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ORIGINAL CONTRIBUTION

Preparation of monodisperse crosslinked polymelamine microcapsules by phase separation method

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Abstract Monodisperse polymelamine microcapsules were prepared by phase separation method. Control of microcapsule diameter was investigated using the uniform-sized oil-in-water emulsion droplets as the capsule core. The monodisperse emulsion droplets were prepared using the Shirasu porous glass (SPG) membrane emulsification technique. The effects of the diameter of the oil droplet and concentration of sodium dodecyl sulfate (SDS), which is a typical emulsifier in SPG membrane emulsification, on microencapsulation were investigated. The microcapsules were aggregated when oil droplets with small size were microencapsulated at high SDS concentration. To reduce the SDS concentration, the creamed emulsion was used. The monodisperse polymelamine microcapsules were successfully prepared by using the creamed emulsion. The microcapsule diameter was almost similar to the diameter of the encapsulated oil droplet. The coefficient of variation values was about 10% for all microcapsules prepared in this study. Control of microcapsule diameter was achieved in the range of 5–60 μm.

Keywords Monodisperse microcapsule · Phase separation method · Control of capsule diameter · Shirasu porous glass membrane · Sodium dodecyl sulfate concentration

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Introduction

Microcapsules are tiny packaged materials that have been used in a wide variety of fields such as in chemical and pharmaceutical industries and in cosmetics and printing. In the 1950s, they were used in carbonless copy paper developed by the National Cash Register Company [1]. The microcapsules in the carbonless copy paper were powder-like substances that protected the core material from damage caused by oxidation and rough handling and treatment. Several microencapsulation methods were subsequently developed and applied in the fields in which they are used today. Microcapsules with a variety of functions can be produced by using different microencapsulation methods.

Of the several microencapsulation methods, the phase separation method is one of the most useful. Crosslinked polyamino resin microcapsules prepared by phase separation method are mono-core microcapsules that enclose water-insoluble organic solvents. They have smooth, thin, and transparent membranes. The capsule membrane is formed at the liquid–liquid interface of an oil-in-water (O/W) emulsion from a continuous phase. These characteristics are suitable for the preparation of a microcapsule that encloses an organic solvent with electrophoretic microparticles, which is used as an element of paper-like display systems [2–4]. However, there are still some problems in applying the microcapsule prepared by the phase separation method to the paper-like display system. Controlling the diameter of the microcapsule is one of the most serious technical issues. The diameter of the microcapsule directly affects the thickness of the display. It also affects the intensity of the electric field and the electrophoretic performance of the microparticles in the microcapsule. In

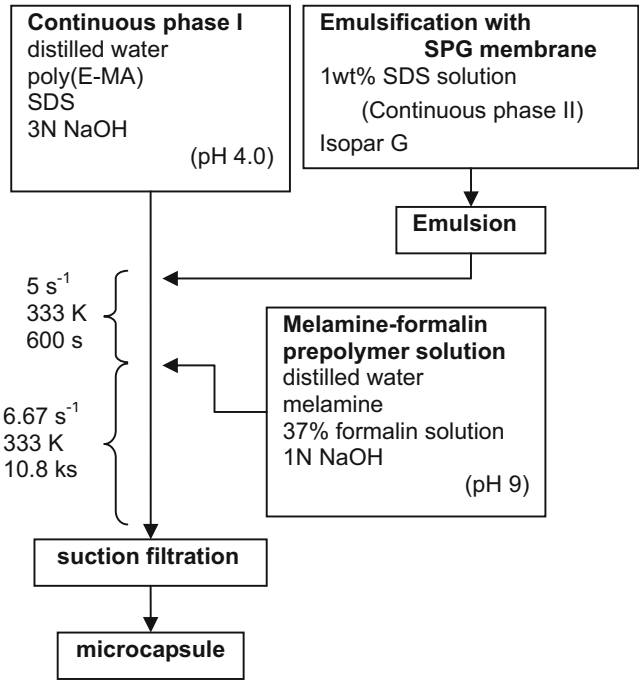

Fig. 1 Protocol for the preparation of monodisperse crosslinked polymelamine microcapsules

