

Hydrothermal synthesis of carbonaceous spheres starting from different starches

Takayuki OKANO* and Yoshikazu SUZUKI^{*,**,†}

*Graduate School of Pure and Applied Sciences, University of Tsukuba, Ibaraki 305-8573, Japan

**Faculty of Pure and Applied Sciences, University of Tsukuba, Ibaraki 305-8573, Japan

Carbonaceous spheres (CSs) were prepared by hydrothermal treatment of corn, potato and rice starches. Each starch powder (corn: 1.0–4.0 g, potato: 1.0 g, or rice: 1.0 g) was dispersed in 40 mL H₂O in a Teflon-lined stainless autoclave, and the autoclave was heated at 160°C for 4–16 h. The solid products after hydrothermal treatment were washed and dried to obtain CSs. CSs from the potato starch showed the narrowest particle-size distribution, which can be attributed to its B-type starch structure. Although the particle-size distribution of CSs was affected by starting starches, chemical characteristics were almost identical for all starches.

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1. Introduction

Hollow particles have some unique properties such as high surface area, low relative density, high heat resistance, and effective light scattering. They are applied for light-weight structural components, heat insulators, soundproofing materials, photocatalysts, drug delivery system, ultrasound contrast agents and so on. Hollow particles have been synthesized by various methods such as spray pyrolysis,^{1,2)} bubble template method,^{3,4)} lost-wax method,⁵⁾ template-free solvothermal method⁶⁾ and template method.^{7,8)} Among them, the template method is particularly useful to obtain homogeneous and well-controlled hollow particles. Polystyrene (PS),^{8,9)} silica,¹⁰⁾ polymethyl methacrylate (PMMA)¹¹⁾ and carbonaceous spheres (CSs)¹²⁾ have been used as templates. CSs are used as environmentally-friendly templates, because organic solvents or toxic inorganic solvents are not needed for the template-removal step. Sun et al.¹²⁾ reported that the surface of CSs had hydrophilic groups, such as OH and C=O, and hence, it is not necessary to modify the surface structure in order to adsorb precursors or ions for target hollow particles. Furthermore, CSs gradually shrink during the burning-out step with keeping their spherical morphology, which is suitable as templates. CSs can be prepared through hydrothermal treatment of saccharides.¹³⁾ This hydrothermal treatment is a low-temperature environmentally-friendly process using only saccharides and water. So far, Sevilla et al.¹⁴⁾ have succeeded in preparing CSs (called as hydrochar) from glucose, sucrose and potato starch. However, as far as we know, the effect of the type of starch has not yet been studied in detail.

In this study, we have prepared CSs from corn, potato and rice starches, and clarified the particle size distribution of CSs. Crystal structure of starches was analyzed by X-ray diffraction method. Previous studies reported that the CSs were synthesized at $\geq 160^\circ\text{C}$ from glucose¹²⁾ and $\geq 120^\circ\text{C}$ from fructose.¹⁵⁾ In

this work, 160°C was selected as the hydrothermal treatment temperature.

2. Experimental

Corn starch (JIS Special Grade, Wako Pure Chemical Industries Ltd., Osaka, Japan), potato starch (1st Grade, Wako) and rice starch (Sigma-Aldrich Japan LLC, Tokyo) were used as starting materials. We have used the same starches as sacrificial pore-forming agents of porous ceramics in a previous paper, where the size distribution of the starches is given.¹⁶⁾ Crystal structure of starches was analyzed by X-ray diffraction (XRD, Multiflex, Cu-K α , 40 kV, 40 mA, Rigaku, Tokyo, Japan). Each starch powder (corn: 1.0–4.0 g, potato: 1.0 g, or rice: 1.0 g) was dispersed in 40 mL H₂O in a Teflon-lined stainless autoclave by using a magnetic stirrer for 10 min. The autoclave was heated at 160°C for 4–16 h. The ramp rate to 160°C was 10°C/min, and after keeping, the autoclave was naturally cooled to the room temperature. The resultant dark brown suspensions were centrifuged at 10,000 rpm for 20–60 min to obtain light brown transparent solution and black solid products. The solid products were dispersed in ethanol, and re-centrifuged. This cleaning process was repeated until ethanol remained colorless. The products were dried at 80°C for 20 h to obtain CSs.

