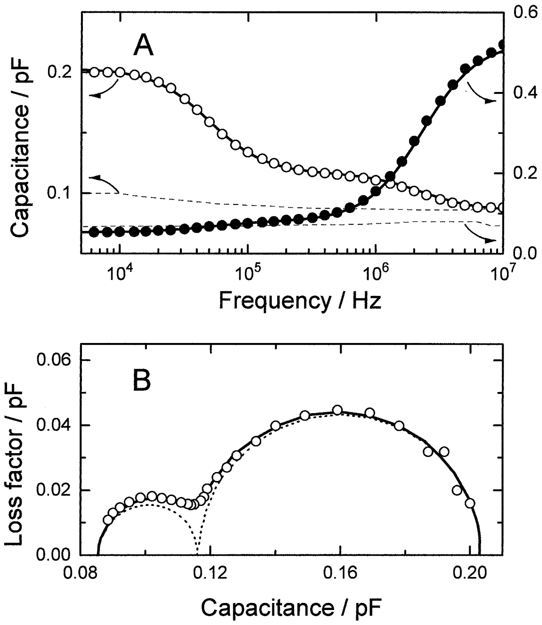

Fig. 3 Dielectric dispersion measured by locating the probe electrode above the top of a polystyrene microcapsule in water. The probe height is 1000 μm. (A) Frequency dependence of the capacitance (○) and conductance (●). The solid lines are the best-fit curves calculated from Eq. (1) with the parameters shown in Table 1 (Specimen 1). The thin broken lines indicate the data without microcapsule. (B) Cole–Cole plots in which loss factor ($= (G - G_l)/2\pi f$) is ploted for capacitance C. The solid line indicates the curve calculated from Eq. (1), which is a sum of the two subdispersions (P- and Q-dispersions) indicated by the dotted lines

Results and discussion

Dielectric images of a polystyrene microcapsule

When dielectric measurement was made in the spot mode by locating a probe electrode just above the top of a microcapsule in distilled water, the measured capacitance C and conductance G showed a two-step dielectric dispersion (Fig. 3). This dispersion is expressed by a sum of two subdispersions of Debye type, termed P- and Q-dispersions for the low- and high-frequency dispersions, respectively.

$$C^* = C - \frac{G}{2\pi f} = C_h + \frac{\Delta C_p}{1 + jf/f_{cp}} + \frac{\Delta C_q}{1 + jf/f_{cq}} + \frac{G_l}{j2\pi f}, \quad (1)$$

where C_h is the high frequency limit of capacitance, ΔC is the magnitude of the dispersion, f_c is the characteristic frequency, f is frequency, $j = (-1)^{1/2}$, G_1 is the low frequency limit of conductance and the subscripts p and q refer to the P- and Q-dispersions, respectively. The parameters (C_h, ΔC_p, f_{cp}, ΔC_q, f_{cq}, G_1) obtained for several microcapsules are listed in Table 1. The dielectric dispersion is in shape similar to those obtained by the suspension method [1, 2] and by the single-capsule measurement [5].

After the spot measurement the probe was scanned along a line through the top of the microcapsule at a constant height and capacitance and conductance were measured between 10 kHz and 10 MHz. Figure 4 shows frequency dependence of the single-line images of the capacitance and conductance. Further, when the probe was rasta-scanned over the microcapsule, two-dimensional images of the conductance and capacitance were obtained at various frequencies as shown in Fig. 5. The images are symmetrical about the microcapsule center because of its spherical shape. At low frequencies the capacitance of the central part is higher than that of the surrounding, because of the buildup of charge on the boundaries between the microcapsule shell and the aqueous phases. The conductance of the central part is lower than that of the surrounding at low frequencies and increases with increasing frequency. This means that the internal conductive phase becomes electrically visible at high frequencies, where the thin insulating shell is apparently short circuited.

The frequency dependence of the dielectric images includes important information on the structural and electrical properties of the microcapsules. Hence, we attempted to estimate the electrical parameters of the microcapsules from the data obtained by the spot and line-scan measurements in the following subsections.