Table 1 Preparation condition of crosslinked polymelamine microcapsules

	Total amount (g)	Content	Amount (g)
(A)			
Continuous phase I	77.5	Distilled water (+ NaOH)	67.5
		Poly(E-MA)	2.5
Emulsion	37.5	Isopar G	15.0
		Continuous phase II[a]	30.0
Melamine–formalin prepolymer solution	50	Melamine	5.0
		37% formalin solution	12.5
		Distilled water (+ NaOH)	32.5
(B)			
Continuous phase I	92.5	Distilled water (+ NaOH)	90.0
		Poly(E-MA)	2.5
Creamed emulsion	22.5	Isopar G	15.0
		Continuous phase II[a]	7.5
Melamine–formalin prepolymer solution	50	Melamine	5.0
		37% formalin solution	12.5
		Distilled water (+ NaOH)	32.5

Microencapsulation was carried out with (A) emulsion in state of SPG emulsification and (B) creamed emulsion.
[a] Continuous phase II is 0.5 wt.% SDS solution.

Table 2 Preparation condition of crosslinked polymelamine microcapsules with different amounts of oil phase

	Continuous phase I[a]			Emulsion[b]			Prepolymer solution[c] (g)	Poly(E-MA)/total surface area (g/m^2)
	Total (g)	Content (g)		Total (g)	Content (g)			
		Poly(E-MA)	SDS		Oil phase	Aqueous phase		
(A)	96	2.5	0.14	5	1	4	50	3.17
(B)	92	2.5	0.13	10	2	8	50	1.58
(C)	80	2.5	0.11	25	5	20	50	0.63
(D)	60	2.5	0.07	50	10	40	50	0.32

[a] Solvent was distilled water and its pH was adjusted with 3×10^3 mol/m^3 NaOH solution to 4.0.
[b] Emulsion was prepared using SPG membrane with 2.6-μm diameter pore. Aqueous phase (continuous phase II) was 0.2 wt.% SDS solution.
[c] Composition was 5.0 g of melamine, 12.5 g of 37% formalin solution, and 32.5 g of distilled water with its pH adjusted with 1×10^3 mol/m^3 NaOH solution to 9.0.

Table 3 Preparation conditions of crosslinked polymelamine microcapsules at different SDS concentrations

	Total amount (g)	Content	Amount (g)[a]		
			(1)	(2)	(3)
Continuous phase I	90	Distilled water (+ NaOH)	87.30	87.07	86.85
		Poly(E-MA)	2.5	2.5	2.5
		SDS	0.20	0.43	0.65
Creamed emulsion[b]	25	Isopar G	15.0	15.0	15.0
		Continuous phase II	10.0	10.0	10.0
Melamine–formalin prepolymer solution	50	Melamine	5.0	5.0	5.0
		37% formalin solution	12.5	12.5	12.5
		Distilled water (+ NaOH)	32.5	32.5	32.5

[a] Panels (1), (2), and (3) correspond to the conditions (1), (2), and (3) in Fig. 6.
[b] Emulsion was prepared using SPG membrane with 4.8-μm diameter pore. Continuous phase II was 1 wt.% SDS solution.

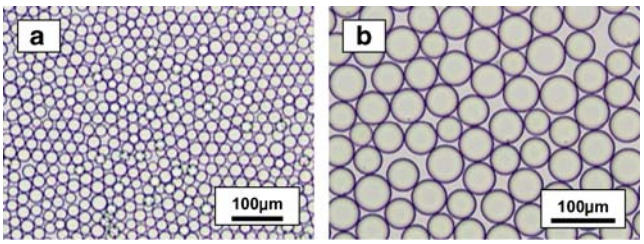

Fig. 2 Optical microscope photographs of emulsions prepared using SPG membrane. SPG membrane pore sizes were **a** 4.8 μm and **b** 13 μm