Microstructure of the starches and the CSs was observed by scanning electron microscopy (SEM, JSM-5600LV, JEOL, Tokyo, Japan). Size distribution of CSs was calculated from SEM images by using Image-J software. Chemical structure of CSs was analyzed by Fourier transform infrared spectroscopy (FT-IR, FT/IR-300, 400–4000 cm⁻¹, JASCO, Tokyo, Japan).

3. Results and discussions

Figure 1 shows XRD patterns and SEM images of three starches used in this study. The XRD patterns for potato and corn starches are in good agreement with reported data, ICDD-JCPDS nos. 39-1912 and 39-1911 (both were not indexed), respectively. Starches are generally composed of amylose and amylopectin, and the amylose content is typically 20–25%. The structures of amylopectins depend on starches, and are generally categorized

[†] Corresponding author: Y. Suzuki; E-mail: suzuki@ims.tsukuba.ac.jp

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into A-type, B-type and C-type.¹⁷⁾ The A-, B- and C-types are characterized by short molecular chains (~ 20), long molecular chains (~ 35), and mixture of them, respectively. The patterns of corn and rice had a peak at $2\theta \sim 23^\circ$ (categorized as A-type) and that of potato had a peak at $5\text{--}6^\circ$ (categorized as B-type). These structural differences affect the decomposition behavior and products after hydrothermal treatment. In fact, the SEM images clearly show the difference of sizes and morphologies, i.e., small and angular for the A-type corn and rice starches, whereas large and roundish for the B-type potato starch. Judging from these characteristics, the decomposition of B-type potato starch during the hydrothermal treatment is expected to be slower than the others.

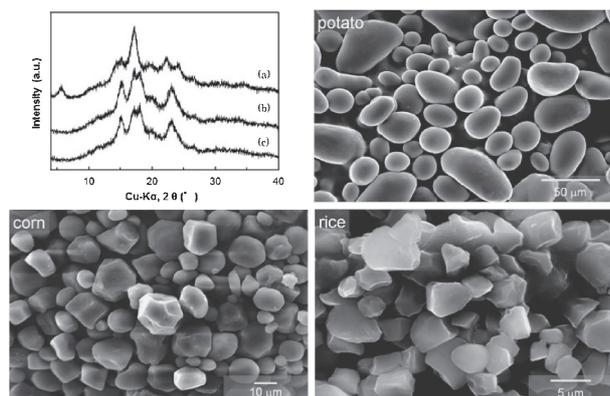


Fig. 1. XRD patterns of (a) potato (b) corn and (c) rice starches, and corresponding SEM images.

At first, CSs were prepared from the corn starch with changing sample mass and hydrothermal durations. **Figure 2** shows SEM images and particle-size distributions of CSs from the corn starch. With increasing starting starch mass and hydrothermal duration, larger CSs were obtained. When the hydrothermal duration was 4 h or less, almost no CSs were obtained. Second, CSs were prepared from the potato and rice starches (1 g each) with changing hydrothermal durations. With increasing hydrothermal duration, larger CSs were also obtained, as shown in **Fig. 3**. **Table 1** summarizes the size and the yield of CSs synthesized by the hydrothermal treatment.

The formation mechanism of CSs from glucose is discussed in detail by Sun et al.¹²⁾ and Sevilla et al.¹⁴⁾ Intramolecular/intermolecular dehydration, polymerization and aromatization take place under hydrothermal conditions. When the solution reached a critical supersaturation, nucleation and growth of CSs proceeded.¹²⁾ In this study, starches gradually decomposed into glucose, fructose and so on. When the hydrothermal durations were 4 h or less, the solution did not reach the critical supersaturation to form the nuclei. As shown in Table 1 and Figs. 2 and 3, with increasing starting sample mass and hydrothermal duration, larger CSs were obtained. These results agreed with the formation mechanisms reported in previous studies.^{12)–14)} Since the hydrothermal temperature of this study (i.e. 160°C) was close to the lower limit of the formation temperature of CSs, precise control of the particle size became somewhat difficult for lower sample concentrations. In fact, for the corn starch, mean size decrement with increasing hydrothermal duration was observed for 1 and 2 g samples (i.e., C-1-08 \rightarrow C-1-12 and C-2-12 \rightarrow C-2-16 in Table 1), which can be attributed to the inhomogeneous

