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Microwave Assisted Synthesis of Organic-Inorganic Polymer Hybrids

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Summary

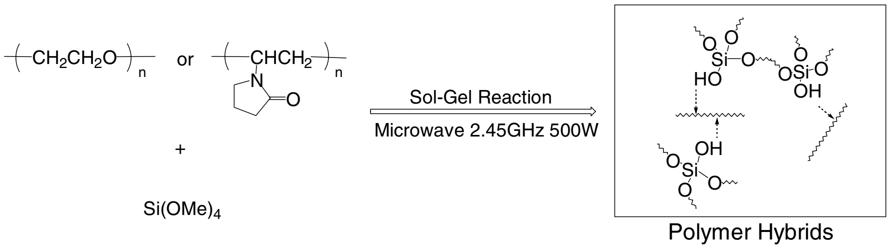
Organic-inorganic polymer hybrids from various organic polymers such as poly(ethylene oxide) and poly(*N*-vinylpyrrolidone) were prepared with the assistance of microwave heating. With the 500 W, 2.45 GHz of microwave irradiation, the formation of polymer hybrids was accelerated. The obtained polymer hybrids were optically transparent and no phase separation was observed. From the SEM images and IR spectra of the obtained polymer hybrids, the composition and the properties of the polymer hybrids synthesized with microwave heating were found to be mostly the same as that synthesized with conventional heating.

Introduction

Microwave technology has been applied to various chemical reactions [1-4]. Many review papers were published about microwave assisted chemical reactions. In most cases, the microwave was used for accelerating reactions. Microwave irradiation gives rapid energy transfer and high energy efficiency. Microwave also gives direct heating of solvents and reactants. Due to this interesting heating mechanism, which is clearly different from other conventional heating, selective heating can be accomplished and many reactions can be accelerated.

Organic-inorganic polymer hybrids have been attracting a great deal of attention because of their high performances. Various kinds of polymer hybrids prepared from organic polymer and inorganic materials such as silica gel, have been investigated [5-11]. Generally, the polymer hybrids have high performances especially in the field of thermal stability, mechanical property and so on. Sol-gel method is one of the most useful methods to prepare such hybrid materials [12]. The polymer hybrids can be prepared by the sol-gel reaction of alkyl silicate in the presence of organic polymer when the appropriate interaction exists between organic moiety and inorganic one. In our previous research, various interactions such as covalent bonding, hydrogen bonding interaction and aromatic interaction between organic polymers and silica matrix were utilized for nano-ordered combination of the two moieties. For example, poly(*N*-vinylpyrrolidone), poly(2-methyl-2-oxazoline), and poly(*N*,*N*-dimethylacrylamide) were hybridized with silica gel utilizing hydrogen bonding interaction.

Polystyrene-silica hybrids utilizing π-π interaction and ionic interaction were reported [13,14]. Besides, the preparation of polymer hybrids utilizing various stimuli has been also investigated. Preparation of the organic-inorganic polymer hybrids under various stimuli can give different materials compared to that prepared without stimuli due to the different preparation conditions. In various stimuli such as UV and heat, the homogeneity of the polymer hybrid was controlled by photodimerization reaction and Diels-Alder reaction [15,16]. Here, the microwave heating was applied to the preparation of the organic-inorganic polymer hybrids. Sol-gel reaction is also accelerated by microwave irradiation. Clark et al. reported the microwave irradiated sol-gel reaction of alkoxysilane and they report that the microwave accelerated the sol-gel reaction of tetraethoxysilane and the decreased the pore radius [17]. In this paper, the preparation speed and the properties of the polymer hybrids prepared with microwave irradiation are reported.



Scheme 1. Microwave assisted preparation of polymer hybrids.

Experimental

Materials

Tetramethoxysilane (TMOS) was distilled and stored under nitrogen atmosphere. Methanol was distilled over magnesium methoxide and stored under nitrogen atmosphere. Other reagents were used as supplied. Poly(*N*-vinylpyrrolidone) (PVP) (MW. av. 630,000) was purchased from Tokyo Kasei Kogyo Co., Ltd. Poly(acrylic acid) (PAA) (MW. av. 25,000) was purchased from Wako Pure Chemical Industries, Ltd. Poly(ethylene oxide) (PEO) (MW. av. 8,000) and poly(vinylidene fluoride) (PVdF) (MW. av. 180,000) were purchased from Sigma-Aldrich Co., Ltd. Poly(vinyl alcohol) (PVA) (MW. av. 22,000) was purchased from Nacalai Tesque, Inc.