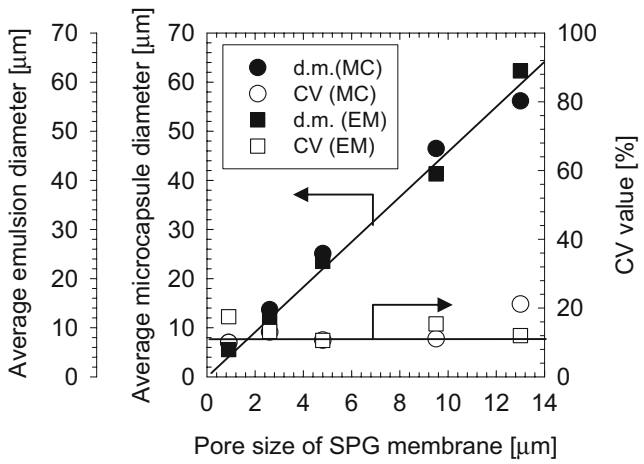

Fig. 3 Relationships between average emulsion droplet and microcapsule diameters and pore size of SPG membrane. *MC* Microcapsule, *EM* emulsion droplet, *d.m.* diameter

addition, to closely pave an electrode with microcapsules, the microcapsules must have a uniform diameter.

A few researchers have reported on controlling the diameter of a microcapsule prepared by phase separation method [5–8]. They reported that the microcapsule diameter

