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Hayato Marumoto

mrhyttttt@gmail.com

Kagoshima University

Takumi Sayo

Kagoshima University

Takayoshi Kawasaki

Tokuyama (Japan)

Yoshihiro Ohzuno

Kagoshima University

Takayuki Takei

Kagoshima University

Masahiro Yoshida

Kagoshima University

Research Article

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Posted Date: June 17th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-9495726/v1

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Additional Declarations: No competing interests reported.

Development of hollow microcapsules using melamine-formaldehyde prepolymer

Hayato Marumoto[1*], Takumi Sayo[1], Takayoshi Kawasaki[2], Yoshihiro Ohzuno[3], Takayuki Takei[3], Masahiro Yoshida[3]

[1] Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan

[2] Tsukuva Research Lab., Tokuyama Corporation, Ibaraki 300-4247, Japan

[3] Department of Chemical Engineering, Kagoshima University, Kagoshima 890-0065, Japan

*Corresponding author. E-mail: mrhyttttt@gmail.com

Contributing authors: t.sayo.tk@gmail.com, t.kawasaki.6s@tokuyamagr.com, ohzuno@cen.kagoshima-u.ac.jp, takei@cen.kagoshima-u.ac.jp, myoshida@cen.kagoshima-u.ac.jp

Abstract

The preparation of hollow microcapsules using melamine-formaldehyde (MF) prepolymer was investigated. Chlorobenzene was used as the core material, and large emulsion droplets were prepared by the Shirasu-porous-glass (SPG) membrane emulsification method. The effects of polymerization conditions were evaluated using MF prepolymer as the capsule wall material. Good capsule formation was possible even under mild conditions near neutral pH and at room temperature. Measurements of the bulk density and core retention rate of the capsules confirmed that a certain amount of core material could be removed. This technology is considered to be highly cost-effective and industrially useful.

Keywords: melamine formaldehyde, prepolymer, hollow microcapsule, SPG membrane emulsification, mild condition

Introduction

Chemical mechanical polishing (CMP) is an essential process for manufacturing semiconductors. In this process, a semiconductor wafer is pressed against a polishing pad and both are moved relative to each other while a polishing slurry is provided, simultaneously causing reactions with chemicals in the slurry and mechanical abrasion by the abrasive particles, resulting in an ultra-flat wafer [1]. CMP pads are equipped with pores and grooves that retain the polishing slurry and discharge polishing byproducts, which substantially influence the CMP polishing characteristics [2]. Prasad et al. investigated the effect of pore size in urethane pads on the polishing characteristics and reported that pads with large pores enhance polishing performance, whereas pads with small pores have issues with polishing uniformity [3]. One method for introducing pores into CMP pads is the solid-state microcellular foaming process, in which inert gas is injected at high pressure to create pores. Although this technique allows for adjustment of the pad properties through control of the pore size and distribution, and the degree of porosity, optimizing process parameters such as the gas saturation pressure, gas desorption time, and foaming temperature is difficult. However, the literature includes examples where pores are introduced by adding thermally expandable microcapsules [4]. This is a simple process that involves merely kneading uniformly expanded microcapsules; because the capsule diameter directly determines the pore size, control is straightforward. However, because the capsule walls are flexible, enabling them to follow the volumetric expansion of the core material, the capsules themselves exhibit low strength and are prone to deformation during incorporation into the resin, which leads to the formation of distorted pores.

We focused on melamine-formaldehyde (MF) as a new microcapsule material for introducing pores into CMP pads. MF is an inexpensive material with excellent mechanical strength and can encapsulate various substances such as fragrances [5], phase-change materials [6, 7], and self-healing agents [8]. For MF capsules to be used to impart pores to CMP polishing pads, their interiors should be hollow. Hollow capsules can be produced by removing the core material after capsule formation, and methods such as acid treatment or heating have been used for this purpose [9, 10]. In the present study, we used a volatile organic solvent as the core material and removed it by drying to create hollow capsules.

