

Preparation of bio-based thermal energy storage microcapsules by spray drying and its property evaluation

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Abstract

This study focuses on developing bio-based thermal energy storage microcapsules (MCs) by spray drying. New MCs were successfully prepared using ethyl laurate as the core material (phase change material; PCM), and gelatin as the outer shell. Various physical cross-linkers for the outer shell and spray-drying temperatures were tested to improve the stability of MCs and retention of the PCM. It was found that physical cross-linking by tannic acid under acidic to neutral pH conditions was the most effective in strengthening the outer shell and that a spray-drying temperature of 120 °C was optimal for obtaining well-dried MCs with minimal PCM loss. Higher core/shell ratios resulted in higher encapsulation efficiency, indicating that more PCM could be effectively encapsulated. These MCs showed the improved PCM content and thermal stability, reaching 70.1% PCM content at a core/shell ratio of 5. Heat storage tests for MCs showed significant suppression of temperature change between -5 °C and 3 °C.

Keywords: Bio-based thermal energy storage microcapsule; Gelatin; PCM; Spray drying; Tannic acid

Introduction

As the world's population grows and the economy and technology develop, the energy demand has been increasing. Most of the energy in the world is derived from fossil fuels, but their amount is limited. In addition, CO₂ emission has been a burden on the environment [1]. Therefore, renewable energy sources, such as solar energy, have been currently attracting attention. However, as solar energy can only be obtained during the daytime, renewable energy often cannot be supplied continuously and stably [2]. To solve these problems, thermal energy storage technology has attracted attention [3, 4].

Latent-heat-based thermal energy storage systems are those utilizing phase change materials (PCMs) as the key materials [5]. However, using PCM alone has some drawbacks, such as PCM leaking during melting [6]. To overcome these disadvantages, thermal energy storage microcapsules (MCs) are frequently used [1, 7]. The microencapsulation of PCM facilitates a wide range of applications and is expected for use in many fields, such as building materials and clothing [8]. MCs can be produced by three main methods, ie., physical, chemical, and physicochemical methods [9, 10]: Physical methods include spray drying [11] and solvent separation [12], chemical methods include interfacial polymerization [13] and *in situ* polymerization [14], and physicochemical methods include coacervation [15].

Currently, paraffin is often used as the PCM, and polymers such as melamine and urea resins are used for the outer shell as the major materials for MCs. Although paraffin has higher heat storage density, it is not biodegradable in the natural environment due to its stability. In addition, it is produced from petroleum resources. Similarly, synthetic polymers as the shell material are not biodegradable and can cause microplastic problems when leaked into nature. Therefore, bio-based MCs have been investigated using materials derived from animal and plant resources [16-18]. However, reports on

the preparation of thermal storage MCs using only biodegradable materials are still limited [19-22]. Although complex coacervation has been often used for the preparation of MCs using gelatin-gum arabic, this process requires precise pH adjustment to form the complex coacervate and is not suitable for mass production. Moreover, one of its raw materials, gum arabic, is facing supply concerns, including price fluctuations [23]. On the other hand, it is also known that capsules can be prepared only from gelatin, which can be stably supplied, and there is potential for application to gelatin-based thermal storage MCs [24, 25].

If thermal energy storage MCs could be prepared using only edible materials such as gelatin, they could be used for food-related applications. Currently, however, there is little information on the preparation of edible thermal energy storage MCs. In addition, there are few reports on the preparation of edible MCs by spray drying, which is considered suitable for industrial scale-up. Hence, it is required to obtain detailed information on spray drying when only edible materials are used. In this study, gelatin and ethyl laurate, both of which are biodegradable and edible, were used to prepare the MCs. In encapsulation, physical cross-linking treatment is often performed to strengthen the outer shell. Therefore, physical cross-linking conditions were optimized. The ratio of the PCM to shell (core/shell ratio) was also evaluated to produce the edible MCs with higher heat storage capacity.

Materials and Methods

Materials

The major reagents (ethyl laurate, gelatin, tannic acid, glutaraldehyde, sodium tripolyphosphate, gallic acid, citric acid, sodium hydroxide, and hydrochloric acid) used for the preparation of MCs were purchased from FUJIFILM Wako Pure Chemicals

(Osaka, Japan). Transglutaminase (ACTIVA-TI) was purchased from Ajinomoto (Tokyo, Japan).

Effect of type of physical cross-linking agent and spray-drying temperature on MC formation

MCs containing ethyl laurate as the PCM were prepared by spray-drying an emulsion as follows: Ethyl laurate (equal mass to gelatin) was mixed with a 5 mass% gelatin solution in distilled water (about 200 mL, 40 °C). Emulsions were prepared by stirring the mixture at 16,000 rpm for 3 min using a homogenizer (T25 digital with an S25N-18G shaft, IKA Japan, Osaka). Then, a predetermined amount (1–10 mass% of gelatin) of the physical cross-linking agent was added to the resulting emulsion and stirred for a fixed time (1–24 h), where tannic acid, glutaraldehyde, transglutaminase tripolyphosphate, citric acid, or their mixtures were used as the physical cross-linking agents. As necessary, pH of the resulting mixture was adjusted with 0.2 mol/L hydrochloric acid or 0.2 mol/L sodium hydroxide solution. Note that, when pH is <7, tannic acid and gelatin form a strong structure via hydrogen bonding [26]. Because the interaction via hydrogen bonding is not strictly "cross-linking", it is treated as "physical cross-linking" in this study.

The suspension was dried by a spray dryer (LB-8, Okawara Kakoki, Kanagawa, Japan). The inlet temperature of the dryer was 80–180 °C, and the flow rate of the solution was 20 mL/min, with an atomizer speed of 30,000 rpm. The final MCs were obtained as a powder. Note that the LB-8 is a large spray dryer for lab-scale use (3 kg/h water evaporation), and at least 10 L of solution would be required to properly calculate the powder yield. However, in this study, the amount of solution was about 200 mL, which was considerably small for calculating the yield. Therefore, the powder yield was

not calculated in this study.

Effects of core/shell ratio and physical cross-linking conditions by tannic acid on the properties of MCs

MCs with the outer shell physically cross-linked by tannic acid were prepared under various conditions. The amount of added ethyl laurate (PCM) was 1–5 times the mass of gelatin, and the amount of added tannic acid was 5–20 mass% of the gelatin mass. The pH was adjusted to 4.0–9.0 by 0.2 mol/L hydrochloric acid or 0.2 mol/L sodium hydroxide solution during the physical cross-linking treatment. The resulting suspension was spray-dried to produce MCs.

Evaluation of the thermal storage properties of MCs by differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was performed to measure the thermal storage behavior of the MCs using a DSC-60plus differential scanning calorimeter (Shimadzu, Kyoto, Japan) with the following conditions: Holding at 35 °C; temperature drop to -35 °C at -10 °C min⁻¹; holding at -35 °C for 1 min; temperature increase from -35 °C to 35 °C at 10 °C min⁻¹. The measurements were performed in triplicate. Area of the melting peak of PCM was measured, and the enthalpy of melting (ΔH_m ; J g-MC⁻¹) was then calculated by dividing the area by the sample mass.

Evaluation of the thermal stability of MCs by thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to evaluate thermal stability of the MCs. An STA6000 thermogravimeter (Perkin Elmer, Waltham, MA, USA) was used for the analysis. MC sample was weighed into crucibles and heated at a constant rate of

10 °C min⁻¹ from 50 °C to 600 °C while nitrogen gas (flow rate 18 mL min⁻¹) was supplied to the device.

Measurement for the particle size distribution of MCs

Particle size of the MCs was measured using a laser diffraction particle size analyzer (SALD-2000, Shimadzu). The sample was prepared by dispersing a small amount of MCs in warm water.

Measurement of the surface morphology

The surface morphology of the MCs was analyzed using an analytical scanning electron microscope (SEM, SU-6600, Hitachi High-Tech, Tokyo, Japan) under a low vacuum.

Evaluation of thermal storage capacity against temperature change

Cylindrical epoxy resin rods (9 mm ϕ × 35 mm, about 2.4 g) enclosing a K-type thermocouple were prepared to evaluate thermal storage capacity. The resin rod was placed in a 50-mL plastic centrifuge tube (27 mm I.D. × 120 mm), and the tube was filled with the powdery MCs to cover the rod. The tube was then placed in an environmental test chamber (SH-242, ESPEC, Osaka, Japan), and the ambient temperature of the tube was changed. The temperature program was as follows: holding at an initial temperature of 10 °C, holding at -25 °C for 1 h, holding at 10 °C for 1 h, and holding at -25 °C for 1 h. Temperature change of the resin rod was recorded by a data logger (GL240, Graphtec, Kanagawa, Japan).

