

Formation of Macroporous Organic-Inorganic Polymer Hybrids Using Tea Extract

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ABSTRACT: Macroporous organic-inorganic polymer hybrids were prepared from poly(vinyl pyrrolidone), and inorganic alkoxides. To a reaction mixture of poly(vinyl pyrrolidone) and tetramethoxysilane, extract from tea leaves and HCl aqueous solution in methanol were added. The resulting mixture was constantly stirred at room temperature for 1 h and heated at 60°C for two weeks. Consequently, the corresponding polymer hybrid became a

macroporous material having a pore size from 3.26 to 20.86 μm . We succeeded in finding that the pruned tea leaves were able to utilize the synthesis of novel macroporous materials. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 926–931, 2011

Key words: composites; macroporous polymers; polyamides

INTRODUCTION

Tea is a very popular beverage and about 2.5 million tons of tea are produced in the world every year. Tea leaves contain tea polyphenols, tea caffeine, amino acids, saponins, tannins, etc., with about 10–30% (w/w) polyphenols and 2–4% (w/w) caffeine.¹ Tea polyphenols isolated from tea leaves are natural antioxidants, and have an anticarcinogenic effect.² Moreover, tea polyphenols have antibacterial activity.^{3,4} Generally, in tea cultivation, after picking tea leaves, tea plants are maintained by pruning the tea leaves and branches. The tea leaves and branches which were pruned are usually discarded into the corner of the tea garden. Since these discarded leaves and branches contain many nitrogen components, they may be effective as manure. However, on the other hand, these leaves and branches make the tea garden fertile more than required. Furthermore, the nitrogen component which overflows from the tea garden pollutes groundwater, ponds, etc.⁵ Pruned tea leaves are generally treated as waste and our aim is to use them as valuable resources. Many polyphenols are likely to be contained in the pruned tea leaves. In fresh tea leaves and green teas, catechins are the major polyphenols and are mainly composed of (–)-epicatechin, (–)-epigallocatechin, (–)-epicatechin gallate, and (–)-

epigallocatechin gallate.¹ (–)-Epicatechin, which is a major polyphenol, is soluble in ethyl acetate, acetone, methanol, and water. It is expected from the dissolution behavior of (–)-epicatechin that tea polyphenols have amphiphilic property. Alkyltrimethylammonium salts have been used as a surfactant for the preparation of mesoporous silicates.⁶ Tea polyphenols may be effective as a surfactant for the preparation of porous materials. Many interesting porous inorganic oxides based on the sol-gel reaction have been reported.⁷ Compared with the use of inorganic oxide independent materials, it is easy to control the properties of organic-inorganic polymer hybrid materials by changing organic or inorganic compounds. The organic-inorganic polymer hybrids from organic polymers and inorganic alkoxides are very interesting materials.^{8–10} Polymer hybrids are prepared by the sol-gel reaction in the presence of an organic polymer. Thus, it enables the introduction of organic elements into inorganic materials without deteriorating their functionalities. A novel polymer material using tea may be created by utilizing the properties of polymer hybrids. Until now, there have been many materials and products which utilized the properties which tea polyphenols have such as antibacterial property. From such a background, to examine the possibility of effective using a vast quantity of tea leaves which would ordinarily be thrown away, we tried to develop a novel porous polymer material using the extract from tea leaves without considering the other properties of tea such as antibiotic properties, etc. Herein, a novel porous organic-inorganic polymer hybrid material using a tea extract by utilizing the property of organic-inorganic polymer hybrid materials is reported.

Additional Supporting Information may be found in the online version of this article.

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EXPERIMENTAL

Materials

Poly(vinyl pyrrolidone) (PVP), tetraisopropyl titanate ($\text{Ti}(\text{OPr}^i)_4$), tetramethoxysilane ($\text{Si}(\text{OMe})_4$), and caffeine were purchased from Tokyo Chemical Industry Co., Ltd. Catechin 40B was purchased from Shirai-matsu Pharmaceutical Co., Ltd. (catechin content is above 40%). Saponin was purchased from Tokyo Chemical Industry Co., Ltd. All other solvents and reagents were purchased from Wako Pure Chemical Industries, Ltd.

Preparation of tea extract

The tea extract was prepared by modifying the method used in reported procedure.¹ Microwave irradiation was performed using a SANYO EMO-FZ40, equipped with a magnetron (2.45 GHz, 500 W). Green tea leaves (1.00 g) from the Ohkubo tea garden (Shizuoka, Japan) were mixed with ethanol (20 mL). The suspension was irradiated for 30 s (100 W). The resulting suspension was filtrated. The obtained filtrate was used as a tea extract with ethanol. When the 20 mL of tea extract was evaporated, 8.8 mg of a nonvolatile solid was obtained.