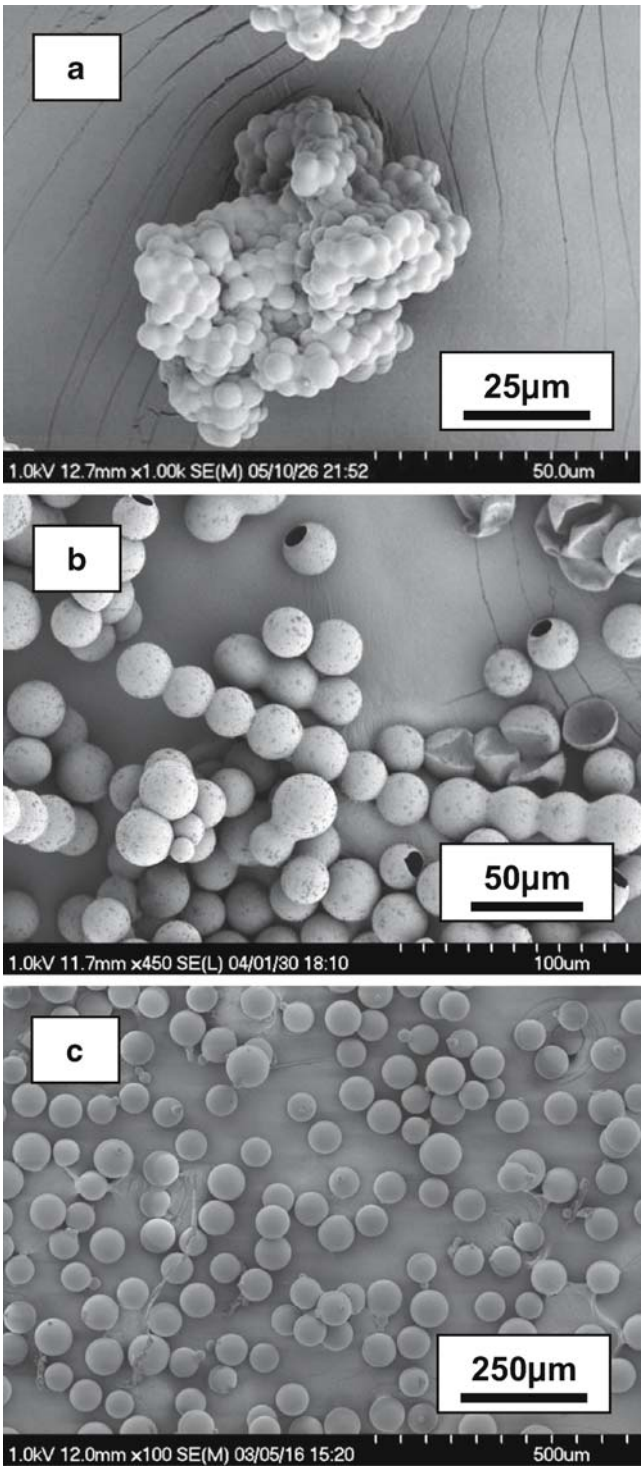

Fig. 4 SEM observations of microcapsules prepared in conditions shown in Table 1(A). Average diameters of emulsion droplets used as core were **a** 5.5 μm, **b** 23 μm, and **c** 62 μm

was controlled by adjusting stirring speed during the microencapsulation process and that the average diameter of the microcapsules decreased as stirring speed increased. However, the prepared microcapsules were not monodisperse ones.

The objective of our work was to implement a technique that controls the diameter of crosslinked polymelamine microcapsules prepared by phase separation method. We tried to fabricate microcapsules with a desired capsule diameter in a narrow size distribution. We used the Shirasu porous glass (SPG) membrane emulsification technique to control the diameter of a microcapsule.

Experimental

Reagents

Melamine and 37% formalin solution were used as the monomer and the condensing agent, respectively. Sodium dodecyl sulfate (SDS) was used as an emulsion stabilizer. Sodium hydroxide was used to adjust the pH of the continuous phase of the microencapsulation process (hereafter called continuous phase I). All of these analytical grade reagents were purchased from Wako Pure Chemical Industry, Ltd. The polymeric surfactant, poly(ethylene-*alt*-maleic anhydride) (poly(E-MA)), was purchased from Aldrich Co. Ltd. Isopar G, the core material of the microcapsule, was purchased from Exxon Mobil Co.

SPG membrane emulsification

The SPG membrane is highly porous and is made from deposits of volcanic ash and sand. SPG membranes have a huge number of pores of uniform micron size. One can select an SPG membrane of a desired pore size to prepare the O/W emulsions with uniform-sized oil droplets [9–15]. We used tubular SPG membranes with 0.9, 2.6, 4.8, 9.5, and 13-μm pores. An SPG membrane emulsification module (SPG mini-kit, SPG Technology Co. Ltd.) was used to prepare the O/W emulsions with uniform-sized oil droplets. First, the continuous phase of the emulsification process (hereafter called continuous phase II) was introduced inside the SPG membrane. The oil phase was inserted into the continuous phase II from the outside of the SPG membrane by compressed N_2 gas at a pressure that was kept constant during the emulsification process. The resulting emulsion was circulated inside the SPG membrane using a pump. In this study, an aqueous solution dissolving a desired amount of SDS was used as continuous phase II.

Preparation of crosslinked polymelamine microcapsule

Crosslinked polymelamine microcapsules were prepared with the following procedure. An aqueous solution containing poly(E-MA) was used as continuous phase I. Its pH was adjusted to 4.0 with 3×10^3 mol/m^3 NaOH aqueous solution. The emulsion prepared by using the SPG membrane was added to a desired amount in continuous