Results and discussion

Effects of various physical cross-linking agents on the properties of MCs

Figure 1 shows typical DSC curves of MCs prepared with and without physical cross-linking agents. Melting and crystallization (solidification) peaks of PCM (ethyl laurate) were observed for each sample. Although an endothermic peak associated with the melting of PCM was observed at about $-2\text{ }^{\circ}\text{C}$ ($T_{m,peak}$) in all cases, the solidification behavior differed greatly depending on the sample. In all thermograms, a large difference in crystallization and melting peak temperatures was observed due to great supercooling. This difference would be ascribed to the fast temperature decrease rate of $-10^{\circ}\text{C min}^{-1}$, which is considered to be larger than the intrinsic difference. In the case of bulk PCM (PCM only), an exothermic peak was observed at about $-10\text{ }^{\circ}\text{C}$ ($T_{c,peak}$) when decreasing the temperature. On the other hand, encapsulation lowered the peak temperature, $T_{c,peak}$, below $-10\text{ }^{\circ}\text{C}$, and in some cases, multiple solidification peaks appeared. This reason would be that the isolation of PCM by microencapsulation suppressed nucleation during solidification [27]. The mechanisms are as follows: In the case of bulk PCM, if nucleation occurs at even one location, the entire PCM begins to solidify. However, in the case of MC, the PCM is isolated by the outer shell of the capsule. If nucleation does not occur within the individual capsule, the PCM inside the capsule will not solidify. Therefore, the solidification temperature would decrease by microencapsulation. Furthermore, focusing on the number of peaks, a small peak of crystallization was observed around $-22\text{ }^{\circ}\text{C}$ in the case, for example, without physical cross-linking, in addition to that around $-12\text{ }^{\circ}\text{C}$. Since PCM is a pure substance (ethyl laurate), the observation of these two peaks for the MC form suggests the existence of at least two types of MCs; one that is prone to nucleation and the other that is less prone to it.

The phase change enthalpies of solidification (crystallization) and melting of bulk PCM were 149.4 J g^{-1} and 153.3 J g^{-1} , respectively. The measurement error due to

supercooling was small and both enthalpies were almost the same. Therefore, in the following study, we mainly evaluated the thermal storage capacity by the enthalpy of melting, ΔH_m . Table 1 shows the peak temperature for crystallization ($T_{c,peak}$), peak temperature for melting ($T_{m,peak}$), and thermal storage capacity (enthalpy of melting and PCM content in MC) for the MCs obtained using various physical cross-linkers. PCM content is defined as follows:

$$\text{PCM content (mass\%)} = \frac{\Delta H_{m,MC}}{\Delta H_{m,PCM}} \times 100 \quad (1)$$

where $\Delta H_{m,MC}$ and $\Delta H_{m,PCM}$ are the enthalpies of melting for PCM in MC and bulk PCM, respectively, obtained by the DSC measurement. PCM content is the mass fraction of PCM in the encapsulated MC.

When capsules were prepared without physical cross-linking treatment at PCM:shell (gelatin) = 1:1 (mass/mass), the PCM content was small (about 13%). On the other hand, when tannic acid, transglutaminase, tripolyphosphoric acid, or their mixture was used as a cross-linking agent, the PCM content was greatly improved over the uncross-linked case. In particular, when tannic acid was used alone, the PCM content was about 30%. This result would indicate the moderate physical cross-linking of the outer shell is better for reinforcement of the outer shell. When cross-linking was performed by glutaraldehyde, transglutaminase, citric acid, or gallic acid alone, however, the PCM content was much lower than the case without physical cross-linking. This could be due to various factors: For example, treatment with glutaraldehyde could cause much stronger covalent cross-linking and aggregation of gelatin. If aggregation becomes extreme, there is insufficient gelatin to maintain the structure of outer shell, probably resulting in tearing of the outer shell. It was reported that citric acid and gallic acid form

hydrogen bonds with proteins [28, 29]. However, the number of hydroxyl groups in these molecules is smaller than in the case of tannic acid. Therefore, insufficient physical cross-linking between gelatin molecules was formed and consequently softened the outer shell. These effects would decrease the PCM content.

Effect of spray-drying temperature on the heat storage capacity of MCs

When the MCs were prepared at the mass ratio of ethyl laurate/gelatin/tannic acid=1/1/0.1, the PCM content should theoretically be 48%. However, as shown in Table 1, the actual PCM content was about 30%. This lower PCM content probably resulted from the evaporation of ethyl laurate during spray drying. However, there was no clear information on how much PCM evaporates during spray drying. Therefore, we evaluated the effect of spray-drying temperature on the PCM content.

The effect was examined in the inlet temperature range of 80–180 °C (Fig. 2). At the drying temperatures above 100 °C, the PCM content gradually decreased with increasing temperature. The fact that the PCM content decreased at higher temperatures is a clear indication of the PCM evaporation during spray drying. The vapor pressure of ethyl laurate is 1.33 kPa at 146 °C [30], making it a rather evaporative ester. Hence, the loss due to evaporation would be more pronounced during the drying. On the other hand, the PCM content was somewhat lower for drying at 80 °C. This suggests that the drying was insufficient, softening the outer shell. Even though the highest PCM content was achieved by drying at 100 °C, part of the resulting MCs was still incompletely dried.

Here, the formation of the outer shell and the evaporation of PCM are both faster at higher temperatures, and there is a tradeoff with respect to temperature. In other words, the higher the temperature, the stronger the outer shell becomes, but the PCM also evaporates more easily during drying. This study suggests that the optimal spray-drying

temperature is 120 °C for reliable drying. Based on these findings, subsequent studies were conducted using MCs dried at 120 °C.

Effect of pH on the properties of MCs

Figure 3 shows the effect of pH on the properties of MCs. For the MC without physical cross-linking, the PCM content was only 6.8%. The enthalpy of melting, $\Delta H_{m,MC}$, was about 10 J g⁻¹MC, which was much lower than that of bulk PCM ($\Delta H_{m,PCM} = 153$ J g⁻¹PCM). This may be because MC exists as an O/W emulsion with a fragile oil-water interface (outer shell). The outer shell would be destroyed during spray drying, resulting in the evaporation of most PCM.

When physical cross-linking with tannic acid was applied at the pH range of 4–7, the PCM content was over 30%, indicating that the physical cross-linking process positively contributed to PCM retention. This also indicates that about 2/3 (70% ± 5%) of the added PCM was encapsulated. The encapsulation efficiency reflecting this degree of encapsulation is defined hereafter to further discuss encapsulation behaviors by the following equation:

$$\text{Encapsulation efficiency (\%)} = \frac{\text{Amount of encapsulated PCM (g)}}{\text{Amount of added PCM (g)}} \times 100$$

When MCs were prepared at pH 8 or pH 9, on the other hand, the PCM content steeply dropped (PCM content was 25% and 23% at pH 8.0 and 9.0, respectively). Furthermore, the encapsulation efficiency was also lower (around 50%). In general, it is well known that the pyrogallol group of tannic acid is oxidized at pH 8 or higher, forming a Schiff base or occurring Michael addition with proteins to form covalently cross-linked structures [26]. In such covalent cross-linking, gelatin molecules more tightly bind each other and form gelatin aggregate, resulting in the collapse of MCs.

The particle size distribution of physically cross-linked MCs at various pH is shown in Fig. 4, and SEM images of MCs are shown in Fig. 5. For the MCs without physical cross-linking, a single broad peak was observed around 1.6 μm in diameter. Whereas physical cross-linking by tannic acid increased the particle size and changed the properties of the outer shell. This change would suppress PCM evaporation during spray drying and improve the PCM content, resulting in larger particle size. In addition, the particle size changed depending on pH. The bimodal distribution was observed from pH 4 to 8, whereas at pH 9, there was only one peak. In the pH range showing a bimodal distribution, there were two peaks, 2.4 to 2.9 μm (peak 1) and 8.3 to 12 μm (peak 2). Peak 2 became smaller and peak 1 became larger as pH increased. At pH 9, a single peak was observed near 2.9 μm . In the SEM images in Fig. 5, it was observed that the particle size tended to be larger than that observed in laser diffraction (Fig. 4), especially at higher pH. This suggests that the particles could aggregate during spray drying.

The reason for these trends would be that the physical cross-linking mechanism of tannic acid depends on pH [26]. Physical cross-linking by hydrogen bonding under acidic to neutral conditions optimally preserved the outer shell structure of the MCs and suppressed the evaporation of PCM during spray drying. On the other hand, under basic conditions, covalent cross-linking occurred. As above mentioned, the strong covalent bonding affected the formation of gelatin aggregate, resulting in leakage of PCM during spray drying. In addition, the specific surface area of the interface (outer shell) at higher pH was larger due to the small particle size, resulting in thinning of the outer shell. This would also weaken the capsule and lower the encapsulation efficiency.