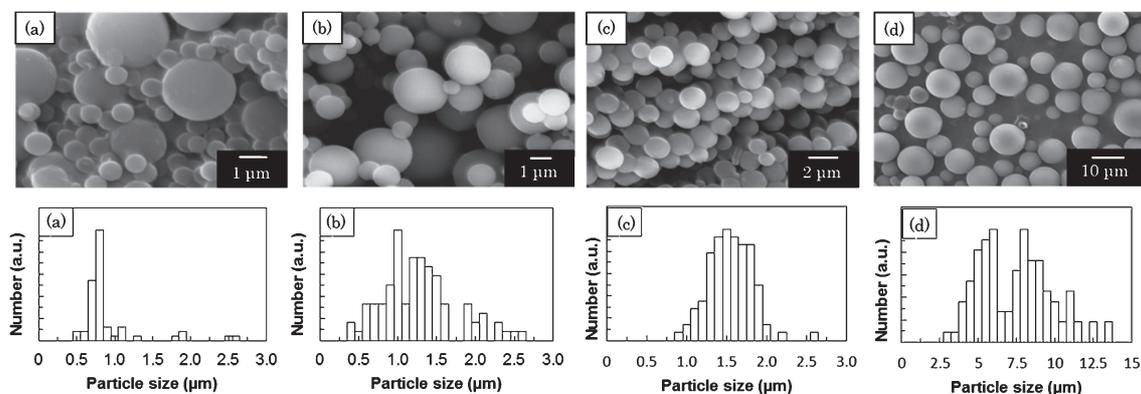


Fig. 2. SEM images and particle-size distributions of CSs from corn starch: (a) 1 g-12 h, (b) 1 g-16 h, (c) 2 g-16 h, and (d) 4 g-16 h.

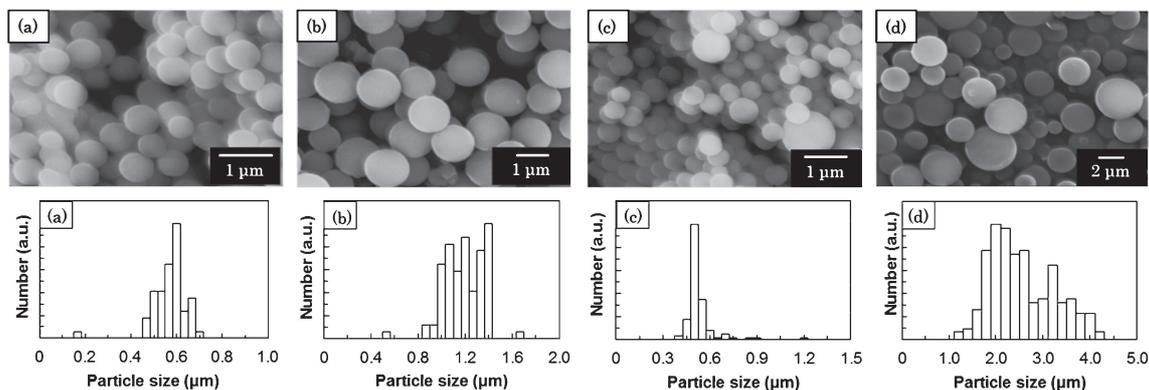


Fig. 3. SEM images and particle-size distributions of CSs from potato starch: (a) 1 g-12 h, (b) 1 g-16 h, and from rice starch: (c) 1 g-12 h and (d) 1 g-16 h.