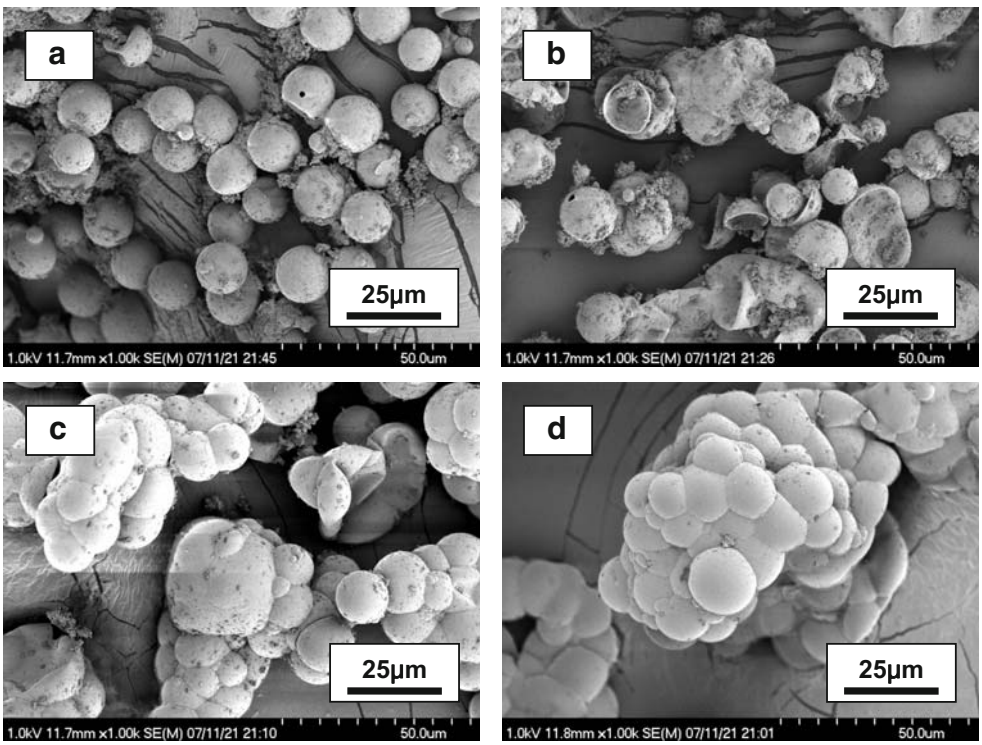

Fig. 5 SEM observations of microcapsules prepared with various amounts of emulsion droplet. The total amount of the oil phase: **a** 1.0 g, **b** 2.0 g, **c** 5.0 g, and **d** 10.0 g. The average diameter of the encapsulated emulsion droplet was 13 μm

phase I. The mixture was stirred for 600 s at 333 K under agitation at 5 s^{-1}. Then, microencapsulation was started by adding the melamine–formalin prepolymer solution, which was prepared separately. The prepolymer solution was prepared as follows: 5.0 g of melamine, 12.5 g of formalin solution, and 32.5 g of distilled water with an adjusted pH of 9 with 1×10^3 mol/m^3 NaOH aqueous solution were mixed and stirred at 333 K for 900 s. During the microencapsulation, the temperature was kept constant at 333 K. The microencapsulation was carried out for 10.8 ks under agitation at 6.67 s^{-1}. After 10.8 ks, the prepared microcapsules were collected by suction filtration and washed with distilled water. The morphology of the microcapsules was observed by a field emission scanning electron microscope (FE-SEM S-4700, Hitachi).

The preparation process of the crosslinked polymelamine microcapsule is shown in Fig. 1. The preparation conditions are summarized in Tables 1, 2, and 3.

Results and discussion

Figure 2 shows the O/W emulsion prepared using the SPG membrane emulsification technique. As shown in Fig. 2, the size of the prepared oil droplets was uniform. The average diameter and the coefficient of variation (CV) value of the emulsion droplets prepared using the SPG membranes with several pore sizes are summarized in Fig. 3. The average diameters of the emulsion droplets were in proportion to the pore diameters of the SPG membrane. They were about five times as large as the pore diameters. The CV values were almost 10%. Until now, some researchers reported the relationship between the pore diameter of SPG membrane and the diameter of the emulsion droplet. For example, Nakashima and Shimizu reported that the diameter of the kerosene droplet was 3.25 times as large as the pore diameter of the SPG membrane [13]. Omi et al. reported that the droplet diameter of the mixture of styrene–divinylbenzene–hexadecane and the mixture of benzene and hexadecane were linear to the pore size of the SPG membrane with slopes of 6.62 and 5.2, respectively [14]. Shiomori et al. reported that the diameter of the oil droplet of isooctane containing olive oil was proportional to the pore diameter of the SPG membrane with a slope of 3.4 [15]. These results show a validity of the result in this study. If the obtained emulsion droplet is not destroyed during the microencapsulation process and the capsule membrane is successfully formed, a microcapsule with the same diameter and size distribution as the used emulsion droplet can be prepared.