Preparation of catechin extract

Microwave irradiation was performed using a SANYO EMO-FZ40, equipped with a magnetron (2.45 GHz, 500 W). Catechin 40B (1.00 g) was mixed with ethanol (20 mL). The suspension was irradiated for 30 s (100 W). The resulting suspension was filtrated. The obtained filtrate was used as a catechin 40B extract with ethanol.

Preparation of organic-inorganic polymer hybrids

PVP (0.50 g) was dissolved in 20 mL of methanol with $\text{Ti}(\text{OPr}^i)_4$ (1.81 g) or $\text{Si}(\text{OMe})_4$ (1.27 g), and 0.1M aqueous HCl solution (10 equiv to alkoxy-silane). After being stirred at room temperature for 1 h, the mixture was placed in a polypropylene vessel covered with a wiping paper and left in air at 60°C for two weeks. The obtained polymer hybrid was dried *in vacuo* at 60°C for two days.

Preparation of tea extract-incorporated organic-inorganic polymer hybrids (typical procedure)

PVP (0.50 g) was dissolved in 20 mL of methanol with $\text{Ti}(\text{OPr}^i)_4$ (1.81 g) or $\text{Si}(\text{OMe})_4$ (1.27 g), tea extract (5 mL) and 0.1M aqueous HCl solution (10 equiv to alkoxy-silane). After being stirred at room temperature for 1 h, the mixture was placed in a

polypropylene vessel covered with a wiping paper and left in air at 60°C for two weeks. The obtained polymer hybrid was dried *in vacuo* at 60°C for two days.

Preparation of additive-incorporated organic-inorganic polymer hybrids

PVP (0.50 g) was dissolved in 20 mL of methanol with $\text{Si}(\text{OMe})_4$ (1.27 g), caffeine (2.2 mg), or saponin (2.2 mg or 50.3 mg), and 0.1M aqueous HCl solution (10 equiv to alkoxy-silane). After being stirred at room temperature for 1 h, the mixture was placed in a polypropylene vessel covered with a wiping paper and left in air at 60°C for two weeks. The obtained polymer hybrid was dried *in vacuo* at 60°C for two days.

Preparation of catechin-incorporated organic-inorganic polymer hybrids

PVP (0.50 g) was dissolved in 20 mL of methanol with $\text{Si}(\text{OMe})_4$ (1.27 g), catechin extract (5 mL), and 0.1M aqueous HCl solution (10 equiv to alkoxy-silane). After being stirred at room temperature for 1 h, the mixture was placed in a polypropylene vessel covered with a wiping paper and left in air at 60°C for two weeks. The obtained polymer hybrid was dried *in vacuo* at 60°C for two days.

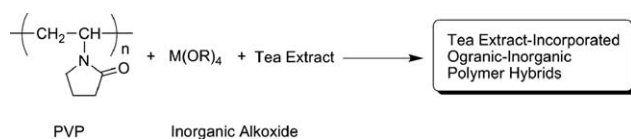
Measurements

The morphology of the obtained organic-inorganic polymer hybrids was observed using a JEOL JSM-5310LV scanning electron microscope (SEM) system. Thermogravimetric analysis (TGA) was performed using a TG/DTA200, SEIKO Instruments, Inc., with heating rate of 10°C min⁻¹ in air. The FT-IR spectra were obtained on a JASCO FT/IR-4200 infrared spectrometer. Nitrogen adsorption porosimetry was conducted with BEL Japan Inc.

RESULTS AND DISCUSSION

The tea extract-incorporated organic-inorganic polymer hybrids were prepared via an acid-catalyzed sol-gel reaction of $\text{Ti}(\text{OPr}^i)_4$ or $\text{Si}(\text{OMe})_4$ in the presence of the organic polymer by a modification of Chujo's protocol.¹¹ PVP was used as the organic polymer and methanol was used as the solvent. PVP was dissolved in methanol with inorganic alkoxides, 0.1M HCl aqueous solution (1.5 mL), and tea extract (Scheme 1).

