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Microwave-enhanced hybridizations of biopolymers with silica: effective method for rapid preparation and homogeneous dispersion

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Abstract Effective hybridization of biopolymers such as chitosan or lignin was conducted by microwave-assisted sol–gel reaction of several alkoxysilanes such as tetramethoxysilane (TMOS), methyltrimethoxysilane (MeTMOS), and 3-aminopropyltrimethoxysilane (APTMS). The hybridization proceeded rapidly and efficiently via inhibition of aggregates derived from intermolecular hydrogen bonding in the biopolymers as compared with the conventional heating as a traditional method due to activated hydroxyl groups of both the biopolymers and alkoxysilanes by microwave irradiation. The composition and the thermal properties of the polymers hybridized under microwave irradiation were almost identical to those prepared by the conventional method using TGA analysis and FT-IR spectroscopy. However, the homogeneity on the surface of the hybrid obtained under microwave irradiation was better than that under conventional heating by measuring the SEM and nitrogen adsorption porosimetry analysis.

Keywords Microwave · Organic–inorganic hybrid · Biopolymers

Introduction

Microwave irradiation technique is of considerable interest in the field of organic [1, 2], inorganic [3, 4], and polymer synthesis [5, 6] because the effect of this

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technique is a combination of the thermal effect and non-thermal effects, i.e., overheating, hot spots and selective heating, and non-thermal effects of the highly polarizing field, in addition to effects on the mobility and diffusion that may increase the probabilities of effective contacts. The mechanism based on the combinational effect is microwave dielectric heating. The substances with high dielectric constant are heated more rapidly under microwave irradiation compared to conventional heating as a traditional method. For example, general alcohols such as methanol or ethanol, whose respective dielectric constants are 32.35 and 25.00 [7], can be heated at higher boiling point, i.e., higher than 100 °C, under microwave irradiation in the sealed vessel [2, 8].

Organic–inorganic polymer hybrids have been widely studied because of their high performance and unique properties [9]. In general, the sol–gel reaction of alkoxysilane in the presence of various polymers, e.g., poly(*N*-vinylpyrrolidone) [10], poly(2-methyl-2-oxazoline) [11], polystyrene [12], and so on, is used to prepare hybrid materials utilizing the interactions such as hydrogen bonding, covalent bonding, π–π interaction, etc. However, long reaction times are required to complete the reaction when the reaction is carried out under conventional heating. In order to overcome this problem, microwave irradiation has been applied to the preparations of some polymer hybrids [13–16]. The acceleration of sol–gel reaction by microwave irradiation can be attributed to the increase of alkoxysilane concentration due to the evaporation of solvents, and the activation of the polar silanol groups generated by hydrolysis of alkoxysilane.

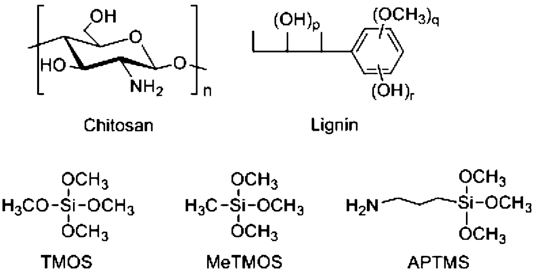
In recent years, the use of biomass has been widely expanded from the view of effective use of energy resources. Chitosan and lignin are abundant substances in nature. Therefore, such biopolymers have been interested in the field of material science. Although chitosan [17–23] and lignin [24–27]/silica hybrids have been prepared under conventional heating, the preparation of the hybrids was achieved with long reaction time. Further, chitosan and lignin have poor solubility due to their high crystallinity constructed by intermolecular hydrogen bonding. In previous report, homogeneous and transparent chitosan/silica hybrids [17] and lignin/silica hybrids [24] could be obtained by introducing urethane groups into hydroxyl groups in the chitosan or lignin to enhance the compatibility of the polymer with silica gels. However, this method requires somewhat laborious process. Therein, the other report exhibits that microwave irradiation is effective to the dissolution of chitosan in the solution due to inhibition of aggregates generated by intermolecular hydrogen bonding [28].