Based on the above results, it is best to perform physical cross-linking of the gelatin outer shell with tannic acid under acidic to neutral conditions (pH 4–7). Furthermore, operation without pH adjustment (pH 5.6) is the simplest and most realistic. Therefore,

the following studies were conducted without pH adjustment.

Optimization for core/shell ratio of MCs

To fabricate microcapsules with higher heat storage capacity, it is necessary to increase the PCM content. Therefore, MCs were prepared by changing the mass ratio of PCM to gelatin (core/shell ratio). Figures 6 and 7 respectively show the properties of MCs prepared with various core/shell ratios (PCM/shell=1–5, mass/mass) and SEM images of the MCs. The peak melting temperature, $T_{m,peak}$, of PCM was around -1 °C, independent of the core/shell ratio and almost the same as that of bulk PCM. The peak solidification temperature, $T_{c,peak}$, increased and became -10 °C, almost nearly to that of bulk PCM, when the core/shell ratio was more than 2. This indicates that the properties of PCM in MCs would approach that of bulk PCM with an increasing core-shell ratio.

The PCM content and encapsulation efficiency increased with increasing core/shell ratio, indicating that encapsulation is possible even at a higher core/shell ratio. The reason for the higher values of encapsulation efficiency may be as follows: when the ratio is high, the emulsion droplets in suspension before spray drying are larger, and the specific surface area relative to the volume of the emulsion is small. As a result, the PCM slowly evaporates and PCM content increases. Indeed, when the core/shell ratio=5, the PCM content exceeded 70% and the melting enthalpy, ΔH_m , increased up to 107.4 J g⁻¹ MC⁻¹. The SEM images also suggest that as the core/shell ratio increased, the MC surface convexity decreased, and the size of MC particles also increased. The encapsulation efficiency reached 86% at the core/shell ratio=5, suggesting that most of the PCM was incorporated into the capsule. Thus, by increasing the core/shell ratio, MCs with higher heat storage capacity can be efficiently fabricated. In addition, the MC structure was retained even at large core/shell ratios, proposing that the flexibility of the outer shell

could play an important role.

Thermal stability of MCs

Figure 8 shows curves for thermogravimetric analysis (TGA; gas = nitrogen) of MCs at various core/shell ratios. The curve of PCM (bulk ethyl laurate; black curve) suggests that ethyl laurate evaporates completely below 200 °C. On the other hand, thermal decomposition of gelatin proceeded gradually below 270 °C and decomposed abruptly between 270–400 °C. Here, below 300 °C, it is presumed that the water bound to the gelatin molecule evaporated mainly.

Next, we discuss each MC. In the case of MC with the core/shell ratio=1, the PCM content was about 36 mass% (Fig. 6). If the PCM completely evaporated from MC without any interference of the outer shell, the relative mass in TGA should finally reach 64% (i.e., $100\% - 36\% = 64\%$). However, the curve shows that the mass loss curve flexed at just under 90% (about 150 °C; blue arrow 1 in Fig. 8), and then decreased gradually. This means that some PCM was still encapsulated within the MC and gradually evaporated. This evaporation would reflect the strong interference by the outer shell. On the other hand, when the core/shell ratio was 2 to 5, part of the PCM evaporated as well as the bulk PCM (area within the dotted oval indicated by red arrow 2).

Once a certain amount of PCM evaporated, the mass loss slowed down, resulting in the appearance of a bending point (orange arrow 3) as did in blue arrow 1. This may be because the evaporation of PCM made the outer shell slightly denser, resulting in slower evaporation of PCM (orange oval indicated by arrow 4). This gradual mass loss continued in the temperature range below 240 °C. However, the effect of PCM retention by the outer shell was not comparable to the case with the core/shell ratio=1. This may be due to the relatively insufficient denseness of the outer shell. Although the denseness of the

outer shell was still retained to some extent when the core/shell ratio was 2 or 3, no effect of PCM retention was observed when the core/shell ratio was 4 or higher, and it is considered that the denseness of the outer shell was almost completely lost.

A drastic mass loss occurred again at 240–270 °C (orange oval indicated by arrow 5). This phenomenon was observed at all core/shell ratios with a similar trend and the same temperature range, indicating a common phenomenon due to the thermal decomposition of gelatin, the outer shell material. Above 270 °C, the mass loss became slower again for all cases, indicating that the hard-to-degrade components of the outer shell (e.g., highly cross-linked gelatin) may have slowly decomposed (orange oval indicated by arrow 6).

Heat storage capacity of MCs

Figure 9 shows the heat storage capacity of MCs to suppress the change in ambient temperature at various core/shell ratios. Although the temperature change was suppressed for all core/shell ratios, there were differences between the suppression behaviors. The larger the core/shell ratio, the more remarkably the temperature change was suppressed during cooling (0–60 min). In the case of core/shell ratio = 5, the temperature change became smaller from around 18 min, and the suppression effect continued until around 25 min. Although the suppression effect was also observed in the case of core/shell ratio = 3 or 4, the temperature change was slightly larger. In the case of core/shell ratio = 2 or 1, sufficient suppression effect was not observed and the temperature slowly changed. This trend was also observed during the temperature increase (60–120 min). These results indicate that the temperature change can be suppressed using MCs with a core/shell ratio = 3 or higher.

As shown above, the change in temperature was suppressed. This effect was especially pronounced between -5 °C and 3 °C. This temperature range was the same as

the melting temperature range of PCM. Although the solidification peak temperature in DSC measurements was much lower than the melting peak temperature (Fig. 1), the effective temperature range in this test was almost the same during solidification and melting. This would be due to the slower temperature change during this test than the DSC measurement, allowing sufficient time for nucleation of PCM and heat transfer.

Conclusion

A new bio-based edible microcapsule was developed using ethyl laurate as the PCM and gelatin as the outer shell. The PCM content could be increased using tannic acid as a physical cross-linking agent. Physical cross-linking by hydrogen bond under acidic to neutral conditions was favorable for strengthening the outer shell, making it suitable for MC preparation. When the core/shell ratio was increased to 5, MCs with a PCM content of 70.1% could be achieved. These microcapsules are expected as biodegradable thermal storage MCs for uses around -5 to 3 °C. As shown, we have succeeded in producing a thermal energy storage MC consisting only of edible materials. Since there is no problem even if the MC is in direct contact with food, temperature of the food can be controlled more precisely. In addition, this MC can be used as a food ingredient itself, contributing to the creation of novel food products.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

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References

1. Dresselhaus MS, Thomas IL. Alternative energy technologies. *Nature*. 2001;414(6861):332-7. doi:10.1038/35104599.
2. Waterson M. The characteristics of electricity storage, renewables and markets. *Energy Policy*. 2017;104:466-73. doi:10.1016/j.enpol.2017.01.025.
3. Anisur MR, Mahfuz MH, Kibria MA, Saidur R, Metselaar IHSC, Mahlia TMI. Curbing global warming with phase change materials for energy storage. *Renew Sustain Energy Rev*. 2013;18:23-30. doi:10.1016/j.rser.2012.10.014.
4. Yan J, Hu D, Wang Z, Ma W. Construction strategies and thermal energy storage applications of shape-stabilized phase change materials. *J Appl Polym Sci*. 2022;139(4):51550. doi:10.1002/app.51550.
5. Baetens R, Jelle BP, Gustavsen A. Phase change materials for building applications: A state-of-the-art review. *Energ Build*. 2010;42(9):1361-8. doi:10.1016/j.enbuild.2010.03.026.
6. Wang X, Li C, Zhao T. Fabrication and characterization of poly(melamine-formaldehyde)/silicon carbide hybrid microencapsulated phase change materials with enhanced thermal conductivity and light-heat performance. *Solar Energ Mater Solar*

Cell. 2018;183:82-91. doi:10.1016/j.solmat.2018.03.019.