Table 1. Size and yield of CSs synthesized by hydrothermal treatment at 160°C

Raw materials (starches) and processing condition			Products (carbon spheres)			
Sample mass [g]	Hydrothermal duration [h]	Product code name	Mean Diameter [μm]	Standard deviation	Yield (%)	
Corn	1	C-1-08	1.30	0.78	0.80	
		C-1-12	0.87	0.43	3.14	
		C-1-16	1.25	0.52	4.65	
	2	C-2-08	1.35	1.14	1.84	
		C-2-12	2.09	0.48	5.64	
		C-2-16	1.50	0.27	10.1	
	4	C-4-04	2.61	1.08	0.08	
		C-4-08	4.41	1.57	0.99	
		C-4-12	5.83	1.82	5.65	
Potato	1	P-1-08	0.22	0.035	0.60	
		P-1-12	0.56	0.075	1.72	
	16	P-1-16	1.16	0.17	4.12	
Rice	1	R-1-08	0.46	0.42	0.79	
		R-1-12	0.50	0.096	2.23	
		R-1-16	2.46	0.67	4.18	

growth of some large spheres [see. Fig. 2(a)].

Among three starches, potato starch was favorable to obtain narrow particle-size distribution [Figs. 3(a) and 3(b)]. As described for Fig. 1, the structure of potato starch (B-type) is different from that of corn and rice starches (A-type). Under hydrothermal conditions, starches are decomposed into glucose, fructose, maltose and 5-hydroxymethylfurfural (5-HMF) and so on.¹⁸⁾ Similarly to glucose, fructose also form CSs via 5-HMF formation.¹⁵⁾ In other words, there should be glucose-derived and fructose-derived CSs (or even other), when starches are used as starting materials. From this study, it can be deduced that the B-type starch (with longer chains) decomposes somewhat slowly compared with A-type, and thus, the nucleation behavior (and also the composition) of B-type should be different from A-type.

Figure 4 shows FT-IR spectra of some CSs. As is reported by Sevilla et al.¹⁴⁾ the band at $\sim 790\text{ cm}^{-1}$ is assigned to aromatic C–H out-of-plane bending vibration, and the band at ~ 1500 and $\sim 1600\text{ cm}^{-1}$ are assigned to aromatic C=C breathing vibrations. These bands indicate the aromatization under the hydrothermal condition. The bands at ~ 1700 , ~ 3400 , and $1000\text{--}1300\text{ cm}^{-1}$ are assigned to C=O, O–H, C–O vibrations, respectively, which demonstrate the existence of surface functional groups.¹⁹⁾ The wide band at $\sim 3400\text{ cm}^{-1}$ implies the existence of hydrogen bonds among many molecules. The band at $\sim 2900\text{ cm}^{-1}$ is assigned to aliphatic C–H stretching vibration. Despite some intensity differences, all samples showed similar IR spectra.

4. Conclusions

In this study, carbonaceous spheres (CSs) were synthesized by the hydrothermal treatment of corn, potato and rice starches. When the hydrothermal duration was 4 h or less, almost no CSs were obtained. When the hydrothermal duration was 8 h or more, CSs were obtained. With increasing starting sample mass and hydrothermal duration, larger CSs were obtained. Even for the relatively low hydrothermal temperature of 160°C, homogeneous CSs were synthesized from potato starch with B-type structure. This result confirmed that the initial crystal structure of starch affected the hydrothermal reactions. FT-IR spectroscopy revealed the existence of plenty of surface functional groups and low

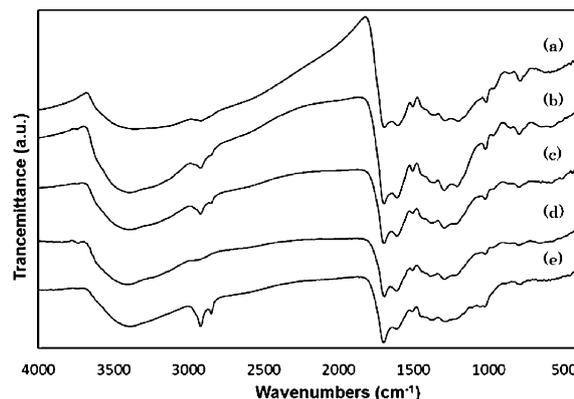


Fig. 4. FT-IR spectra of CSs: (a) C-4-12, (b) C-2-16, (c) C-1-12, (d) P-1-12 and (e) R-1-08.

crystallinity of CSs. Although the particle-size distribution of CSs was affected by the starting starches, the chemical properties were almost identical for different starches.

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