In this article, we report more efficient and easy preparation of chitosan or lignin/silica hybrids under microwave irradiation, and their properties were investigated by comparing with conventional heating.

Experimental

Materials

Chitosan (Chitosan 50, Wako Pure Chemical Industries, Ltd.), Lignin Alkali (Kanto Chemical Co., Inc.), tetramethoxysilane (TMOS, Tokyo Kasei Kogyo Co., Ltd),



Scheme 1 Chemical structures of biopolymers and alkoxysilanes

methyltrimethoxysilane (MeTMOS, Wako Pure Chemical Industries, Ltd.), 3-aminopropyltrimethoxysilane (APTMS, Sigma-Aldrich Co., Ltd.), and methanol (Wako Pure Chemical Industries, Ltd.) were used as received without further purification. The chemical structures of the biopolymers and alkoxysilanes used in this article are shown in Scheme 1.

Measurements

Thermogravimetric analysis (TGA) was performed on a SEIKO TG/DTA 6200 with a heating rate of 10 °C/min in air. Scanning electron microscopy (SEM) measurements were conducted using a JEOL JSM-5600 system. Fourier transform infrared (FT-IR) spectra were recorded on an IRPrestage-21 infrared spectrometer (Shimadzu Corp.). Nitrogen absorption porosimetry was carried out with BELSORP-18PLUS (BEL JAPAN INC.). The powder of the hybrids was heated at 600 °C in an ambient atmosphere to remove the organic parts. The samples were then dried at 150 °C for 5 h at reduced pressure under nitrogen atmosphere. Surface areas were calculated with BET equation equipped on the apparatus in the range of 0.05–0.30 (p/p_0).

The sol–gel reaction behavior under microwave irradiation and conventional heating

The sol–gel reaction behavior of TMOS, MeTMOS, and APTMS under microwave irradiation and conventional heating was investigated by weight change. The solutions of 2.0 g of alkoxysilane and catalysis (0.1 N HCl or NH_3) were stirred for 1 h. The amount of the catalyst was adjusted to contain four equivalent molar of water to TMOS, and three equivalent molar of water to MeTMOS and APTMS. After stirring, microwave was irradiated with chasing the weight of the solution for adjusted time. In the case of conventional heating, the solution was put into an oven at 60 °C.

Preparation of chitosan/silica hybrids

The preparation of chitosan/silica hybrids is as follows. 0.1 g of chitosan was dissolved in 10 ml of 0.5% aqueous acetic acid solution, followed by adding methanol and alkoxysilane. Diluted acetic acid plays a role of dissolution of chitosan and catalysis of the sol–gel reaction of alkoxysilanes. After stirring for 1 h, the solution was poured into polypropylene vessel, and it was put into a microwave reactor (Milestone General MicroSYNTH). Then, 2.45 GHz microwave was irradiated at 200 W for 20 min, subsequently at 800 W for 2 min. In the case of the conventional heating, the solution was put into a 60 °C oven for 24 h. The obtained hybrids were evaluated by TGA, SEM, FT-IR, and nitrogen adsorption porosimetry analysis.

Preparation of lignin/silica hybrids

Similarly to the preparation of above hybrid, the lignin/silica hybrids were prepared. 0.1 g of lignin was dissolved in water, followed by adding methanol, APTMS, and 0.1 N aqueous NH_3 solution. The reaction was carried out under microwave irradiation at a power of 200 W for 20 min, and under conventional heating at 60 °C, respectively.