In our first investigation, we attempted to prepare microcapsules by adding the emulsion, which was in the emulsification state, to continuous phase I. The microencapsulation conditions are shown in Table 1(A). As a result, the microencapsulation was strongly influenced by the diameter of the emulsion droplet: the microcapsules aggregated with each other when the diameter of the

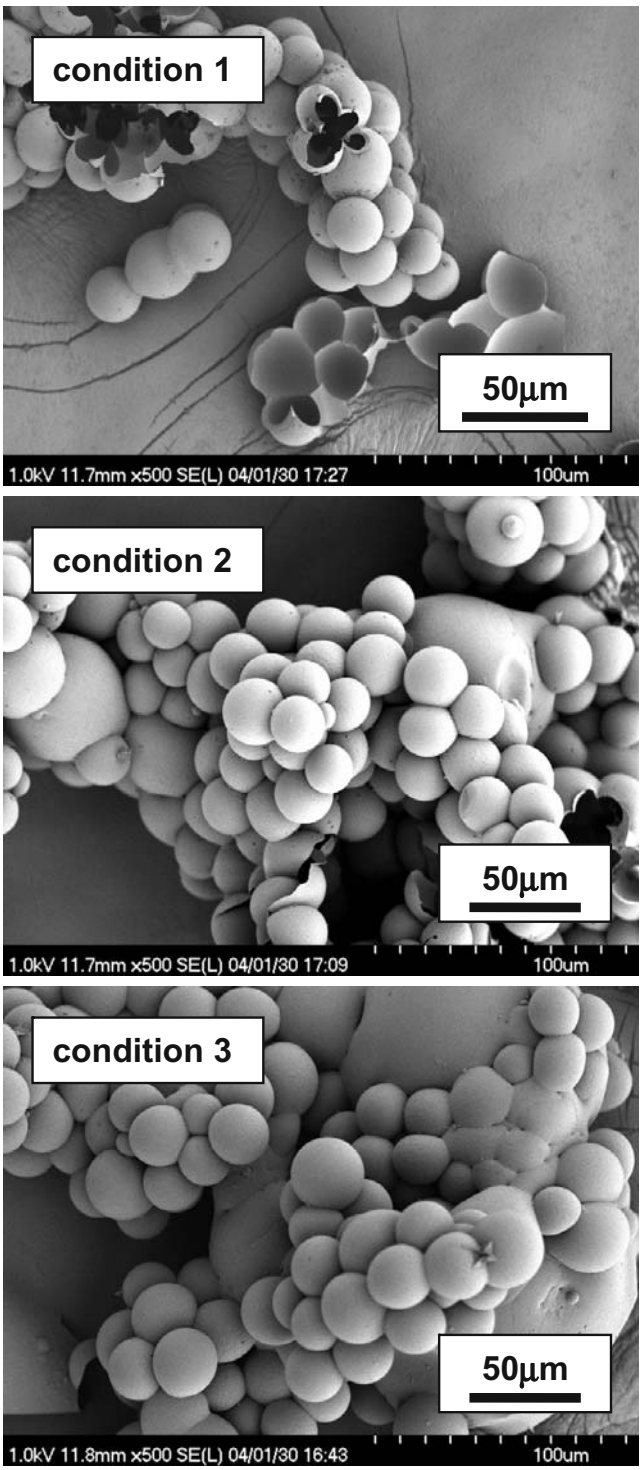

Fig. 6 SEM observations of microcapsules prepared in conditions shown in Table 2. Emulsion was prepared using an SPG membrane with a pore size of 4.8 μm. Average diameter of emulsion droplets was 23 μm. SDS concentration in continuous phase III was 0.2 wt.% (condition 1), 0.35 wt.% (condition 2), and 0.5 wt.% (condition 3)