Irrespective of the use of tea extract, the polymer hybrids from $\text{Ti}(\text{OPr}^i)_4$ were transparent and homogeneous as shown in Table I (Runs 1-2). In the case of the polymer hybrids from $\text{Si}(\text{OMe})_4$, a transparent



Scheme 1 Synthetic scheme of tea extract-incorporated organic-inorganic polymer hybrids.

and homogeneous polymer hybrid was obtained without tea extract (Table I, Run 3). On the other hand, when the tea extract was used, the transparent and homogeneous polymer hybrid was not obtained (Table I, Run 4).

As shown in Figure 1, the polymer hybrid prepared from $\text{Ti(OPr}^i)_4$ showed no recognizable segregation at this level in the SEM image [Fig. 1(a,b)]. Also, in the case of the polymer hybrids from Si(OMe)_4 , the polymer hybrid showed no recognizable segregation at this level in the SEM image [Fig. 1(c)]. Generally, in the case of polymer hybrid synthesis, turbid materials almost showed phase separation of silica and the organic polymer. However, when the sample was prepared from PVP and Si(OMe)_4 with tea extract, silica domains could not be found in a micron order on the surface of the sample. Moreover, spherical pores 3.26–20.86 μm in diameter were observed in sample sections [Fig. 1(d)]. (Tea extract and catechin 40B extract were prepared with water. These extracts were added into the reaction mixture of polymer hybrids, respectively. As a result, in the case of tea extract prepared with water, we could not obtain macroporous polymer hybrids. On the other hand, in the case of catechin 40B extract prepared with water, we could obtain macroporous polymer hybrids. Catechin 40B was manufactured by using only water and ethanol. Therefore, catechin 40B might contain some soluble components which can be dissolved in water and ethanol. However, the tea extract prepared with water might contain water-soluble components which were not present in catechin 40B. Generally, tea leaves contain many compounds such as catechin-related compounds, caffeine, amino acids, saccharides, vitamins, chlorophylls, minerals, and so on. In the case of tea extract prepared with water, the extract might contain the water soluble compounds such as amino acids, saccharides, water-

soluble vitamins, minerals, among others. It seems that the macroporous polymer hybrids were not obtained by the influence of these water-soluble compounds.) On the other hand, BET measurements showed that there are a few pores in the tea extract-incorporated PVP- SiO_2 polymer hybrid (Range: 0.15–100 nm). In the magnified curve of pore-distribution (Supporting information Fig. S2), a few pores 1.72 nm in diameter were observed. Toki et al. reported that a few pores existed to the PVP- SiO_2 polymer hybrid prepared by the conventional method (diameter size 2.0 nm).¹² It is supposed that the tea extract-incorporated PVP- SiO_2 polymer hybrid has almost the same pore-distribution which was reported by Toki et al., i.e., below 100 nm. The obtained sample should originally be transparent and homogeneous. However, since the obtained sample had a large number of spherical macropores, it might become turbid. When a high reactivity alkoxide such as $\text{Ti(OPr}^i)_4$ was used, a transparent and homogeneous polymer hybrid was obtained. Therefore, an alkoxide such as Si(OMe)_4 having moderate reactivity might have to be employed to synthesize macroporous polymer hybrids.

The polymer contents calculated were almost the same as that measured from TGA in the polymer hybrids prepared from PVP and inorganic alkoxides. In contrast, in the polymer hybrids using the tea extract, T_{d10} was shifted to a higher temperature. These results suggest that thermal stability slightly increased when tea extract was used (Table I). That is, the restriction of the molecular motion of PVP which resulted from the hydrogen-bonding interaction between PVP and tea polyphenols containing tea extract might increase the thermal stability of the obtained polymer hybrids.

The FT-IR spectra of the PVP- TiO_2 polymer hybrid (Run 1) and the tea extract-incorporated PVP- TiO_2 polymer hybrid (Run 2) are shown in Figure 2(a). The IR spectrum of PVP- TiO_2 polymer hybrid showed an absorption band at 1650.8 cm^{-1} based on the C=O stretching frequency. In the IR spectrum of the tea extract-incorporated PVP- TiO_2 polymer hybrid, this absorption band was observed at 1650.8 cm^{-1} . The C=O stretching frequency at 1650.8 cm^{-1} was almost unaffected by the use of tea extract. In contrast with the polymer hybrids prepared from

TABLE I
Preparation of Organic-Inorganic Polymer Hybrids

Run	PVP (g)	M(OR) ₄		Tea extract (mL)	Appearance	Ceramic yield (%)			T _{d10} (°C)
		M, R	(g)			Obs.	Calc.	Obs./Calc.	
1	0.501	Ti, Pr ⁱ	1.815	0	Transparent	45.0	50.4	89.3	309.5
2	0.494	Ti, Pr ⁱ	1.813	5	Transparent	50.1	50.8	98.6	315.4
3	0.505	Si, Me	1.263	0	Transparent	50.3	49.7	101.2	366.6
4	0.502	Si, Me	1.261	5	Turbid	49.1	49.8	98.6	367.2