Results and discussion

Reaction behavior of microwave-assisted and conventionally heated sol–gel reactions

The rates of the sol–gel reactions of tetramethoxysilane (TMOS), methyltrimethoxysilane (MeTMOS), and 3-aminopropyltrimethoxysilane (APTMS) were investigated to ensure the effect of microwave irradiation as compared with conventional heating. The weights of the solution, which decrease as the reaction proceeds, were measured until the weight reached the constant value. Figure 1 shows the relationship between reaction time and weight loss of various alkoxysilanes under each condition. Under microwave irradiation at 200 W, the weight of the TMOS solution decreased rapidly (Fig. 1a). When the power of microwave irradiation was enhanced at 500 or 800 W, the sol–gel reaction of TMOS almost finished within 2 min. The accelerations of the sol–gel reactions of MeTMOS and APTMS by means of microwave irradiation were also observed as shown in Fig. 1b and c. In contrast, the sol–gel reaction of these alkoxysilanes using conventional heating required more than 1 h. The results indicate that the accelerations under microwave irradiation can be attributed to high activation of the polar silanol groups generated from alkoxysilanes, and rapid evaporation of both methanol and water in the solvents and/or generated by the hydrolysis of the alkoxysilanes.

Chitosan/silica and lignin/silica hybrids

In order to prepare the biopolymers/silica hybrids under microwave irradiation and conventional heating, chitosan and lignin were employed as the biopolymers. Tables 1 and 2 summarize the results of the feed ratio of the polymer/silica, visible appearance, and 10% thermal decomposition temperature (T_{10}), measured by the

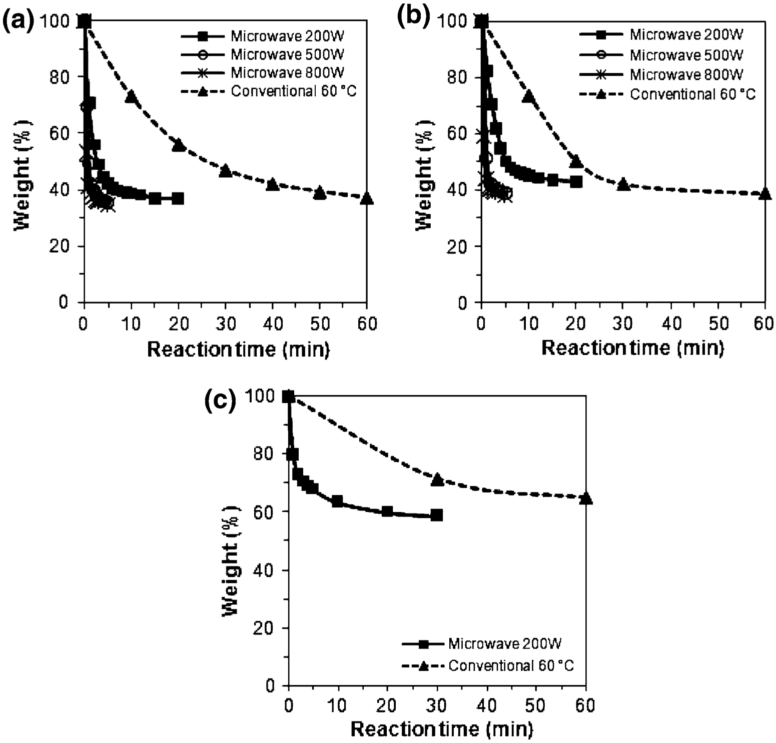


Fig. 1 Weight changes during the sol–gel reaction of alkoxysilanes under microwave irradiation, and conventional heating. **a** TMOS, **b** MeTMOS, and **c** APTMS

thermogravimetric analysis (TGA) measurement. By means of microwave irradiation and conventional heating, homogeneous and transparent chitosan/silica hybrids were obtained at a ratio of chitosan/TMOS = 1/2 (Table 1, run 1), and chitosan/MeTMOS = 1/2–1/10 (Table 1, runs 2–4). Similarly, although TMOS or MeTMOS were also used as alkoxysilanes to obtain lignin/silica hybrids, the reaction solutions were suspended readily during stirring, resulting from rapid gelation of alkoxysilanes due to high alkalinity of lignin. Accordingly, lignin/silica hybrids were synthesized successfully under microwave irradiation and conventional heating when APTMS was used as an alkoxysilane (Table 2, runs 1–3). Figure 2 shows the weight changes during the preparation of chitosan/silica hybrids (Table 1, runs 1, 2) and lignin/silica hybrids (Table 2, run 1) under microwave irradiation and conventional heating. The preparation of the hybrids under microwave irradiation was completed in ca. 20 min. In contrast, the complete preparation of the hybrids under conventional heating required more than 2 h. It was found that the preparation rate of the hybrids was accelerated by microwave irradiation as compared to conventional heating, originating from activated silanol groups generated from alkoxysilanes in the sol–gel reaction according to the mechanism as mentioned above.