7. Xu C, Gou W, Wang X, Zhou J, Liu J, Chen K. Synthesis of paraffin@PS/reduced graphene oxide microcapsules via Pickering emulsion for multi-protective coatings. *Colloid Surf A Physicochem Eng.* 2021;613:126054. doi:10.1016/j.colsurfa.2020.126054.
8. Hunger M, Entrop AG, Mandilaras I, Brouwers HJH, Founti M. The behavior of self-compacting concrete containing micro-encapsulated Phase Change Materials. *Cem Concr Compos.* 2009;31(10):731-43. doi:10.1016/j.cemconcomp.2009.08.002.
9. Kenisarin M, Mahkamov K. Solar energy storage using phase change materials. *Renew Sustain Energy Rev.* 2007;11(9):1913-65. doi:10.1016/j.rser.2006.05.005.
10. Farid MM, Khudhair AM, Razack SAK, Al-Hallaj S. A review on phase change energy storage: materials and applications. *Energ Conv Manag.* 2004;45(9):1597-615. doi:10.1016/j.enconman.2003.09.015.
11. Borreguero AM, Valverde JL, Rodríguez JF, Barber AH, Cubillo JJ, Carmona M. Synthesis and characterization of microcapsules containing Rubitherm®RT27 obtained by spray drying. *Chem Eng J.* 2011;166(1):384-90. doi:10.1016/j.cej.2010.10.055.
12. Lin Y, Zhu C, Alva G, Fang G. Microencapsulation and thermal properties of myristic acid with ethyl cellulose shell for thermal energy storage. *Appl Energ.* 2018;231:494-501. doi:10.1016/j.apenergy.2018.09.154.
13. Cai C, Ouyang X, Zhou L, Liu G, Wang Y, Zhu G et al. Co-solvent free interfacial polycondensation and properties of polyurea PCM microcapsules with dodecanol dodecanoate as core material. *Sol Energ.* 2020;199:721-30. doi:10.1016/j.solener.2020.02.071.
14. Konuklu Y, Unal M, Paksoy HO. Microencapsulation of caprylic acid with different wall materials as phase change material for thermal energy storage. *Solar Energ Mater Solar Cell.* 2014;120:536-42. doi:10.1016/j.solmat.2013.09.035.

15. Wu B, Shi L, Zhang Q, Wang W-J. Microencapsulation of 1-hexadecanol as a phase change material with reversible thermochromic properties. *RSC Adv.* 2017;7(67):42129-37. doi:10.1039/C7RA06764J.
16. Parameshwaran R, Naresh R, Ram VV, Srinivas PV. Microencapsulated bio-based phase change material-micro concrete composite for thermal energy storage. *J Build Eng.* 2021;39:102247. doi:10.1016/j.job.2021.102247.
17. Ismail A, Zhou J, Aday A, Davidoff I, Odukamaiya A, Wang J. Microencapsulation of bio-based phase change materials with silica coated inorganic shell for thermal energy storage. *J Build Eng.* 2023;67:105981. doi:10.1016/j.job.2023.105981.
18. Konuklu Y, Paksoy HO, Unal M, Konuklu S. Microencapsulation of a fatty acid with Poly(melamine-urea-formaldehyde). *Energ Conv Manag.* 2014;80:382-90. doi:10.1016/j.enconman.2014.01.042.
19. Kobayashi T, Nakagawa K. Preparation and evaluation of edible microcapsules for thermal energy storage. *Jpn J Food Eng.* 2018;19(3):165-71. doi:10.11301/jsfe.18528.
20. Németh B, Németh ÁS, Ujhidy A, Tóth J, Trif L, Gyenis J et al. Fully bio-originated latent heat storing calcium alginate microcapsules with high coconut oil loading. *Sol Energ.* 2018;170:314-22. doi:10.1016/j.solener.2018.05.066.
21. Tian Y, Liu Y, Zhang L, Hua Q, Liu L, Wang B et al. Preparation and characterization of gelatin-sodium alginate/paraffin phase change microcapsules. *Colloid Surf A Physicochem Eng.* 2020;586:124216. doi:10.1016/j.colsurfa.2019.124216.
22. Demirbağ S, Aksoy SA. Encapsulation of phase change materials by complex coacervation to improve thermal performances and flame retardant properties of the cotton fabrics. *Fiber Polym.* 2016;17:408-17. doi:10.1007/s12221-016-5113-z.
23. Tarig E, Abdelateif H, Mohamed E, Awad Elkarim S, Hassan E, Pretzsch J et al. Recent changes in local marketing patterns of gum arabic in Kordofan, Sudan. *J Agric Sci Eng.*

2016;2(6):46-56.

24. Cheng SY, Yuen MCW, Kan CW, Cheuk KKL, Chui CH, Lam KH. Cosmetic textiles with biological benefits: Gelatin microcapsules containing Vitamin C. *Int J Mol Med*. 2009;24(4):411-9. doi:10.3892/ijmm_00000247.

25. Sutaphanit P, Chitprasert P. Optimisation of microencapsulation of holy basil essential oil in gelatin by response surface methodology. *Food Chem*. 2014;150:313-20. doi:10.1016/j.foodchem.2013.10.159.

26. Chen C, Yang H, Yang X, Ma Q. Tannic acid: A crosslinker leading to versatile functional polymeric networks: A review. *RSC Adv*. 2022;12(13):7689-711. doi:10.1039/D1RA07657D.

27. Chaiyasat P, Ogino Y, Suzuki T, Minami H, Okubo M. Preparation of divinylbenzene copolymer particles with encapsulated hexadecane for heat storage application. *Colloid Polym Sci*. 2008;286(2):217-23. doi:10.1007/s00396-007-1764-z.

28. Uranga J, Nguyen BT, Si TT, Guerrero P, de la Caba K. The effect of cross-linking with citric acid on the properties of agar/fish gelatin films. *Polymers*. 2020;12(2):291. doi:10.3390/polym12020291.

29. Rui L, Xie M, Hu B, Zhou L, Yin D, Zeng X. A comparative study on chitosan/gelatin composite films with conjugated or incorporated gallic acid. *Carbohydr Polym*. 2017;173:473-81. doi:10.1016/j.carbpol.2017.05.072.

30. Silva LYA, Falleiro RMM, Meirelles AJA, Krähenbühl MA. Determination of the vapor pressure of ethyl esters by Differential Scanning Calorimetry. *J Chem Thermodyn*. 2011;43(6):943-7. doi:10.1016/j.jct.2011.01.017.

Figure legends

Fig. 1 Typical DSC curves of the prepared MCs with and without physical cross-linking agents. Left and right arrows respectively indicate the decrease and increase of temperature

Fig. 2 Effect of spray-drying temperature on the PCM content of MCs. Mass ratio of ethyl laurate/gelatin/tannic acid was 1/1/0.1, and pH of the suspension was not adjusted

Fig. 3 Effect of pH on the various properties of MCs. (A) PCM content; (B) Peak temperatures and enthalpy of melting. Mass ratio of ethyl laurate/gelatin/tannic acid was 1/1/0.1 for the physically cross-linked MCs and was 1/1/0 for one without physical cross-linking. Spray drying was performed at 120 °C

Fig. 4 Particle size distribution of MCs obtained by physical cross-linking treatment at various pHs. Mass ratio of ethyl laurate/gelatin/tannic acid was 1/1/0.1, and spray drying was performed at 120 °C

Fig. 5 SEM images for MCs obtained by physical cross-linking at various pHs. Mass ratio of ethyl laurate/gelatin/tannic acid was 1/1/0.1, and spray drying was performed at 120 °C

Fig. 6 Effect of core/shell ratio on the properties of MCs. (A) PCM content and encapsulation efficiency; (B) Peak temperatures and enthalpy of melting.

Fig. 7 SEM images of MCs with various core/shell ratios

Fig. 8 TGA curves for MCs with various core/shell ratios. Numbers in the figure are referred to in the text

Fig. 9 Evaluation of heat storage capacity for various MCs with various core/shell ratios to suppress temperature change against ambient temperature change

Table 1 Effect of various cross-linking agents on the properties of MCs

Cross-linking agent	$T_{c,peak}^1$ (°C)	$T_{m,peak}^2$ (°C)	Enthalpy of melting (J g-MC ⁻¹) ³	PCM content (mass%)
Bulk PCM (ethyl laurate only)	-9.8	-1.2	153.3±3.2	-
Without cross-linking	-18.6	-2.1	19.4±2.0	12.7
Tannic acid (10 mass%, 1 h) ⁴	-18.7	-1.6	45.6±2.2	29.8
Tannic acid (10 mass%, 1 h) + transglutaminase (1 mass%, 24 h) ⁴	-22.3	-1.3	38.6±1.3	25.2
Tannic acid (1 mass%, 1h) + tripolyphosphate (10 mass%, 1 h) ⁴	-22.8	-1.7	33.0±1.8	21.6
Glutaraldehyde (2.5 mass%, 1 h) ⁴	-25.7	-2.3	9.7±0.8	6.3
Transglutaminase (1 mass%, 24 h) ⁴	-25.5	-2.0	13.0±1.2	8.5
Citric acid (10 mass%, 1 h) ⁴	-22.9	-2.3	7.6±2.2	4.9
Gallic acid (10 mass%, 1 h) ⁴	-25.7	-2.3	7.5±0.4	4.9

¹ $T_{c,peak}$: Peak temperature for crystallizing point; ² $T_{m,peak}$: Peak temperature for melting point; ³ Mean±SE; ⁴ Amount of the cross-linking agent was the relative value against that of gelatin. The ratio of ethyl laurate to gelatin was 1/1. pH was not adjusted, and spray drying was performed at 180 °C