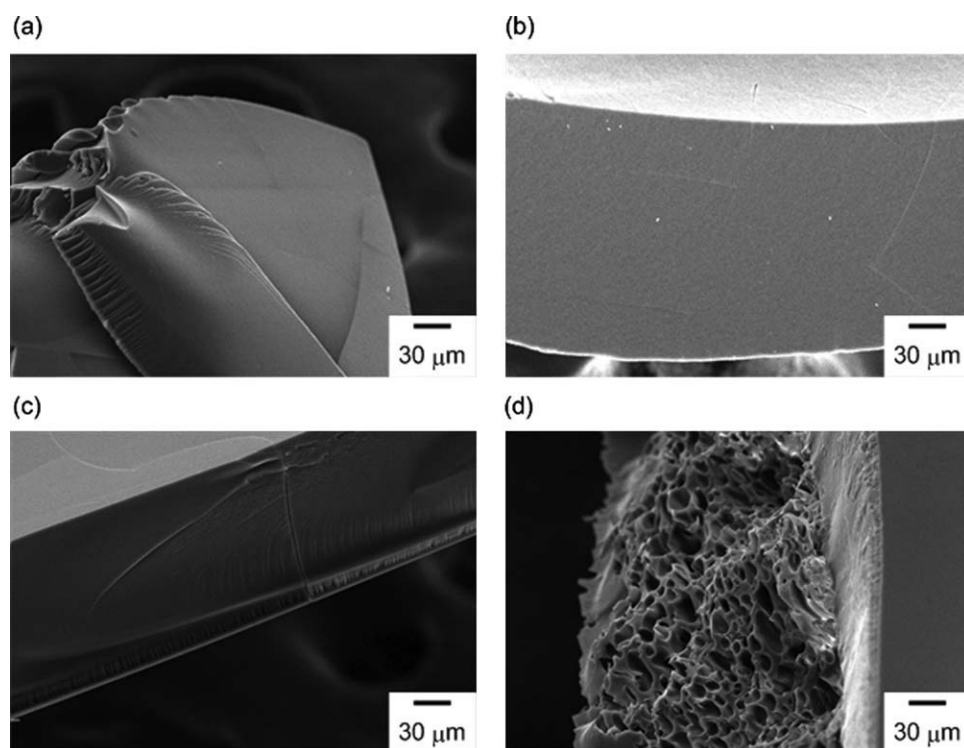


Figure 1 SEM images of (a) the PVP-TiO₂ polymer hybrid (Run 1), (b) the tea extract-incorporated PVP-TiO₂ polymer hybrid (Run 2), (c) the PVP-SiO₂ polymer hybrid (Run 3), and (d) the tea extract-incorporated PVP-SiO₂ polymer hybrid (Run 4).

Ti(OPr)₄, the C=O stretching vibration of PVP-SiO₂ polymer hybrids shifted to a lower frequency from 1662.3 to 1660.4 cm⁻¹ by use of tea extract. These results may indicate the existence of a hydrogen-bonding interaction between the carbonyl group of PVP and the silanol group of SiO₂ or the components of the tea extract [Fig. 2(b)]. Moreover, the C=O stretching vibration of PVP-TiO₂ polymer hybrid systems shifted to a lower frequency than PVP-SiO₂ polymer hybrid systems. Accordingly,

the hydrogen-bonding interaction might mainly be formed between PVP and TiO₂ in the PVP-TiO₂ polymer hybrids. In other words, a hydrogen-bonding interaction might be unable to form between PVP and tea extract in this system. These results may indicate that since the complex was formed between PVP and tea polyphenols containing tea extract via hydrogen bonding, the complex might change the property of PVP from hydrophilic to hydrophobic. Therefore, in the case of tea extract-