Measurements

Scanning electron microscopy (SEM) measurements were conducted using a JEOL JSM-5600 system. Fourier transform infrared (FT-IR) spectra were recorded on a Prekin Elmer 1600 infrared spectrometer. Nitrogen absorption porosimetry was conducted with 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 200 °C for 2 h at reduced pressure under nitrogen atmosphere. Surface areas were calculated with BET equation equipped on the apparatus in the range of 0.05 to 0.30 (p/p_0) and the pore size distribution was calculated by MP method equipped on the apparatus. X-ray diffraction (XRD) analyses were performed by a Rigaku Miniflex system.

Microwave irradiation

Microwave irradiation experiments were performed using a microwave oven (Matsushita NE-NS70), equipped with a magnetron (2.45 GHz, 500 W). The reaction was carried out in a PTFE beaker at the center of the microwave oven.

Preparation of polymer hybrids

Prescribed amount of organic polymer was dissolved in appropriate solvent and TMOS was added. The mixture was stirred for 1 h followed by the addition of acidic water. For the microwave heating, the solution was poured into PTFE beaker. To the solution, 2.45 GHz, 500 W microwave was irrardiated for 5 min with the allowance of the solvent evaporation. After microwave irradiation, the glassy polymer hybrid was collected. For the conventional heating, the solution was poured into plastic container and this container was put into a 100 °C oven for 1 h with the allowance of the solvent evaporation. The obtained polymer hybrids were subjected to further analyses.

Results and discussion

The polymer hybrids were synthesized by utilizing the sol-gel reaction of TMOS in the presence of the organic polymer. Poly(*N*-vinylpyrrolidone) (PVP) was used as an organic polymer and methanol was used as a solvent. The polymer hybrids were prepared under 500 W, 2.45 GHz microwave irradiation. The polymer hybrids under conventional heating were prepared in an oven at 100 °C. The amount of PVP was altered from 0.1 g to 0.9 g and the amount of TMOS was also altered from 1.8 ml to 0.2 ml respectively (Table 1). Under microwave irradiation, the dried polymer hybrid films were obtained within 5 min in comparison with 1 h for conventional heating. In all cases of the obtained polymer hybrids were optically transparent and homogeneous even under microwave irradiation. Figure 1 shows the SEM images of the obtained polymer hybrids prepared under conventional heating and microwave irradiation at the ratio of PVP to TMOS, 1 to 2 (Run 3). In both samples, no image of significant phase separation was observed and both samples were homogeneous in this range. In this case, the difference of the heating method gave no significant difference in homogeneity of the obtained polymer hybrids.

Table 1. Preparation of PVP-silica hybrids

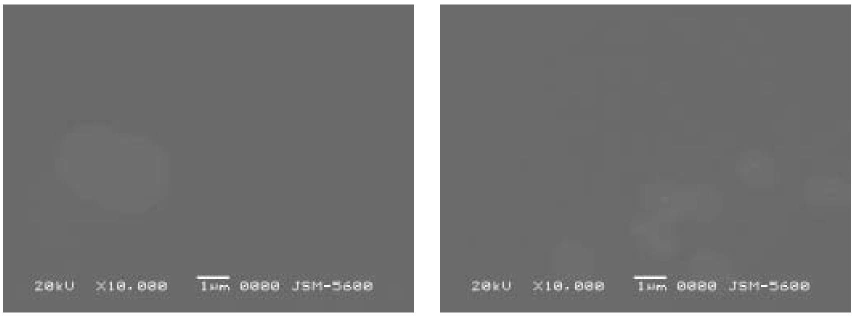
Run	PVP (g)	MeOH (ml)	TMOS (ml)	0.1M HClaq (ml)	Stirring time (h)	Appearance	
						mw a)	100°C b)
1	0.1	10	1.8	0.9	1	○	○
2	0.2	10	1.6	0.8	1	○	○
3	0.5	10	1.0	0.5	1	○	○
4	0.8	10	0.4	0.2	1	○	○
5	0.9	10	0.2	0.1	1	○	○

○:Transparent

a) Microwave heating for 5 min.

b) Conventional heating at 100°C for 1 h.