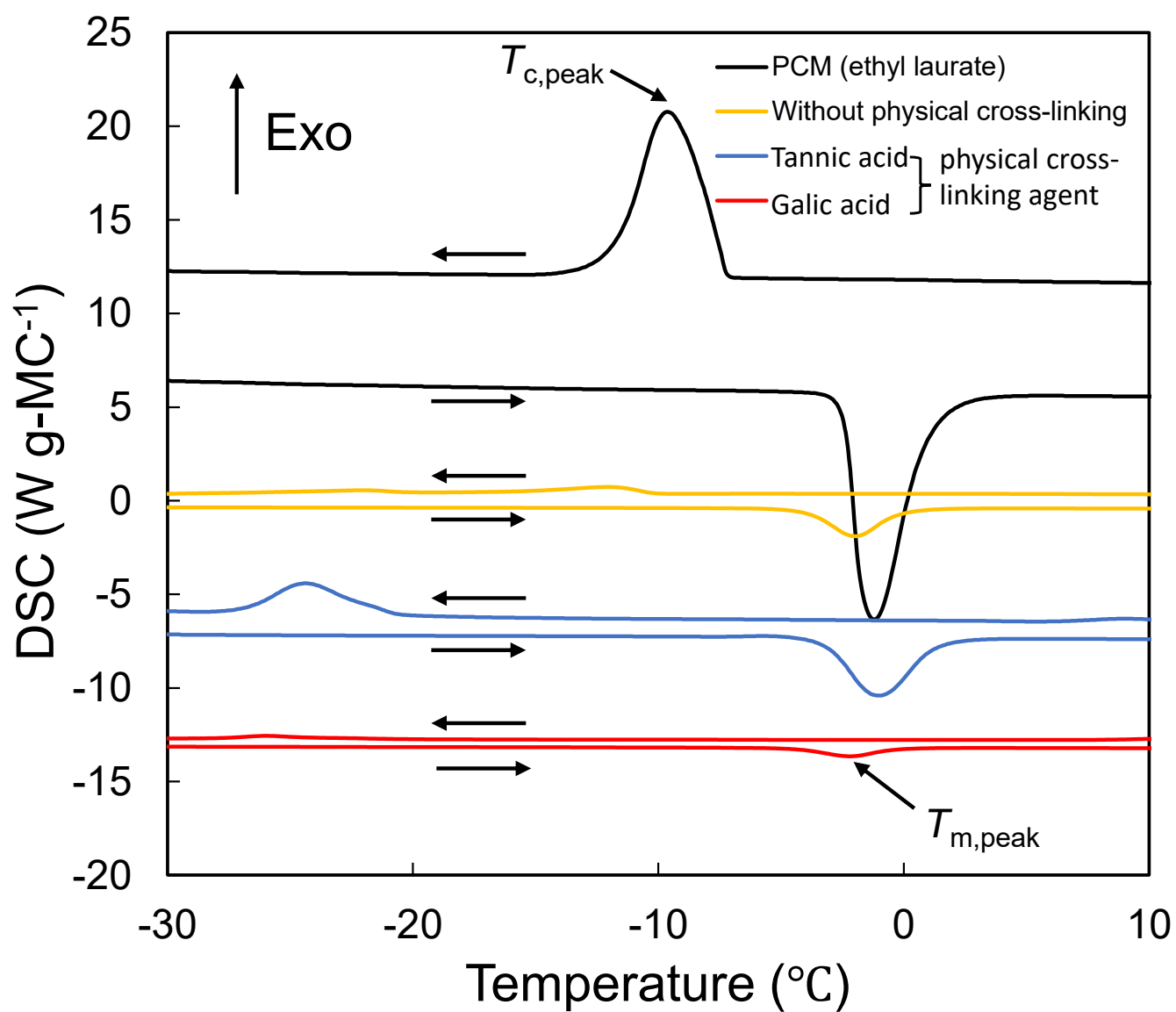


Fig. 1. Takatani *et al.*

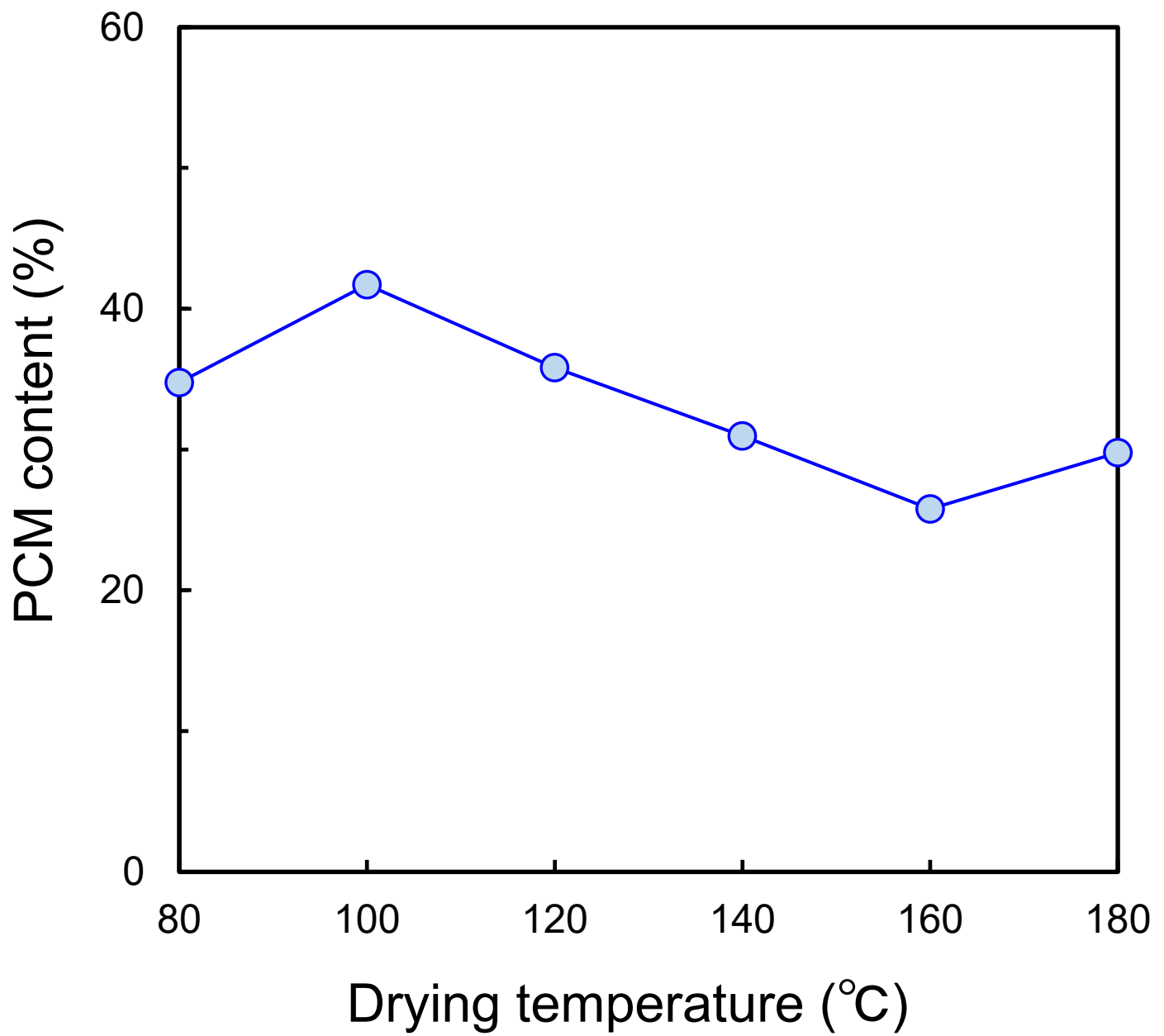


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