Table 1 Preparation of chitosan/silica hybrids under microwave irradiation and conventional heating

Run	Chitosan (g)	Alkoxy-silane (g)	Appearance		Ceramic yield (wt%)^{a}		T_{10} (°C)^{a}	
			MW^{b}	CH^{c}	MW^{b}	CH^{c}	MW^{b}	CH^{c}
1	0.1	TMOS 0.2	Transparent	Transparent	30.9	41.1	248	253
2	0.1	MeTMOS 0.2	Transparent	Transparent	37.4	40.1	261	255
3	0.1	MeTMOS 0.5	Transparent	Transparent	61.2	55.1	280	293
4	0.1	MeTMOS 1.0	Transparent	Transparent	70.6	69.9	326	325

Solvent: 0.5% CH_3COOH aq. 10 mL, CH_3OH 10 mL

[a] Calculated by TGA

[b] Microwave irradiation: 200 W 20 min, and 800 W 2 min

[c] Conventional heating: 60 °C, 24 h

Table 2 Preparation of lignin/silica hybrids under microwave irradiation and conventional heating

Run	Lignin alkali (g)	APTMS (g)	Appearance		Ceramic yield (wt%)^{a}		T_{10} (°C)^{a}	
			MW^{b}	CH^{c}	MW^{b}	CH^{c}	MW^{b}	CH^{c}
1	0.1	0.2	Transparent	Transparent	51.3	49.0	304	300
2	0.1	0.5	Transparent	Transparent	64.1	62.2	382	379
3	0.1	1.0	Transparent	Transparent	53.6	53.0	440	443

Solvent: H_2O 2 mL, CH_3OH 2 mL, 0.1 N NH_3 aq. 0.1 mL

[a] Calculated by TGA

[b] Microwave irradiation: 200 W 20 min

[c] Conventional heating: 60 °C, 24 h

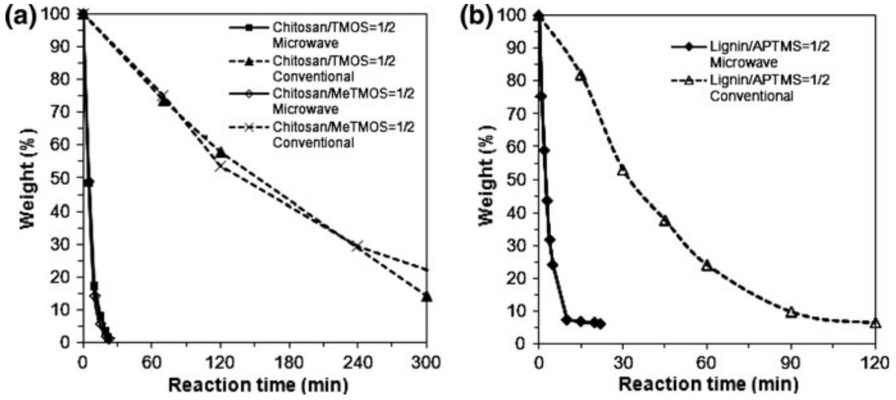


Fig. 2 Weight changes during preparation of hybrids under microwave irradiation, and conventional heating, **a** chitosan/silica hybrids, and **b** lignin/silica hybrids