FT-IR measurement of these polymer hybrids was conducted to confirm the interaction between silanol groups and PVP (Figure 2). It was already reported that the hydrogen bonding interaction between PVP and silanol groups in the polymer hybrids prepared under conventional heating. Also in the case of the polymer hybrid prepared under microwave irradiation, the $\nu_{C=O}$ band was shifted to lower wavenumber region. This result indicates that even under microwave irradiation, the hydrogen bonding interaction affects the homogeneity dispersion of PVP in a silica matrix.



(a) (b)

Figure 1. SEM images of PVP-silica polymer hybrids. (a) Microwave assisted. (b) Prepared by conventional heating at 100 °C.

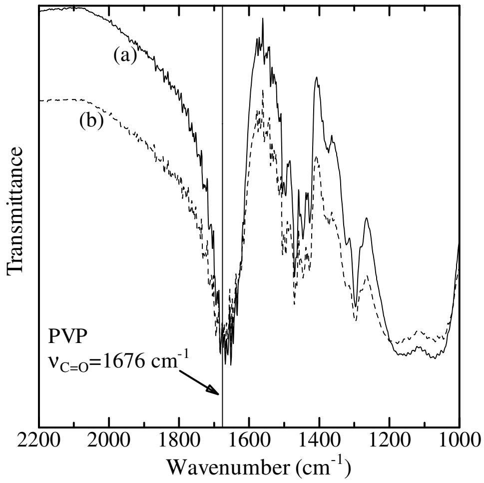


Figure 2. IR spectra of PVP-silica polymer hybrids. (a) Microwave assisted. (b) Prepared by conventional heating at 100 °C.

Pore radius and surface area of the porous silica after calcination of the obtained polymer hybrids were estimated by nitrogen absorption measurement. Table 2 shows these results of the porous silica after calcination of the obtained polymer hybrids at 600 °C for 24 h for removal of the organic moieties. In both cases of microwave heating and conventional heating, the pore radius increased with an increase of the organic content. The surface area was also increased with an increase of organic

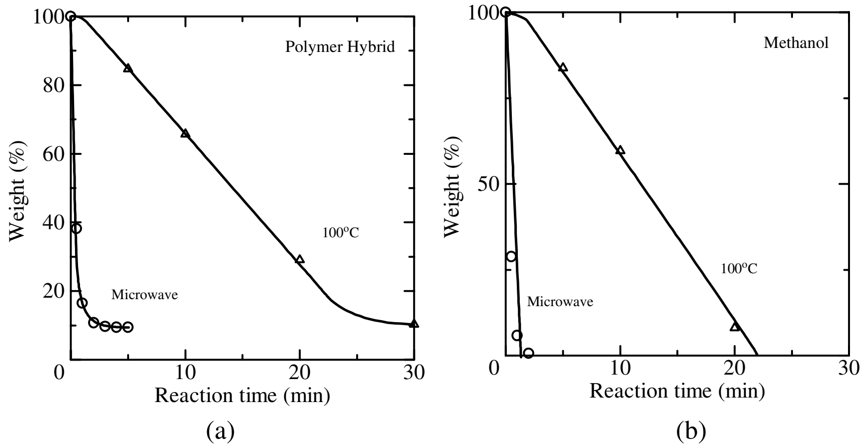
Table 2. Pore size and surface area of the porous silica after calcinations of PVP-silica hybrids

Run	PVP	TMOS	Pore radius (nm)		Surface area (m^2g^{-1})	
	(g)	(ml)	mw$^{a)}$	100°C$^{b)}$	mw$^{a)}$	100°C$^{b)}$
1	0.1	1.8	0.35	0.35	227.8	241.4
2	0.2	1.6	0.39	0.39	279.6	226.6
3	0.5	1.0	0.53	0.56	282.8	328.1

a) Microwave heating for 5 min.
b) Conventional heating at 100°C for 1 h.

content. No significant difference was observed in pore radius and surface area between microwave heating and conventional heating.

Figure 3a shows the weight changes during the preparation of the polymer hybrids. In both cases of microwave heating and conventional heating, the weight change curves are very similar to those of only methanol (Figure 3b). This result indicates that the evaporation of methanol was accelerated by microwave irradiation. With a concern about previous paper Clark et al. wrote[17], the sol-gel reaction should be accelerated by microwave irradiation. In addition to this, the improvement of the preparation rate should also depend on the increase of alkoxysilane concentration due to the evaporation of the solvent. Because the rate of condensation of alkoxysilanes was affected by the concentration.