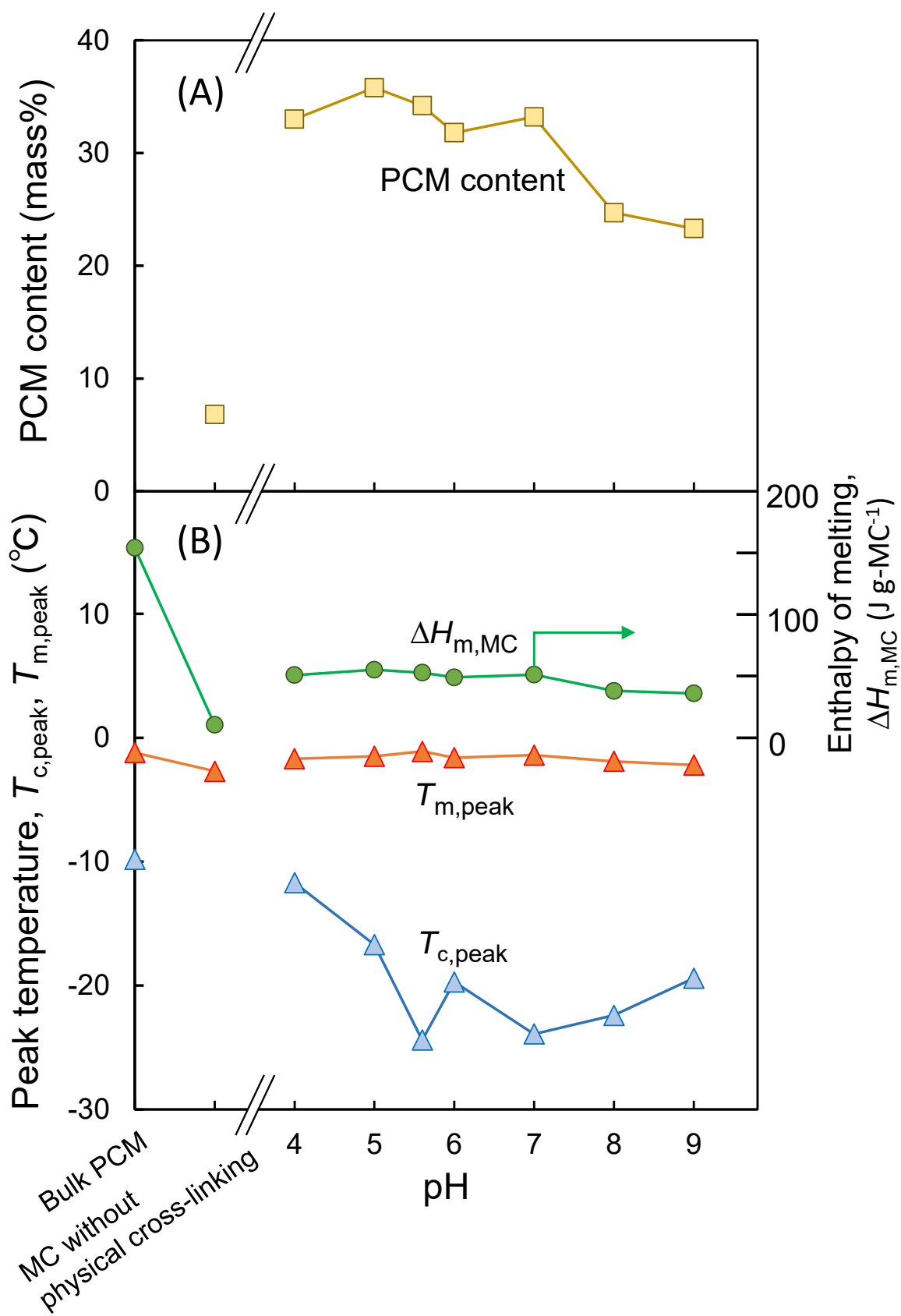


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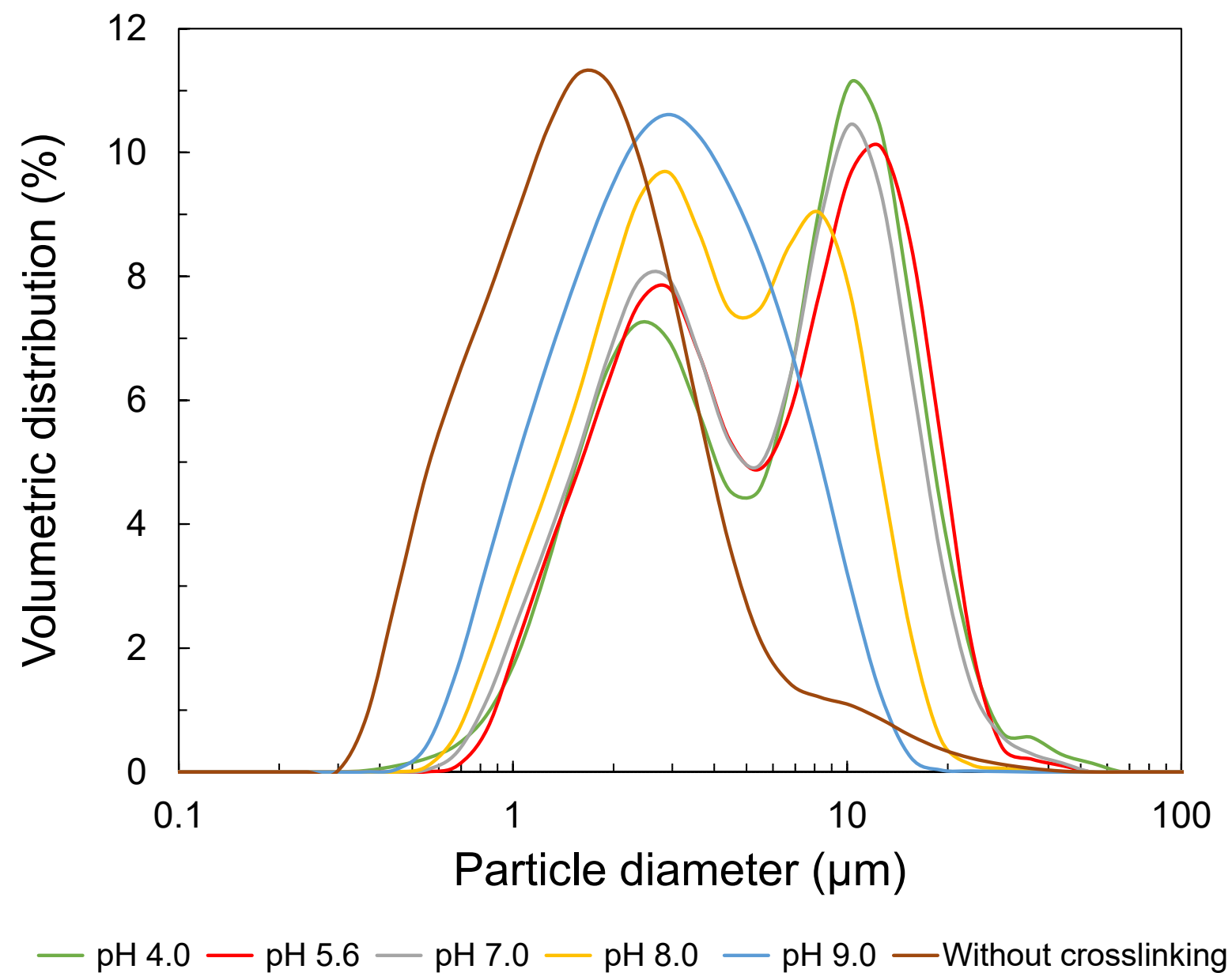