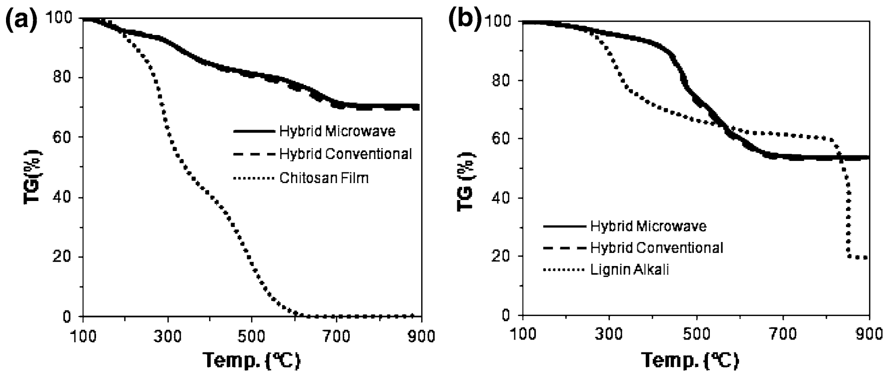


Fig. 3 TGA curves of hybrids and polymers, **a** chitosan/MeTMOS = 1/10, and **b** lignin/APTMS = 1/10, heating rate: 10 °C/min

Further, Fig. 3 illustrates the TGA curves of biopolymers/hybrids obtained by both methods along with chitosan and lignin as the comparable counterparts. T_{10} of the chitosan/silica and lignin/silica hybrids were higher than the counterparts, indicating that increasing the silica contents leads to high thermostability of each biopolymer moiety in the obtained hybrids (Tables 1, 2); e.g., T_{10} of lignin/APTMS = 1/10 hybrid (Table 2, run 3) was above 440 °C. The thermostability of the biopolymer/silica hybrids obtained under microwave irradiation was almost identical to those obtained under conventional heating (Tables 1, 2, and Fig. 3). This result indicates that the difference of each synthetic method does not affect the thermostability of the biopolymer/silica hybrids.

The dispersity of two phases between biopolymer and silica gel at nano-meter level was examined by scanning electron microscopy (SEM) measurement (Fig. 4). The chitosan/MeTMOS and lignin/APTMS hybrids prepared under microwave irradiation were transparent visibly, and the SEM images of both hybrids were homogeneous completely (Fig. 4a, c), indicating that the biopolymers are dispersed homogeneously at nano-meter level in the silica gel. In contrast, the biopolymer/silica hybrids prepared under conventional heating were also visibly transparent. However, some heterogeneous parts were observed (Fig. 4b, d). These heterogeneous parts could result from the aggregates from intermolecular hydrogen bonding in the biopolymers. These results suggest that the sol–gel reactions under microwave irradiation proceed rapidly before biopolymers are aggregated intermolecularly. In the previous reports [17, 24], urethane groups were introduced into hydroxyl groups in chitosan or lignin for homogeneous dispersion of these biopolymers in silica gel, where hydrogen bonding between carbonyl groups of urethane and residual silanol groups in silica gel played an important role on the homogeneity of the hybrids. On the other hand, in the present study, the homogeneous and transparent hybrids were obtained without introduction of the urethane groups since the aggregation of these biopolymers was inhibited by rapid sol–gel reaction of alkoxysilanes. Therefore, microwave irradiation method is very useful technique to obtain highly homogeneous hybrids as compared to conventional heating.