MF capsules are prepared by in situ polymerization, in which the core material is dispersed to form an emulsion and the capsule wall is formed at the droplet interface [11]. Because the droplet size of the core material correlates with the capsule diameter, controlling the emulsion droplet size is important for synthesizing capsules of uniform size. Homogenizers, commonly used for emulsion preparation, are excellent for creating fine emulsions but are not suitable for preparing large emulsions necessary for producing large capsules [12]. We focused on membrane emulsification, which is a superior method for

preparing uniform emulsions [13, 14]. In this technique, the emulsion droplet size is determined by the pore size in the membrane, enabling the synthesis of particles on the order of several tens of micrometers [15, 16]. Following emulsion preparation, methylolated melamine, obtained by reacting melamine and formaldehyde under alkaline conditions, is introduced as the capsule wall material. Acid is then added to adjust the emulsion pH to acidic, which promotes the condensation of methylolated melamine. The synthesis of MF capsules typically requires low-pH, high-temperature reactions [18, 19]. However, because emulsions with the large droplet sizes needed to form large capsules are generally unstable, the emulsion might break down during high-temperature reactions. Additionally, during a typical melamine capsule synthesis, the pH of the reaction solution must be gradually decreased. Lowering the pH to a sufficiently low level requires a long processing time and a large quantity of pH adjusters, which leads to higher costs in industrial production. In industrial production, milder conditions (i.e., a pH near neutral and a reaction temperature below 40 °C) are preferred whenever possible; however, the preparation of melamine capsules under such conditions has not been reported.

In this study, we developed a method for producing hollow microcapsules to be used for pore formation in CMP polishing pads. Initially, the Shirasu-porous-glass (SPG) membrane emulsification method was investigated as a technique for preparing droplets with sizes of several tens of micrometers and a narrow size distribution. For the subsequent melamine capsule preparation, we investigated the use of MF prepolymer as the wall material, aiming to develop a preparation method that involves mild conditions and allows for cost-effective production.

Experimental

Materials

Chlorobenzene (Kanto Chemical) was used as the core material. Sodium hydroxide (Kanto Chemical) and citric acid (Kanto Chemical) were used as pH modifiers. The surfactant used was Scripset 520 (Solenis), a styrene–maleic anhydride copolymer. For the capsule wall material, Nikaredin S-176 (Nippon Carbide Industries), an MF precondensate consisting mainly of monomethylol melamine, was used.

Membrane Emulsification

The preparation scheme for an oil-in-water (O/W) emulsion is shown in Figure 1. Scripset 520 (3.5 g) was dissolved in 2 wt% sodium hydroxide (41.25 g) and distilled water (13.75 g) at 80 °C for 2 h to obtain a

hydrolyzed product, which was then cooled to room temperature to prepare 54 mL of the continuous phase. Chlorobenzene was then added at the specified volume ratio, and the resultant mixture was stirred with a stirrer for 10 min to prepare a premix emulsion. Transmembrane emulsification was subsequently conducted using the external-pressure micro kit shown in Figure 2. For this process, an SPG membrane (outer diameter: 10 mm, membrane thickness: 0.7 mm, total length: 20 mm, pore size: 30 μm) purchased from SPG Technology was used.