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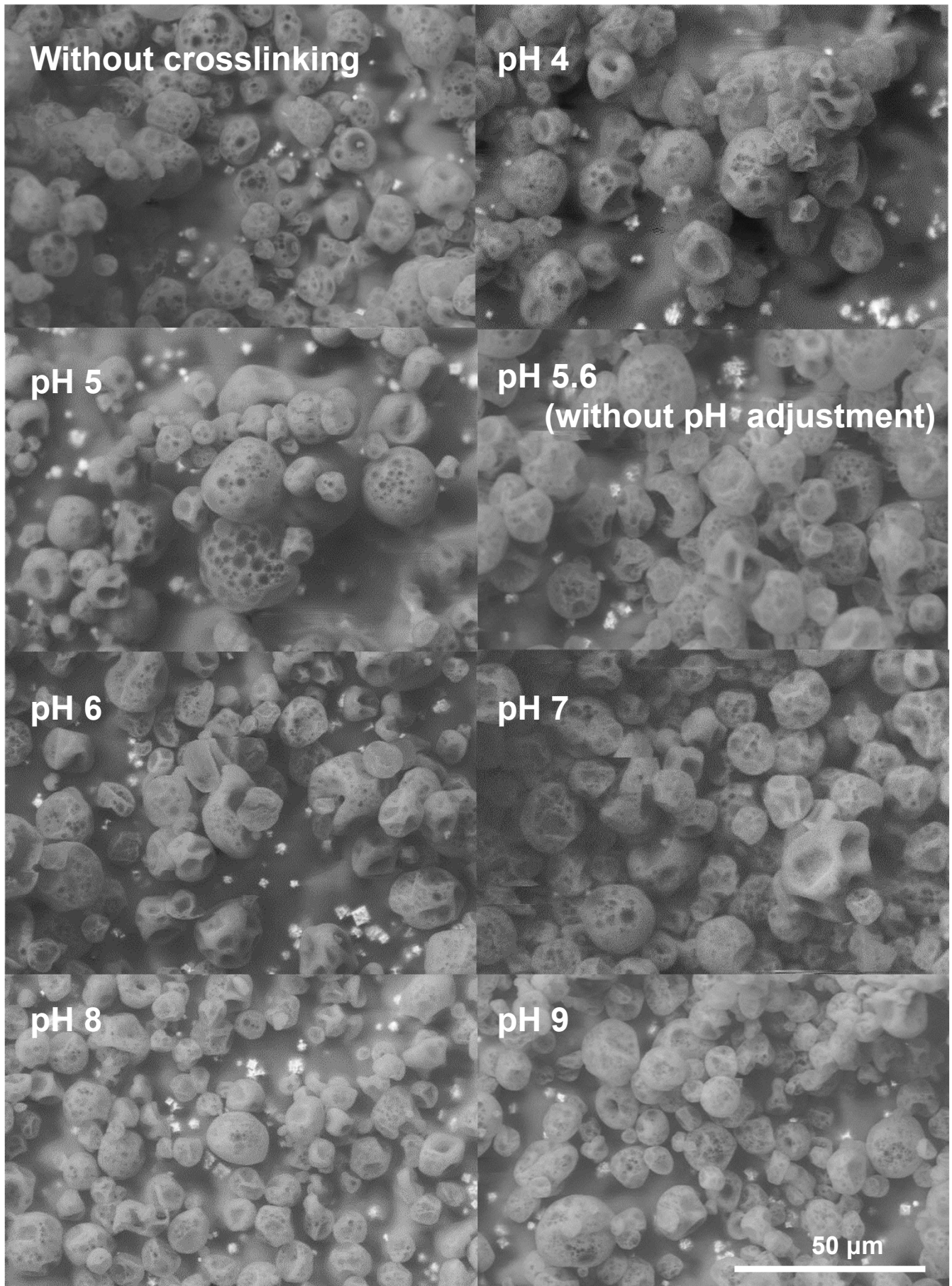


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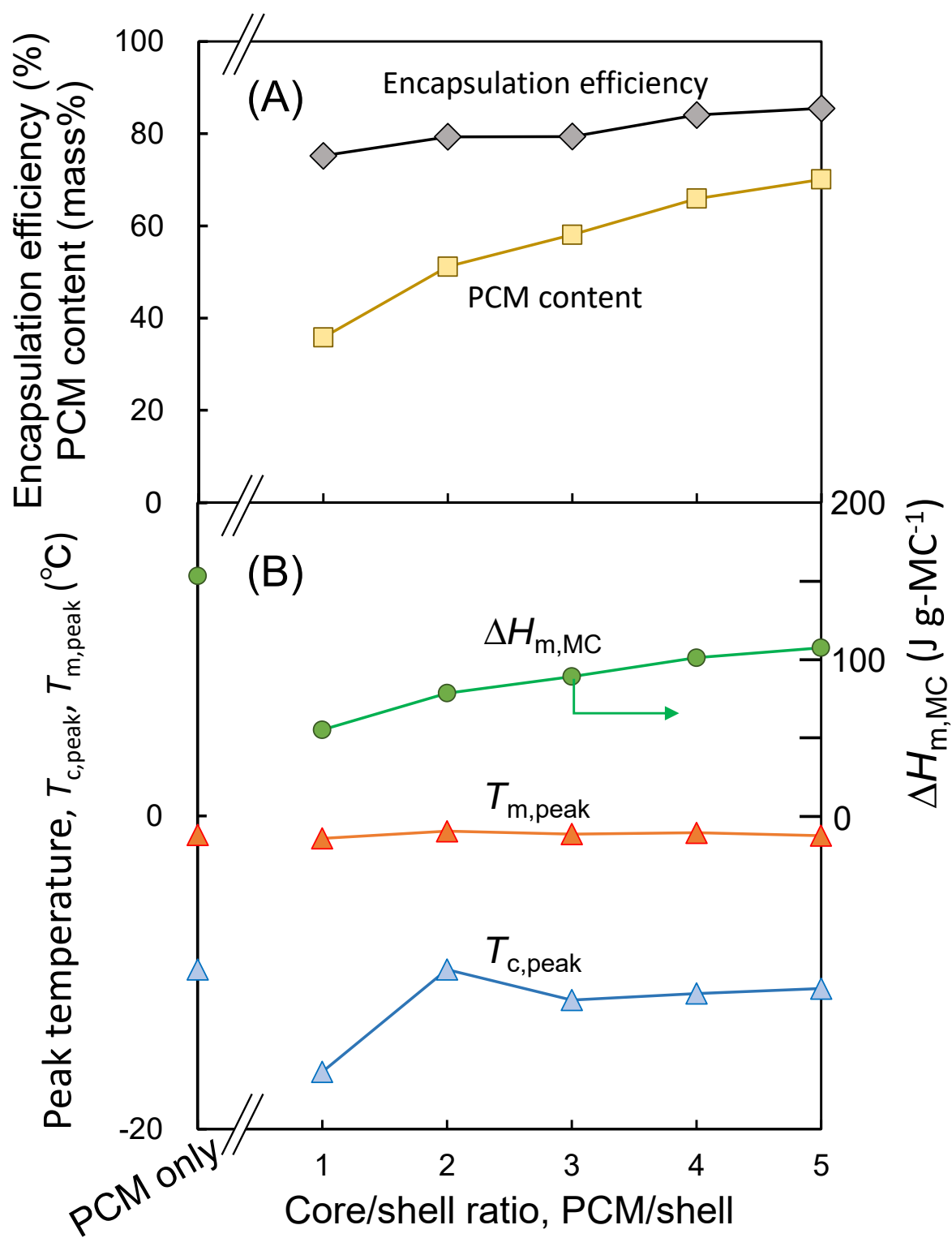


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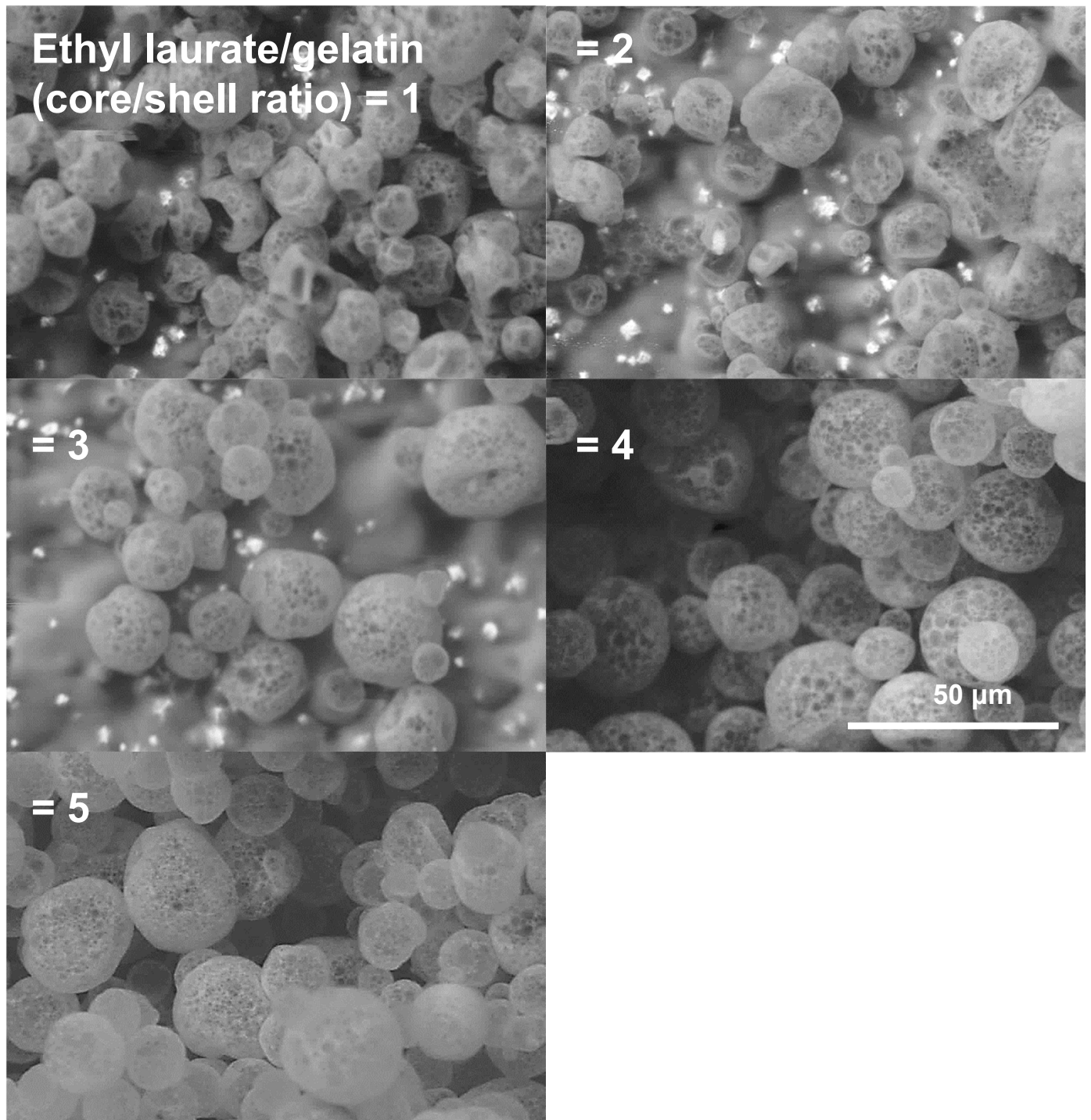