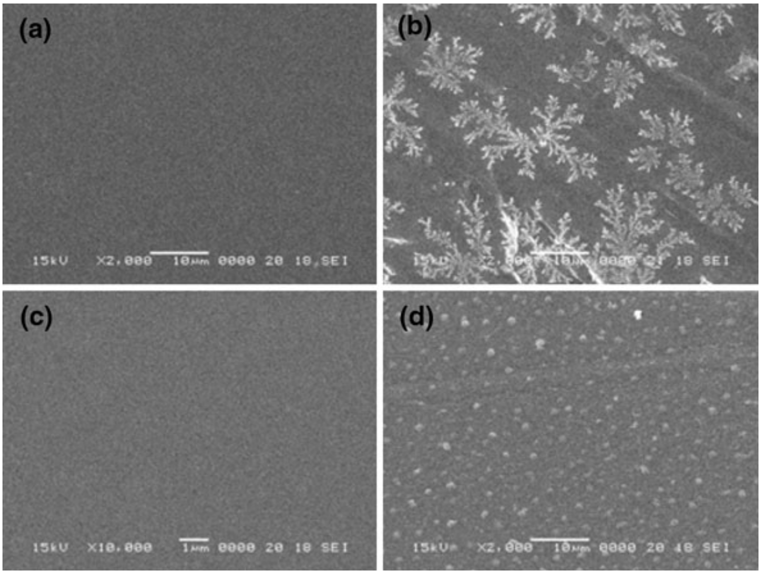
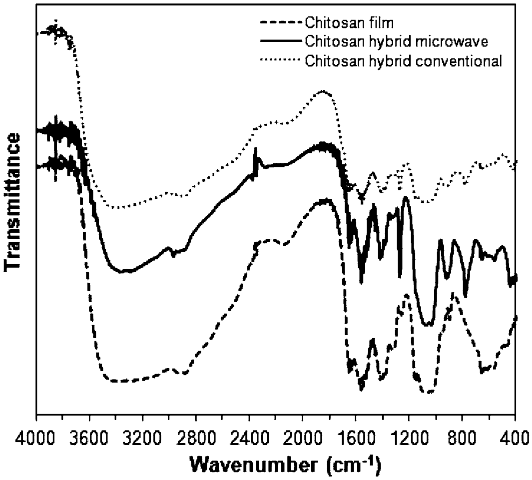


Fig. 4 SEM images of biopolymer/silica hybrids. **a** chitosan/MeTMOS = 1/5, microwave irradiation, **b** chitosan/MeTMOS = 1/5, conventional heating, **c** lignin/APTMS = 1/10, microwave irradiation, and **d** lignin/APTMS = 1/10, conventional heating

Fig. 5 FT-IR Spectra of chitosan film and chitosan/silica hybrids (chitosan/MeTMOS = 1/2)



FT-IR spectra of the obtained hybrids were measured to evaluate whether the difference of each method affected the interaction between polymer and silica matrix (Figs. 5, 6). Chitosan/MeTMOS hybrids show the peak at 3370 cm^{-1} (the stretching vibration of N–H and O–H), the peaks at 1560 and 1415 cm^{-1} (the bending vibration of the N–H and C–H moieties), the wide peak at 1070 cm^{-1} (the stretching vibration of Si–O–Si, Si–O–C, and C–O bonds), and the peaks at

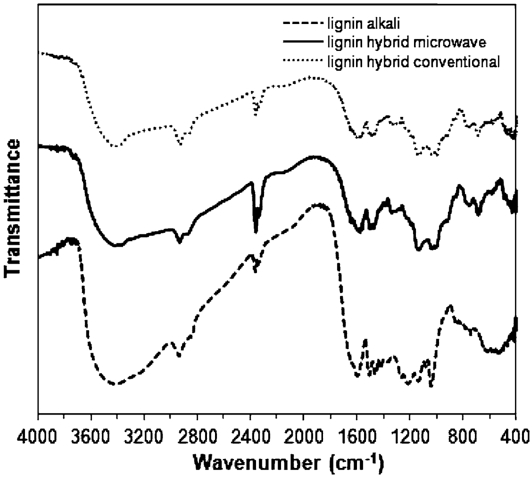


Fig. 6 FT-IR Spectra of lignin alkali and lignin/silica hybrids (lignin/APTMS = 1/2)

1271 and 779 cm^{-1} (the stretching vibrations of C–Si and the bending vibration of the C–H of CH_3–Si groups) [23]. In the case of lignin/APTMS hybrids, the strong and broad band at 3400 cm^{-1} (the stretching vibration of O–H), the peaks at 1456 cm^{-1}, 1504, and 1595 cm^{-1} (C–C stretching in aromatic rings), and the wide peak at 1000–1150 cm^{-1} (the stretching vibration of Si–O–Si, Si–O–C, and C–O bonds) were observed [27]. The spectra of the chitosan/MeTMOS hybrid and the lignin/APTMS hybrid prepared under microwave irradiation are almost identical to those prepared under conventional heating. This result indicates that the interaction between the biopolymer and silica gel was not independent of the preparative methods.