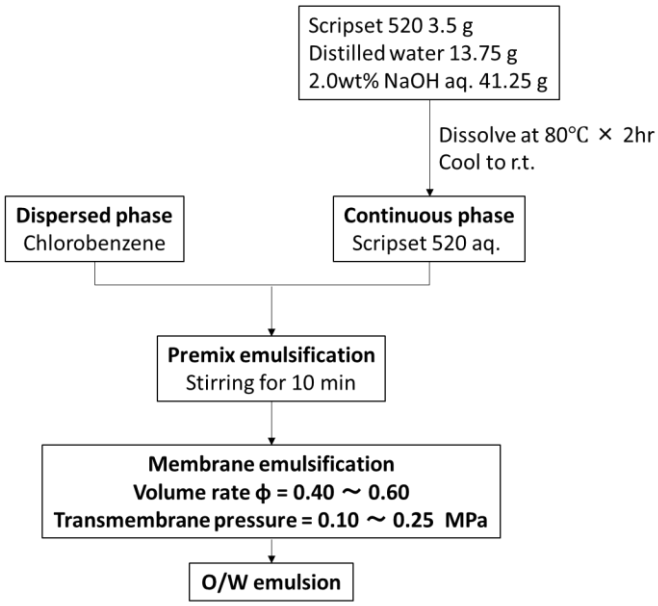


Fig. 1 Scheme of O/W emulsion preparation

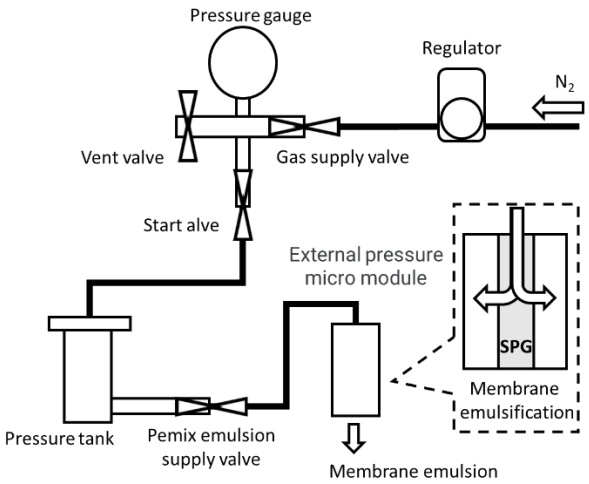


Fig. 2 Overview of external pressure micro kit

Capsule Preparation

The preparation scheme for MF capsules is shown in Fig. 3. A 50 wt% aqueous solution of Nikaredin S-

176 and a 10 wt% aqueous solution of citric acid were prepared as additives. The emulsion obtained by SPG membrane emulsification was transferred to a flask, and, while the emulsion was stirred at 150 rpm with a Teflon two-bladed stirring rod, the Nikaredin S-176 was added as the capsule wall material. The solution was then heated to the specified temperature, and the pH was adjusted to the desired value by dropwise addition of citric acid solution while stirring. After the mixture was stirred for 3 h to allow polymerization to proceed, the continuous phase was removed by centrifugation at 8,000 rpm for 15 min three times and the MF capsules were obtained by freeze-drying for 48 h.

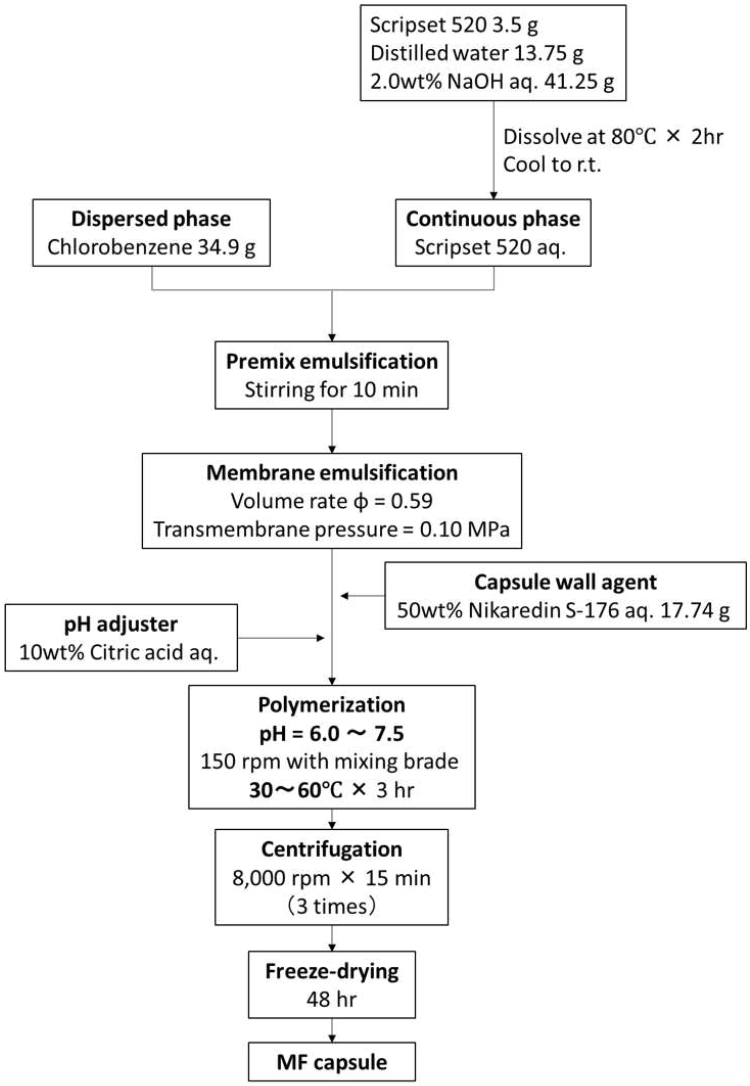


Fig. 3 Scheme of MF capsule preparation

Evaluation

The prepared emulsion was confirmed using an optical microscope (Nikon, ECLIPSE), and the capsule