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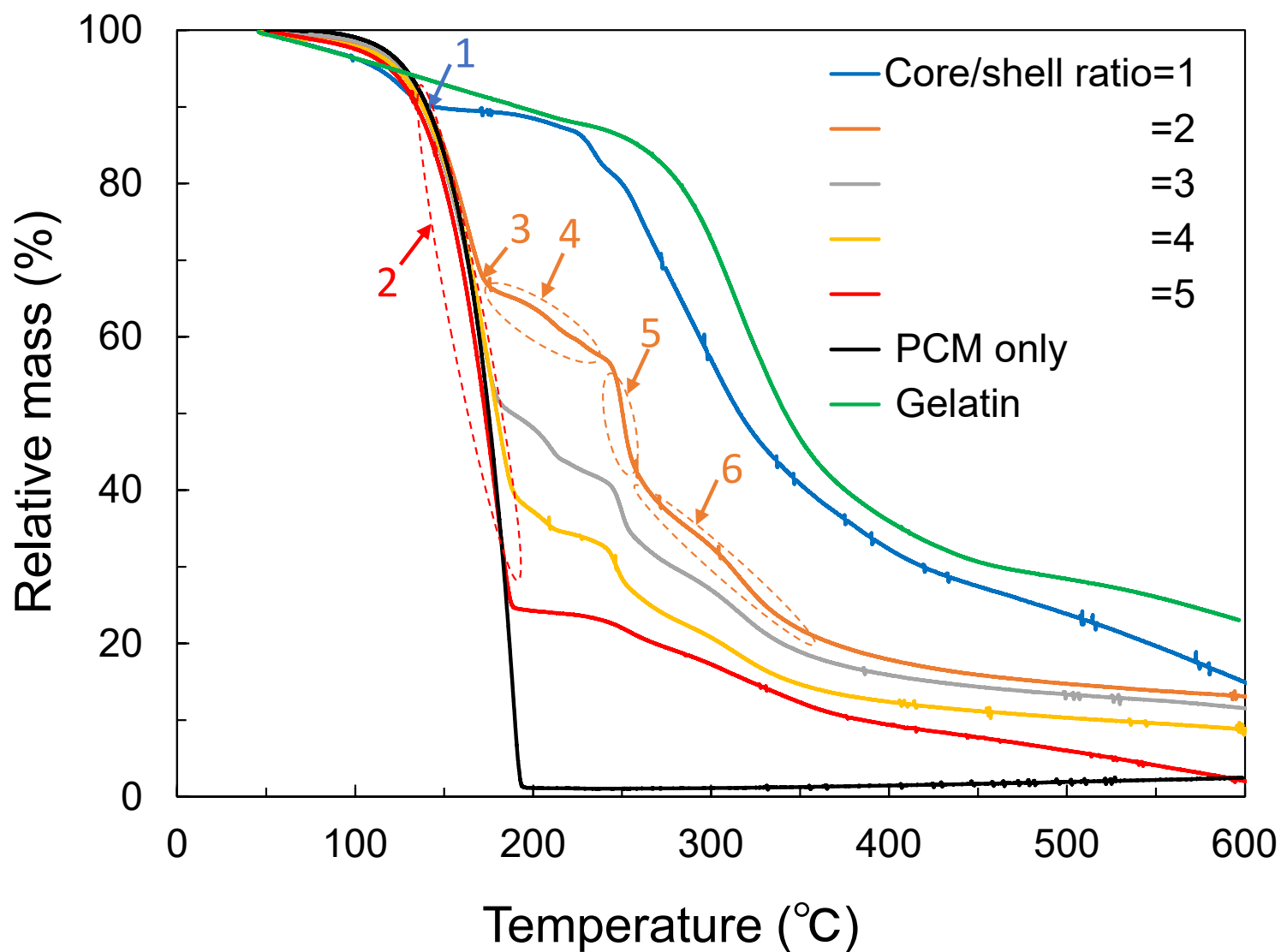


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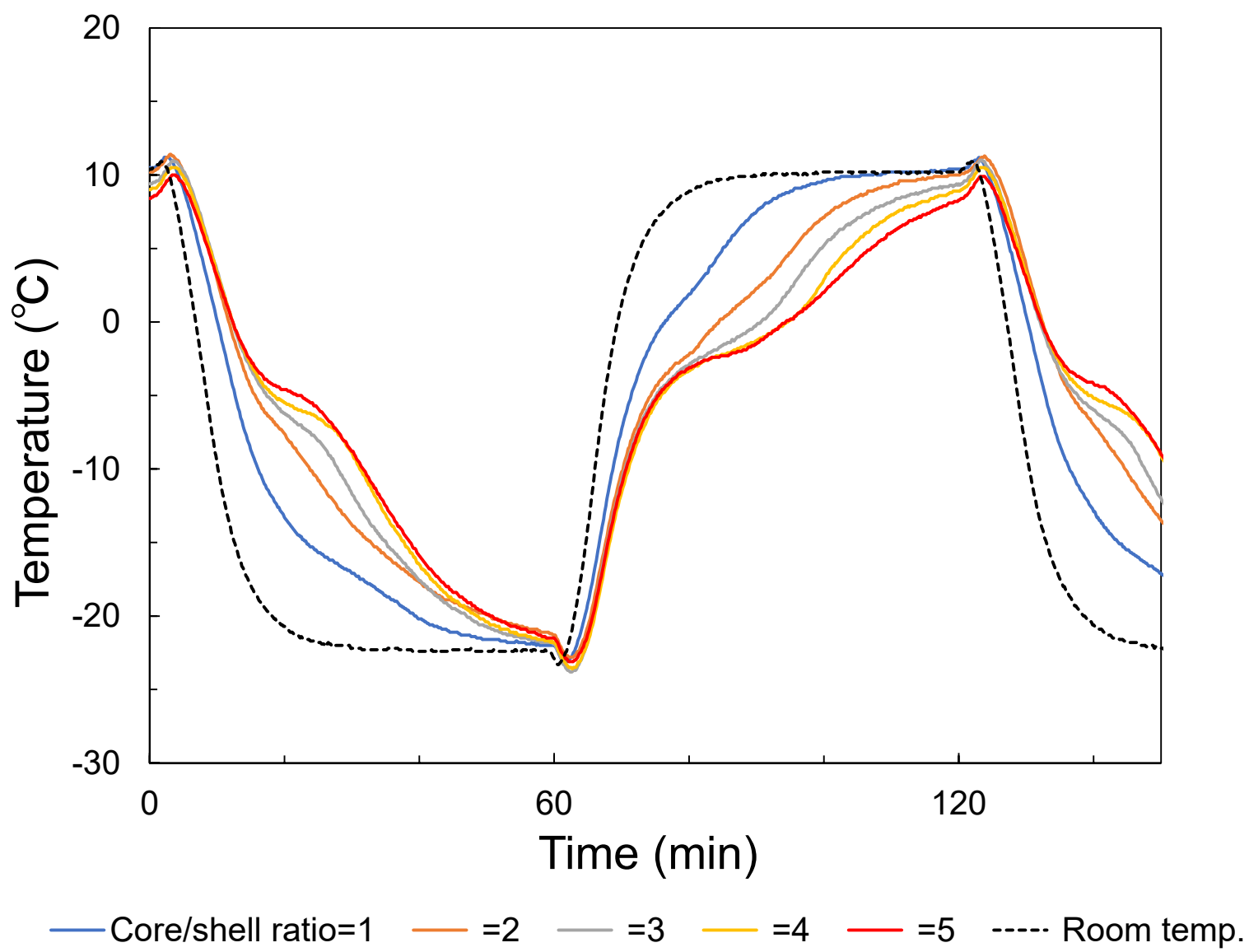


Fig. 9. Takatani *et al.*