(a) (b)

Figure 3. Weight changes during the preparation of the polymer hybrids with microwave irradiation (circle) and conventional heating (triangle). (a) Polymer hybrid solution after 1 h stirring. (PVP, TMOS, methanol and acidic water) (b) Methanol.

The polymer hybrids from various polymers were prepared under microwave irradiation and conventional heating. Poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA) and poly(vinylidene fluoride) (PVdF) were used as organic polymers. Methanol, water, *N*,*N*-dimethylformamide and dimethyl sulfoxide were used as solvents. All these solvents are highly microwave absorptive solvents.

As shown in Table 3, in the case of PEO and PVA, the transparent polymer hybrids were obtained in both cases under microwave irradiation and conventional heating. On the other hand, only turbid materials were obtained under any conditions when PAA or PVdF was used as an organic polymer. In all cases with microwave irradiation, dried gel was obtained within 5 min compared to the conventional heating for 1 week. PEO and PVA can provide hydrogen bonding interaction between organic polymer and silanol group, but such interaction between silanol group and PAA or PVdF is known to be very weak. This might give only turbid materials when PAA or PVdF was used as an organic polymer. These results suggest that even with microwave irradiation, interactions between organic polymer and silica matrix play an important role for the homogeneous dispersion of organic polymer and silica gel.

Table 3. Microwave assisted preparation of polymer hybrids from various polymers

Run	Polymer (g)		Solvent(ml)		TMOS (ml)	0.1M HClaq (ml)	Stirring time (h)	Appearance	
								mw$^{a)}$	60°C$^{b)}$
6	PVP	0.5	MeOH	10	1.0	0.5	2	○	○
7	PEO	0.5	MeOH	10	1.0	0.5	2	○	○
8	PVA	0.1	H_2O	10	1.0	0.5	2	○	○
9	PAA	0.1	H_2O	10	1.0	0.5	2	×	×
10	PVdF	0.1	DMF	10	1.0	0.5	2	×	×
11	PVdF	0.1	DMAc	10	1.0	0.5	2	×	×

○:Transparent ×:Turbid

a) Microwave heating for 5 min.

b) Conventional heating at 60°C for 1 week.

The homogeneous dispersion of PEO in the polymer hybrid prepared with microwave irradiation was evaluated by X-ray diffraction (XRD) measurements. PEO is known as a crystalline polymer and it has crystalline phase at ambient temperature. Figure 4 shows XRD patterns of PEO and PEO-silica polymer hybrid (Run 7) prepared by microwave heating. The PEO-silica polymer hybrid shows only broad amorphous

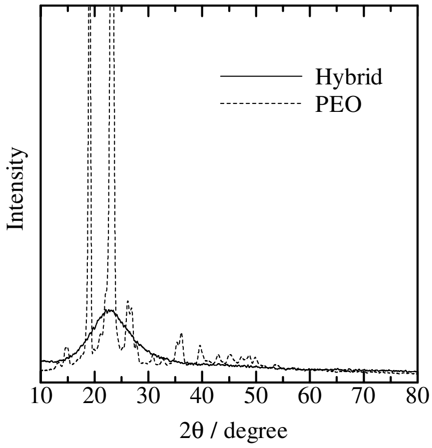


Figure 4. XRD patterns of PEO and PEO-silica polymer hybrid prepared by microwave heating.

halos (2θ=20-30) derived from homogeneously amorphous polymer hybrid, for PEO shows crystal structure diffraction pattern. This indicates that PEO in the polymer hybrid is amorphous state. This result suggests the homogeneous dispersion of PEO in the polymer hybrid.

Conclusion

Transparent organic-inorganic polymer hybrids from PVP, PEO and PVA were prepared under microwave irradiation within 5 min. FT-IR spectra reveal that even with microwave irradiation, the interactions such as hydrogen bonding interaction play an important role for homogeneous dispersion of organic polymers in a silica matrix. The preparation speed was much increased due to an increase of evaporation of the solvents and accelerated sol-gel reaction of TMOS. Interestingly, the homogeneity of the obtained polymer hybrids was almost same as that prepared under conventional heating even though the preparation speed was increased.

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