morphology was observed using a scanning electron microscope (FEI, Quanta 400). The observation images were analyzed using the D-Measure software, and the average emulsion size and capsule size were calculated by measuring 200 samples. In addition, thermogravimetry–differential thermal analysis (TG–DTA; Shimadzu, DTG-60H) was performed by heating the sample to 500 °C at 10 °C/min under a nitrogen atmosphere to measure its weight loss. When weight loss was observed at temperatures below 400°C (i.e., the decomposition temperature of MF), the core retention rate was determined by dividing the weight difference before and after the weight loss by the weight before the onset of weight loss. Additionally, the bulk density was measured by placing the capsules in a graduated cylinder, tapping 3,000 times, and measuring the resultant volume and weight.

Results and Discussion

Membrane Emulsification

Table 1 shows the conditions for membrane emulsification (i.e., the volume ratio and transmembrane pressure). The results show that, as the transmembrane pressure during membrane emulsification increased, the droplet size decreased (Fig. 2). This behavior is speculatively attributed to higher pressures increasing the shear stress applied to the emulsion during membrane emulsification, resulting in smaller droplet sizes as a result of breakup as the emulsion passes through the pores. However, changing the volume ratio did not affect the droplet size in the emulsion after membrane emulsification (Fig. 3). The results indicate that 30 μm emulsions could be prepared using SPG membranes.

Table 1 Membrane emulsification conditions

Entry		A	B	C	D	E	F	G	H
Chlorobenzene	[g]	34.90	34.90	34.90	34.90	23.39	29.30	33.47	35.20
	[mL]	32.00	32.00	32.00	32.00	21.60	27.00	30.78	32.40
Volume rate φ [-]		0.59	0.59	0.59	0.59	0.40	0.50	0.57	0.60
Transmembrane pressure [MPa]		0.10	0.15	0.20	0.25	0.10	0.10	0.10	0.10
Average droplet diameter [μm]		28.38	27.44	26.08	23.32	24.57	24.48	24.49	27.60

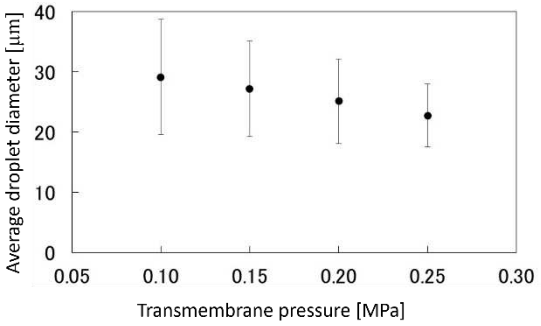


Fig. 4 Average droplet diameter at ϕ = 0.59

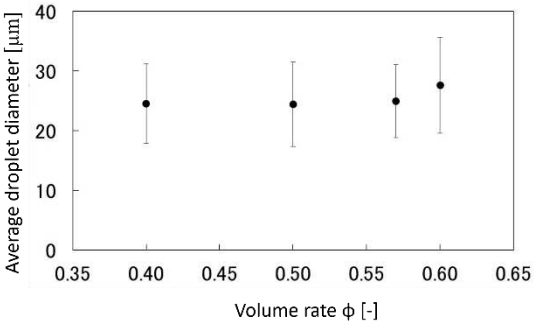


Fig. 5 Average droplet diameter at 0.10 MPa

Capsule Preparation

Table 2 shows the conditions for polymerization (temperature and pH) and the results (average capsule diameter and core retention rate).