emulsion droplet was less than 23 μm. Figure 4 shows examples of prepared microcapsules. The microcapsules prepared using the emulsion droplets with an average diameter of 5.5 μm, which were prepared using an SPG membrane with a 0.9-μm pore diameter, aggregated three-dimensionally. The microcapsules prepared using the emulsion droplets with an average diameter of 23 μm, which were prepared using an SPG membrane with a 4.8-μm pore diameter, were also aggregated, but they were straightly linked together. In contrast, the microcapsules prepared using the emulsion droplets with an average diameter of 62 μm were dispersed from each other. The structurally organized microcapsules shown in Fig. 4b are very interesting. However, the objective of this paper is the preparation of monodisperse microcapsules. Therefore, we did not pursue why such structurally organized microcapsules occurred. That is left to future work.

To improve the aggregation among individual microcapsules, we investigated the effect of the total surface area of the emulsion droplets on the preparation of monodisperse crosslinked polymelamine microcapsule. In the investigation, the SDS concentration in the mixture of continuous phase I, continuous phase II, and the melamine-formalin pre-polymer solution (the mixture is hereafter called continuous phase III) was 0.1 wt.%. The oil droplet with 13 μm of average diameter was used as the microcapsule core. The emulsion was prepared with 50 cm^3 of the oil phase and 200 cm^3 of a 0.2-wt.% SDS solution by the SPG membrane emulsification technique. The emulsion was continuously agitated with four flat-blade stirrers at 5 s^{-1} to maintain homogeneous dispersion of the emulsion droplets. A desired amount of the emulsion was poured into an aqueous solution containing a desired concentration of poly(E-MA) and SDS. The amount of the aqueous phase in the mixture was 100 cm^3. The experimental condition was summarized in Table 2 with the ratio of poly(E-MA) amount/the total surface area of the emulsion. The SEM images of the resulting microcapsules are shown in Fig. 5. The aggregation of microcapsules decreased with the decrease of the concentration of the emulsion droplet in the continuous phase III. This result indicated that the aggregation of microcapsules occurred due to the decrease of poly(E-MA) adsorbed on the surface of the oil droplet. However, as shown in Fig. 5, a large amount of by-produced polymelamine–formaldehyde particles, which were formed in the continuous phase III during microencapsulation, were adhered on the membrane of the microcapsules. The adhesion of the by-produced polymelamine–formaldehyde particle with a large diameter roughens the membrane of the microcapsule. Because SDS strongly affects the increase of the diameter of the by-produced polymelamine–formaldehyde particle as well as the aggregation of the microcapsules, the decrease of SDS concentration in the continuous phase III is essential to prepare monodisperse microcapsule with the smooth membrane.

Subsequently, we investigated the effects of SDS concentration on the aggregation of the microcapsules. The microencapsulation conditions are shown in Table 3. The SDS concentrations in the continuous phase III were adjusted to 0.2, 0.35, and 0.5 wt.% by dissolving different amounts of SDS in continuous phase I. As the capsule core, the emulsion droplet prepared using an SPG membrane with a 4.8-μm pore diameter was used. The average diameter of the emulsion droplets was 23 μm. The prepared microcapsules are shown in Fig. 6. As shown in Figs. 4b and 6, the aggregation of the microcapsules increased remarkably as the SDS concentrations increased. This indicates that the concentration of SDS strongly affects the aggregation of the microcapsules. From these results, we propose the following hypothesis as an effect of SDS on the aggregation of the microcapsules. Poly(E-MA), which is a polymeric surfactant, acts as a protective colloid. It stabilizes an emulsion by electrostatic repulsion and steric repulsion. The steric repulsion, which is caused by the adsorption layer of poly(E-MA) on the surface of an emulsion droplet, would stabilize an emulsion during formation of the microcapsule even if most of the negative charge of poly(E-MA) was cancelled by the melamine–formaldehyde prepolymer and oligomers. On the other hand, SDS stabilizes an emulsion by only the electrostatic repulsion. Because SDS is a surfactant with low molecular weight, a thick adsorption layer is not formed on the surface