Analysis based on an equivalent electrical circuit model

The dielectric dispersion obtained by the spot measurement might be dealt with using an electrical equivalent

Table 1 Dielectric dispersion parameters estimated by fitting Eq. (1) to the data obtained by the spot measurement

Specimen No.	Temp. [°C]	h [μm]	D [μm]	G_l [nS]	C_h [fF]	ΔC_p [fF]	f_{cp} [kHz]	ΔC_q [fF]	f_{cq} [MHz]
1	19.0	1000	821	53	85.6	87.5	49.1	31.0	2.08
2	20.8	900	729	61	103.3	81.7	49.1	31.9	1.72
3	20.4	950	763	71	102.3	52.3	57.7	21.3	3.17
4	20.7	1000	795	227	96.7	84.3	170.5	21.9	2.14

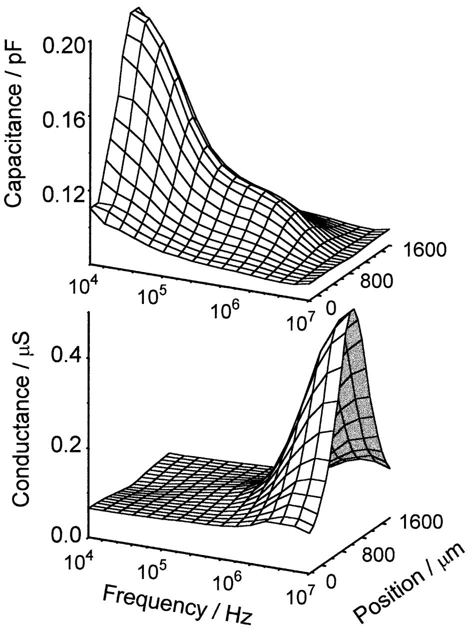

Fig. 4 Frequency dependence of the single-line images of the same microcapsule as in Fig. 3. The probe was scanned along the line across the center of the microcapsule at a height of 1000 μm

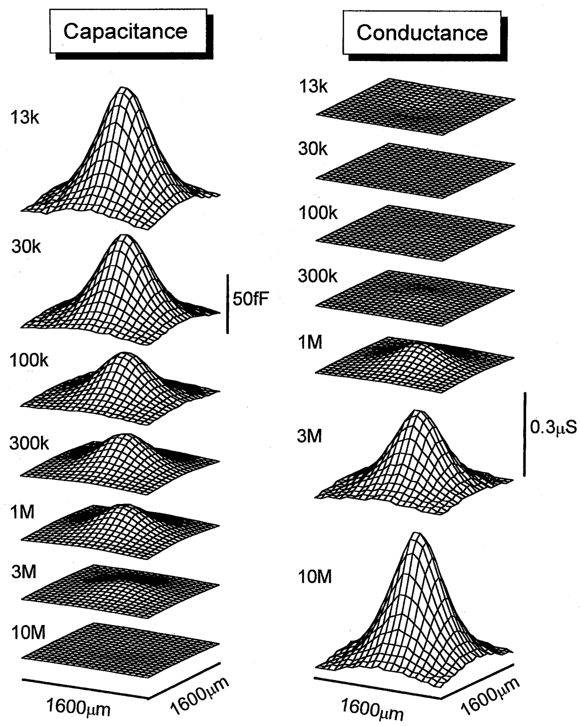

Fig. 5 Two-dimensional dielectric images obtained when the probe was rasta-scanned over the same microcapsule as in Figs. 3 and 4. The images were obtained at frequencies ranging from 13 kHz to 10 MHz. The imaged area is 1600 μm by 1600 μm

circuit model shown in Fig. 1B. This model consists of the admittance for the external aqueous phase between the probe electrode and the microcapsule (its capacitance and conductance are C_a and G_a, respectively), the capacitance ($C_s/2$) for a serial combination of the two insulating shells, and the admittance for the internal aqueous phase (C_i and G_i). The circuit also includes the stray capacitance (C_p) and leakage conductance (G_p) in parallel, which may be equal to C_{st} and G_l. The parameters (C_s, C_a, G_a, C_i, G_i) in the model were determined from the dispersion parameters (C_h, ΔC_p, ΔC_q, f_{cp}, f_{cq}) by the method described by Kiyohara et al. [12]. The results are shown in Table 2. The shell thickness d, the relative permittivity ε_a and conductivity κ_a of the external phase, and the permittivity ε_i and conductivity κ_i of the internal phase were calculated from the estimated values of C_s, C_a, G_a, C_i and G_i by assuming the following simple relationships:

$$C_s = \varepsilon_s \varepsilon_0 S_p / d \ ,$$
$$C_a = \varepsilon_a \varepsilon_0 S_p/(h - D), \qquad G_a = \kappa_a S_p/(h - D) \ ,$$
$$C_i = \varepsilon_i \varepsilon_0 S_p/(D - 2d), \qquad G_i = \kappa_i S_p/(D - 2d) \ , \qquad (2)$$

where ε_0 is the permittivity of vacuum, D is the microcapsule diameter, S_p is the effective measurement area of the probe and h is the distance between the probe end and the counter electrode. As will be discussed in the next subsection, this analysis provides reasonable estimates for the structural and electrical parameters of the microcapsules despite the simplified model.

Analysis based on shell-sphere model

A dielectric spectrum of a single microcapsule in suspension is calculated by averaging the local relative permittivity (calculated from the corresponding capacitance) over the whole area including the microcapsule. The data collected by the line-scan measurements were averaged over

Table 2 Electrical parameters in the equivalent circuit model, shown in Fig. 1B, estimated from the dielectric dispersion parameters in Table 1

Specimen No.	C_a [pF]	G_a [nS]	C_i [pF]	G_i [μS]	C_s [pF]	ε_a	κ_a [μS/cm]	ε_i	κ_i [μS/cm]	d [μm]
1	0.086	71	0.029	1.04	0.276	37	2.7	56	177	4.1
2	0.135	90	0.076	1.54	0.300	55	3.2	129	233	3.7
3	0.123	85	0.093	2.93	0.220	55	3.3	165	462	5.1
4	0.107	306	0.062	1.49	0.278	52	13.1	116	246	4.0
Mean								116	280	4.2

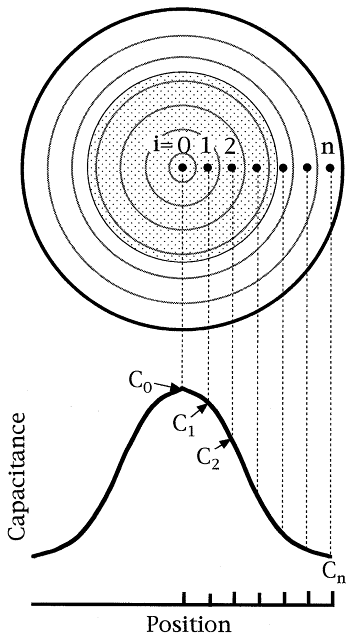

Fig. 6 Calculation of the relative permittivity of a single microcapsule in suspension from the data of the line-scan measurement. The shaded circle indicates an area of the microcapsule. The relative permittivity in each circular band can be calculated from the corresponding capacitance obtained by the line-scan measurement

a circular area shown in Fig. 6. For each numbered circular band in Fig. 6 the same relative permittivity is assumed because the dielectric image is symmetrical about the microcapsule center. Hence, the equivalent permittivity ε of a single microcapsule in a cylindrical parallel plate capacitor of electrode area S and distance h (see Fig. 1C) is given by

$$\varepsilon = \varepsilon_a + \frac{1}{C_c}\sum_{i=0}^{n}(C_i - C_a)S_i \,, \tag{3}$$

where i is the measurement point number and also the area number, C_a is the capacitance without microcapsule, C_c is the cell constant, C_i is the capacitance at the ith measurement point, S_i is the fractional surface area of the ith