Table 2 Polymerization conditions

Entry	I	J	K	L	M	N	O
10wt% Citric acid aq. [g]	10.25	7.29	4.96	2.43	4.85	4.47	4.54
Polymerization pH [-]	6.0	6.5	7.0	7.5	7.0	7.0	7.0
Polymerization temperature [°C]	40	40	40	40	30	50	60
Average capsule diameter [μm]	n.d.	20.27	19.87	24.23	16.10	25.53	24.65
residual rate of core (%)	n.d.	6.25	44.33	n.d.	23.81	38.17	57.94

Our investigation of the solution pH during polymerization confirmed good capsule formation at 6.5 ≤ pH ≤ 7.0 (Fig. 6, entry J, K), whereas aggregates were observed and no capsule formation was confirmed at pH = 6.0 (entry I). At pH = 7.5, irregular fine particles were produced and their size increased (Fig. 7). In the TG–DTA analysis of microcapsules prepared at 6.5 ≤ pH ≤ 7.0, a substantial weight loss was observed at approximately 300°C (Fig. 8). This weight loss is speculatively attributed to the release of the core material remaining inside the capsules. Although the boiling point of chlorobenzene is 130 °C, the MF capsules are covered with a robust wall, allowing them to withstand the expansion of the core material; the chlorobenzene was likely released upon capsule rupture during heating at 300°C. The bulk density and residual rate of core showed that non-hollow particles were obtained at pH = 6.5, whereas capsules prepared at 6.5 ≤ pH ≤ 7.0 exhibited a lower bulk density, indicating that a certain amount of core material had been removed (Fig. 9 and Fig. 10). These results indicate that the use of the MF prepolymer enables encapsulation to proceed even without adjusting the pH to the acidic region. At lower pH, the

polymerization rate increases, which promotes aggregation rather than capsule wall formation at the droplet interface. By contrast, at pH = 7.5, the lower reaction rate causes fusion of the formed capsules, resulting in irregular shapes.

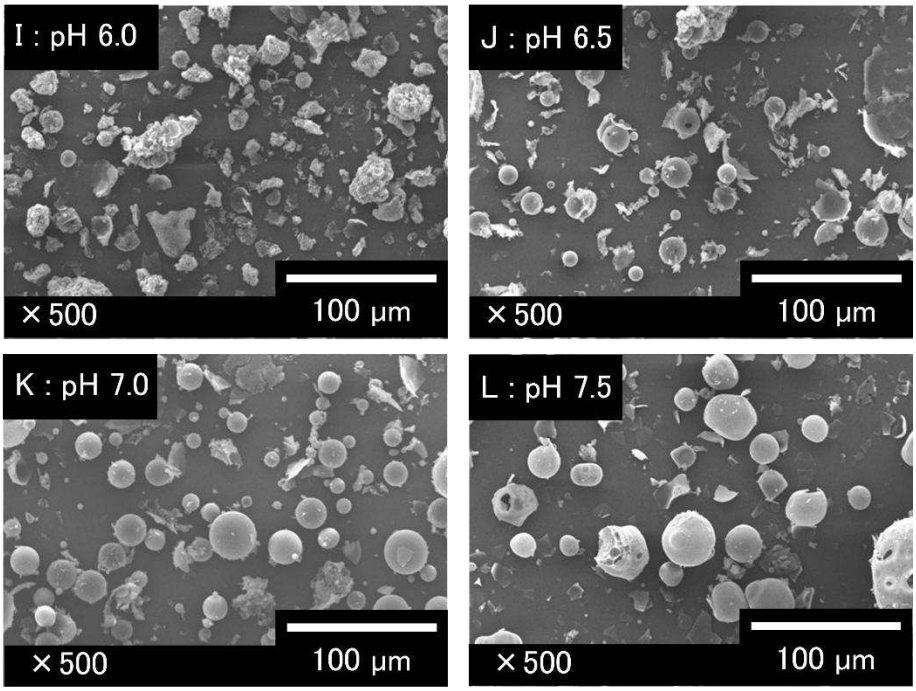


Fig. 6 SEM images of MF capsules (polymerization at 40°C).