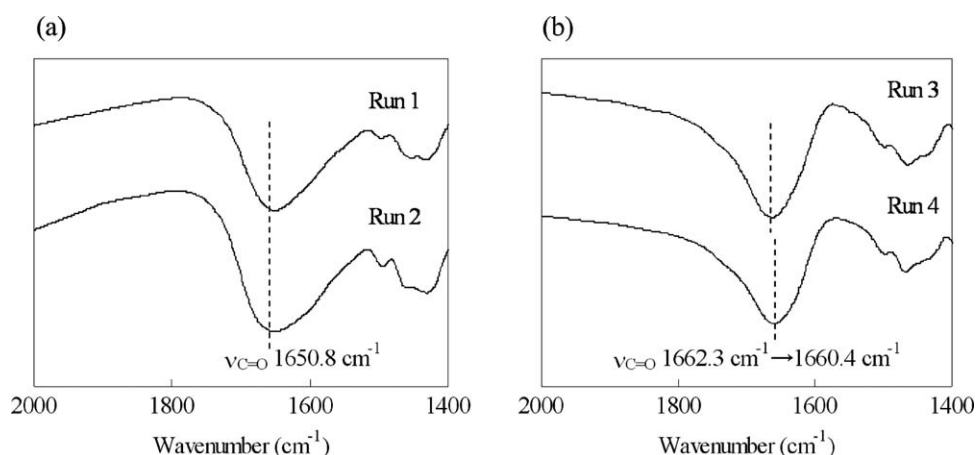
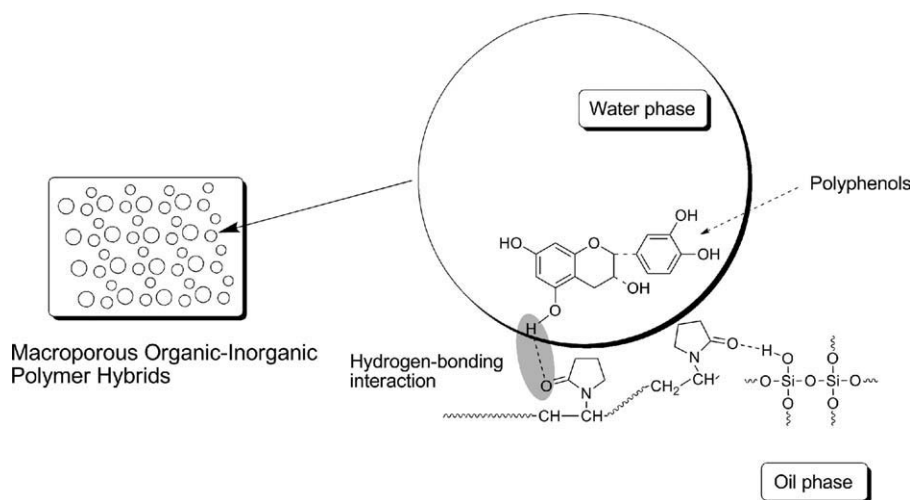


Figure 2 FT-IR spectra of (a) the PVP-TiO₂ polymer hybrid (Run 1), and the tea extract-incorporated PVP-TiO₂ polymer hybrid (Run 2), (b) the PVP-SiO₂ polymer hybrid (Run 3), and the tea extract-incorporated PVP-SiO₂ polymer hybrid (Run 4).



Scheme 2 Schematic drawing of the plausible formation of the pores.