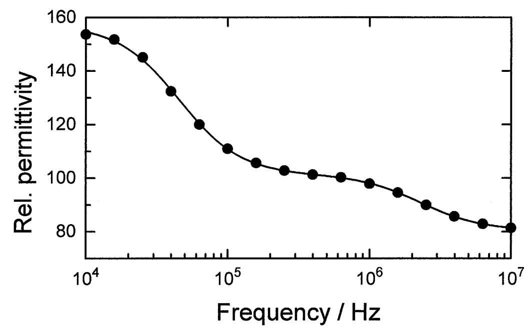

Fig. 7 Frequency dependence of the relative permittivity of a single microcapsule in suspension, which was calculated from the data of the single-line image shown in Fig. 4. The solid curves indicates the best-fit curves calculated from Eq. (4) with the dielectric dispersion parameters shown in Table 3 (Specimen 1). It is the same as the theoretical curve calculated from Pauly–Schwan's equation with the electrical parameters in Table 4 (Specimen 1)

circular band, i.e.,

$S_0 = 0.25/(n+0.5)^2$ for $i = 0$ and $S_i = 2i/(n+0.5)^2$ for $i \neq 0$.

Figure 7 shows frequency dependence of the relative permittivity calculated from Eq. (3) with the data shown in Fig. 4. A two-step dielectric dispersion was also found, which was expressed by an alternative representation to Eq. (1) as

$$\varepsilon^* \equiv \varepsilon - j\frac{\kappa}{2\pi f\varepsilon_0} = \varepsilon_h + \frac{\Delta\varepsilon_p}{1 + jf/f_{cp}} + \frac{\Delta\varepsilon_q}{1 + jf/f_{cq}} + \frac{\kappa_l}{j2\pi f\varepsilon_0} \,, \tag{4}$$

where ε_h is the high frequency limit of permittivity, $\Delta\varepsilon$ is the magnitude of the dispersion, and κ_l is the low frequency limit of conductivity. The parameters of the dielectric dispersion were summarized in Table 3.

The dielectric dispersion for a single microcapsule in suspension can be analyzed using Pauly–Schwan's equation [13] for the shell-sphere model (Fig. 1C). The electrical parameters in the model were estimated by fitting Pauly–Schwan's equation to the dispersion curve. In the

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Table 3 Dielectric dispersion parameters for a single microcapsule in suspension estimated by fitting Eq. (4) to the dielectric dispersions calculated from the data of the line-scan image

Specimen No.	Temp. [°C]	ε_h	$\Delta\varepsilon_p$	f_{cp} [kHz]	$\Delta\varepsilon_q$	f_{cq} [MHz]
1	18.9	80.4	55.9	45.6	20.9	2.29
2	20.6	80.4	45.7	42.2	16.0	1.28
3	21.2	79.5	49.9	49.4	16.8	2.90
4	20.7	80.4	74.7	138.4	18.8	1.84

Table 4 Electrical phase parameters in the shell-sphere model estimated by fitting Pauly–Schwan's equation to the dielectric dispersion parameters in Table 3

Specimen No.	Φ	ε_a	κ_a [μs cm^{-1}]	ε_i	κ_i [μs cm^{-1}]	d [μm]
1	0.144	81	5.04	106	335	3.3
2	0.112	80	4.66	115	205	2.9
3	0.122	80	5.71	103	397	3.0
4	0.131	80	17.86	106	301	2.5
mean				108	310	2.9

curve fitting the relative permittivity of the insulating polystyrene shell was assumed to be 2.65, and the volume fraction Φ was calculated from $\Phi = \pi D^3/6hs$. Table 4 shows the results, in which the estimated parameters are in fairly good agreement with those obtained by the equivalent circuit model. The mean values of the shell thickness and the internal conductivity are close to those estimated by the single-capsule measurement [5].

Conclusion

With polystyrene microcapsules of well-defined structure, we examined the possibility to evaluate electrical properties of the individual microcapsules from their dielectric images obtained by the SDM. The results demonstrated that the analysis described in this paper successfully provided the electrical properties of the polystyrene microcapsules although it needed some knowledge on their structure in advance. The analysis, however, may not be applicable to microcapsules with more complicated structure, such as microcapsules with a porous shell and with an awkward shape, so that we should develop a sophisticated numerical calculation method to analyze a wide variety of microcapsules.

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