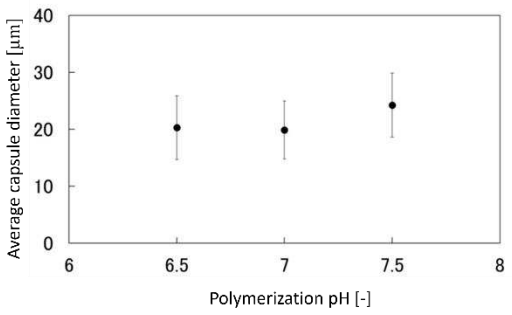


Fig. 7 Average particle diameter (polymerization at 40°C).

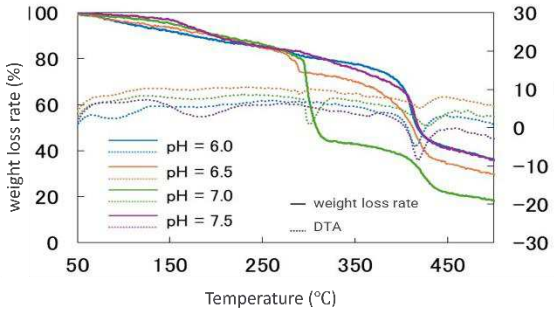


Fig. 8 TG-DTA analysis of MF capsule (polymerization at 40°C).

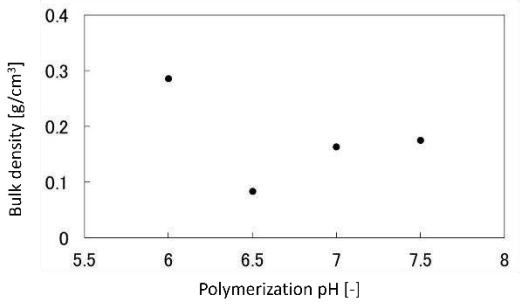


Fig. 9 Bulk density of MF capsule (polymerization at 40°C).

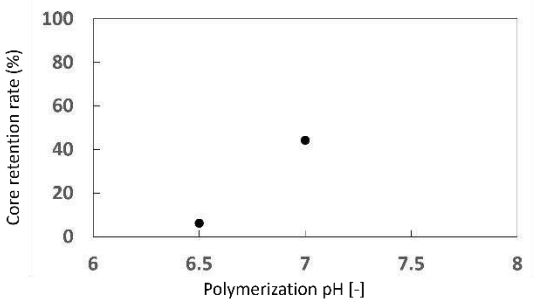


Fig. 10 Residual rate of core (polymerization at 40°C).

Our investigation of the polymerization temperature at pH = 7.0, where the capsule morphology was best, shows that good capsule formation was achieved at all of the investigated temperatures (Fig. 11). Unlike conventional capsule preparation using methylolated melamine, which requires high temperatures, the use of prepolymers enabled encapsulation even at 30°C, close to room temperature. The average capsule diameter increased with increasing temperature, likely because enhanced encapsulation allowed larger droplets to be encapsulated (Fig. 12). The TG–DSC results for all of these good capsules show a weight decrease associated with chlorobenzene release at approximately 300°C (Fig. 13). Both the core retention rate and the bulk density tended to increase with increasing temperature (Fig. 14 and Fig. 15). These results suggest that higher temperatures result in denser and stronger capsule walls, making escape of the core material more difficult.