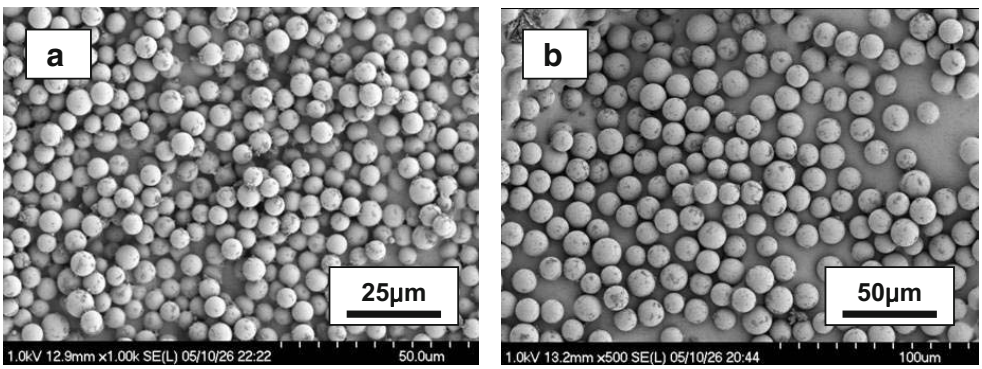

Fig. 7 SEM observations of microcapsules prepared in conditions shown in Table 1(B). Average diameters of encapsulated emulsion droplets were **a** 5.5 μm and **b** 13 μm. Creamed emulsion was used for microencapsulation

of an emulsion droplet. Therefore, it could not stabilize the emulsion any longer, if the negative charge of SDS was cancelled by the melamine–formaldehyde prepolymer and oligomers. When SDS and poly(E-MA) were co-existed in the continuous phase III, they competitively adsorbed on the surface of the emulsion droplet. An increase of the SDS concentration decreases the adsorption amount of poly(E-MA) on the emulsion droplet. As a result, the poly(E-MA) layer would become thin, and the aggregation of microcapsules occurred. That is to say, it was expected that the well-dispersed crosslinked polymelamine microcapsules with uniform particle size could be prepared by decreasing the SDS concentration in continuous phase III.

To reduce the SDS concentration, we poured the emulsion obtained by SPG membrane emulsification into a separation funnel and creamed it. The lower phase in which the emulsion was not present was dumped. Then, the upper layer was collected and dispersed in continuous phase I. This treatment diluted by about 20 times the SDS concentration in continuous phase III. Figure 7 shows the SEM photographs of crosslinked polymelamine microcapsules prepared using emulsions with 5.5 and 12 μm of the average diameter of oil droplets. The experimental condition is shown in Table 1(B). As expected, the prepared microcapsules were dispersed from each other. The microcapsule diameters and CV values are summarized in Fig. 3. The microcapsule diameter corresponded well to the diameter of the used O/W emulsion droplet. The CV values of the diameter of the prepared microcapsules were also about 10%.

We were able to control the diameter of crosslinked polymelamine microcapsules prepared by phase separation method in the range of 5–60 μm. Microcapsules with different diameters may be prepared by using SPG membranes with different pore diameters.

Conclusion

We investigated the control of the diameter of the crosslinked polymelamine microcapsules. Monodisperse oil droplets prepared by the SPG membrane emulsification technique were used as the capsule core. Monodisperse emulsion droplets with CV value of about 10% were successfully prepared. The average diameter of the emulsion droplets was in proportion to the pore diameter of the SPG membrane. The SDS concentration strongly affected the dispersion stability of the prepared microcapsules. Monodisperse microcapsules were successfully prepared by decreasing the SDS concentration. The diameter of the microcapsule corresponded well to the diameter of the O/W emulsion droplets used as the capsule core. In conclusion, we were able to control microcapsule diameter in the range of 5–60 μm.

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