For further analysis and comparison of the nanoscale miscibility by both methods, the N_2 adsorption–desorption isotherms of the porous silica obtained from biopolymer/silica hybrids were measured. As shown in Fig. 7a, type I isotherm was observed in the porous silica obtained from the hybrids at the ratio of chitosan/MeTMOS = 1/2, indicating that chitosan is dispersed in silica matrix at a nanometer scale. The type H2 hysteresis loops, which mean the presence of mesopores [29], were slightly observed in both the porous silica obtained from the hybrids prepared under microwave irradiation and conventional heating. The surface area of the porous silica obtained from the hybrids prepared under microwave irradiation was rather larger than that prepared under conventional heating. The silica gel obtained by calcination of the hybrids prepared at the ratio of lignin/APTMS = 1/2 by both methods showed the type IV isotherm, in which the type H3 hysteresis loop was observed (Fig. 7b). This isotherm suggests that the silica adsorbent has many slit-shaped mesopores [29]. Lignin has many planar aromatic groups. Therefore, when lignin was dispersed homogeneously in the silica matrix, slit-shaped mesopores might be formed. Similarly to the case of chitosan/MeTMOS hybrids, the surface area of the silica obtained from the hybrids prepared under microwave irradiation was larger than that prepared under conventional heating. These results suggest that the nanoscale miscibility of the hybrids prepared

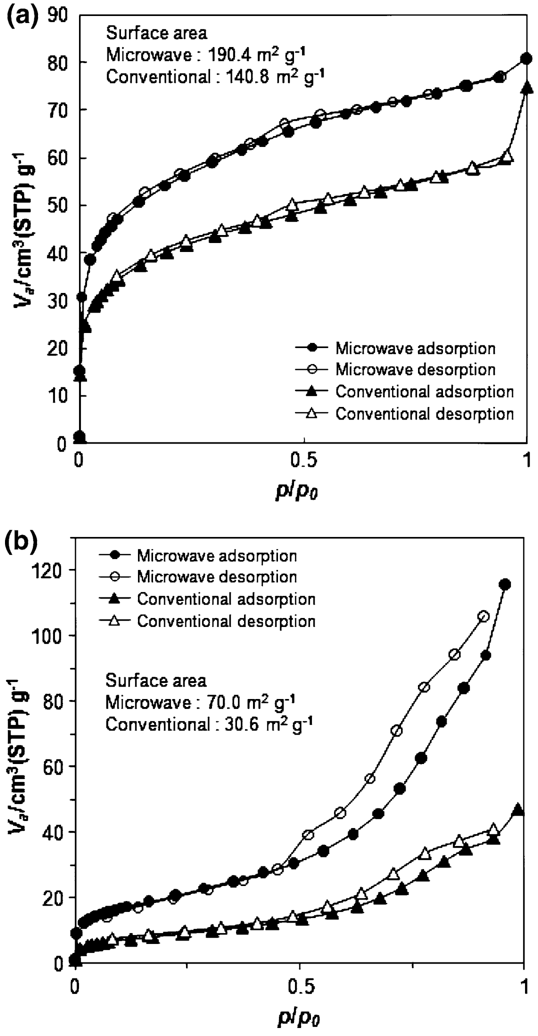


Fig. 7 N_2 absorption–desorption isotherms of porous silica obtained from **a** chitosan/silica hybrids (chitosan/MeTMOS = 1/2), and **b** lignin/silica hybrids (lignin/APTMS = 1/2)

under microwave irradiation was better than that prepared under conventional heating, supporting the results of SEM measurements.

Conclusion

In this study, chitosan/silica and lignin/silica hybrids were prepared under microwave irradiation. The rates of the sol–gel reaction and hybridization were enhanced under microwave irradiation as compared to conventional heating. The properties of the biopolymer/silica hybrids obtained by microwave irradiation were almost same as those prepared by conventional heating. However, the homogeneity of the hybrid was much improved by microwave irradiation.

Chitosan and lignin are abundant materials in nature, and microwave is an attractive energy resource for reduction of the use of fossil fuel. This study will contribute to the effective use of biomass and saving energy.

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