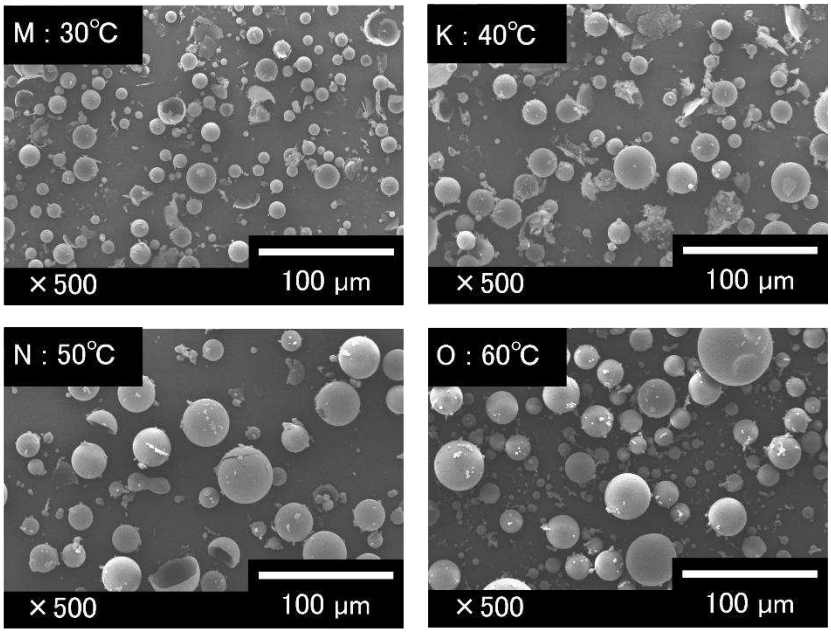


Fig. 11 SEM images of MF capsule (polymerization at pH = 7.0)

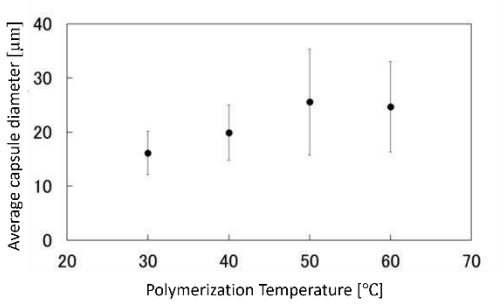


Fig. 12 Average capsule diameter (polymrizaton at pH = 7.0).

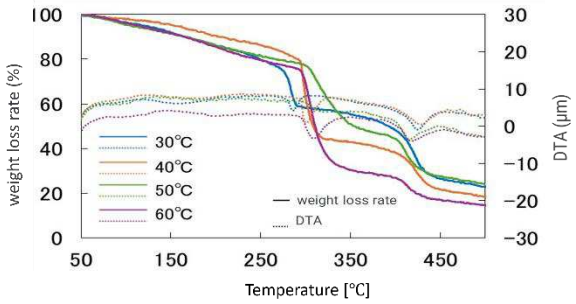


Fig. 13 TG-DTA analysis of MF capsule (polymerization at pH = 7.0).

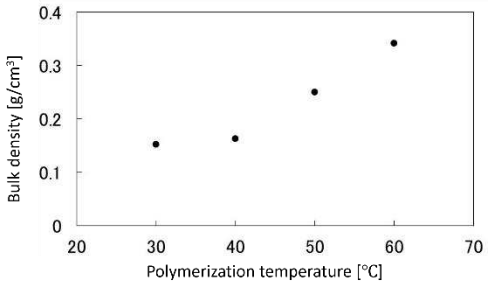


Fig. 14 Bulk density of MF capsule (polymerization at pH = 7.0).

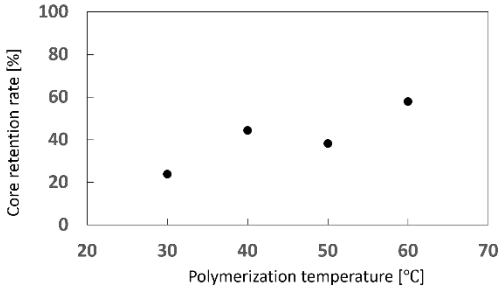


Fig. 15 Residual rate of core (polymerization at pH = 7.0).

Conclusion

Using MF prepolymer, we prepared 20–30 μm hollow microcapsules under mild conditions. Chlorobenzene was used as the core material, and an emulsion with large droplet sizes was prepared using the SPG membrane emulsification method. The effects of pH and reaction temperature on capsule preparation using the prepolymer were investigated, and good capsules were obtained even under neutral conditions (pH = 7.0) and near room temperature (30–40 °C). In addition, measurements of the core retention rate and the bulk density of the capsules showed that a certain amount of the core material could be removed. This technology is not only applicable to the fabrication of hollow microcapsules for introducing pores into CMP pads but can potentially be used to prepare microcapsules that encapsulate various valuable substances. Moreover, because the method can be performed under mild conditions, it would be a cost-effective approach for industrial production.

Author contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Hayato Marumoto and Takumi Sayo. The first draft of the manuscript was written by Hayato Marumoto, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding No funding received.

Data availability All data are included in the manuscript.

Declarations

Conflicts of interests The authors declare no competing interests.

Ethical approval Not applicable.

Consent of publish Obtained.

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