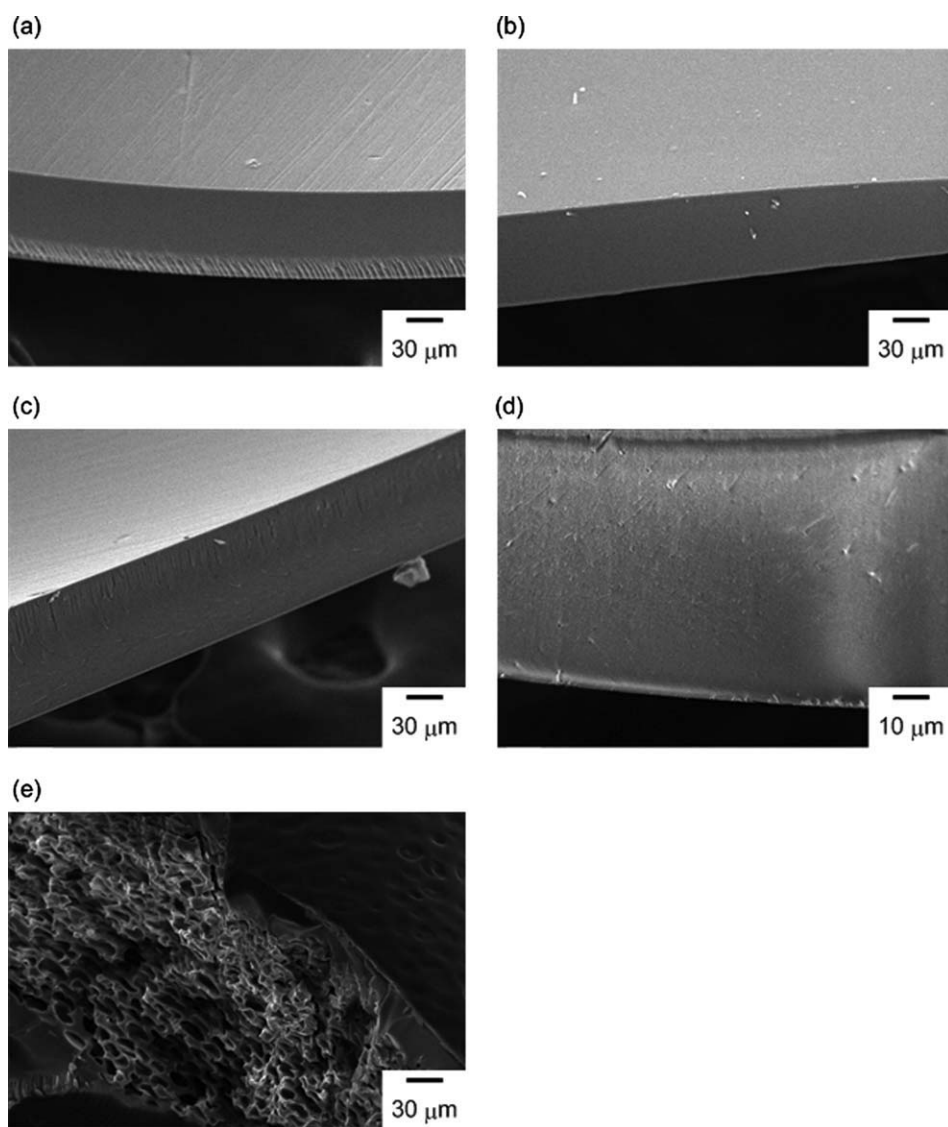


Figure 3 SEM images of (a) the caffeine-incorporated PVP-SiO₂ polymer hybrid (caffeine content: 0.2%), (b) the saponin-incorporated PVP-SiO₂ polymer hybrid (saponin content: 0.2%), (c) the saponin-incorporated PVP-SiO₂ polymer hybrid (saponin content: 5.0%), (d) the saponin-incorporated PVP-SiO₂ polymer hybrid (magnification of Fig. 3c), and (e) the catechin-incorporated PVP-SiO₂ polymer hybrid.

incorporated PVP-SiO₂ polymer hybrid, water in oil phase (W/O) droplets might be formed in the PVP, tea extract, Si(OMe)₄, methanol and 0.1M HCl aqueous solutions (Scheme 2). After the formation of polymer hybrids, interconnected macropores could be formed by eliminating water from bulk polymer hybrids.

The additive-incorporated polymer hybrids were synthesized by using a component included in the tea extract as an additive. In the case of caffeine-incorporated polymer hybrid (caffeine content: 0.2%), the pores were not recognized in SEM observation [Fig. 3(a)]. Also, in the case of saponin-incorporated polymer hybrid (saponin content: 0.2%), the pores were not recognized [Fig. 3(b)]. However, in the case of saponin-incorporated polymer hybrid (saponin content: 5.0%), the pores were slightly recognized [Fig. 3(c,d)]. Generally, saponin has a foaming property and can be emulsified. These properties of saponins might be correlated with the spherical pores formation of the polymer hybrids. In similar manner, the catechin-incorporated polymer hybrid was synthesized from PVP, Si(OMe)₄, and catechin extract. In the SEM observation of the obtained catechin-incorporated polymer hybrid, spherical pores were observed in sample sections [Fig. 3(e)]. This result suggested that the polyphenols such as catechin were deeply related to the spherical pores formation of the polymer hybrids.

CONCLUSIONS

The tea extract-incorporated polymer hybrid prepared from PVP, Si(OMe)₄, and tea extract became a macroporous polymer hybrid. The macroporous

polymer hybrid had a pore size between 3.26 and 20.86 μm. The hydrogen-bonding interaction may be related to the formation of the macroporous polymer hybrid. Usually, pruned tea leaves are thrown away as waste. However, we found out that a novel macroporous material can be synthesized using the pruned tea leaves. Also, we succeeded to develop a novel porous polymer material using the extract from tea leaves without considering the other properties of tea such as antibiotic properties, etc. From environmental science viewpoint, we believe that tea extract is potentially applicable to synthesize novel porous materials.

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