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Stabilization of poly(vinyl chloride) using iodine vapor for preparing carbon aerogels

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Carbon aerogels are promising materials for various applications such as electric double-layer capacitors, chromatographic packing and catalyst supports [1–3]. The classical version of the carbon aerogels is produced through three steps: sol-gel polycondensation of resorcinol with formaldehyde in an aqueous solution, supercritical drying with carbon dioxide and high-temperature heat-treatment in an inert atmosphere [4, 5]. Recently, the present authors have produced carbon aerogels from a solution of poly(vinyl chloride) (PVC) through a novel method in which the sol-gel transformation has been carried out based on dehydrochlorination using a strong organic base [6]. The advantages of this method over the classical one are the wider controllable range of porous structure and the shorter preparation period due to the avoidance of the solvent exchange process prior to the supercritical drying.

For the conversion of the PVC-based organic aerogels into the carbon aerogels without causing large mass loss and fusion, it is especially important to enhance the thermal stability of the organic aerogels, and a stabilization treatment should be aplied prior to carbonization. In the previous study, the stabilization has been carried out via the low-temperature heat-treatment in air and the influences of the stabilization conditions on the structure of the PVC-based carbon aerogels have been reported [6]. It is well known that the atmosphere of the stabilization significantly influences the carbonization behavior of the organic compounds and the resulting carbon structure [7–11]. For the conversion of coal tar pitches into carbons, the use of iodine vapor as the stabilization atmosphere is exceedingly effective to increase the carbon yield [9–11]. In the present study, iodine vapor was used as the stabilization atmosphere for preparing the PVC-based carbon aerogels, and the differences of the carbonization behavior between the aerogels stabilized in air and iodine vapor were investigated.

The organic aerogel was prepared from PVC according to the procedure described in the previous paper [6]. Three types of PVC powder with the number-average molecular weights (M_n) of 22 000, 47 000 and 82 000 were used as the starting polymer. PVC powder was dissolved in dimethylformamide (DMF) and the dehydrochlorinating agent, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) was dropped into the polymer solution with the solution kept stirred. The molar ratio of DBU against chlorine atom in PVC (DBU/Cl) was adjusted to 1.0 or 2.0 since the pore volume in the organic aerogels can be maximized at these values. The concentration of PVC in the PVC/DMF/DBU mixture ([PVC]) was varied in the range of 2.5–15.0 wt%. The results which will be shown below were obtained for DBU/Cl = 2.0, [PVC] = 5.0 wt% and $M_n = 22\,000$ unless otherwise stated. For promoting dehydrochlorination, the mixture, encapsulated in a glass tube, was heated at 30, 50 and 70 °C successively for 24 h each. Immediately after this heat-treatment was started, the PVC/DMF/DBU mixture changed from colorless to black. With the progress of the heat-treatment, the mixture became viscous and eventually gelated. In order to remove the solvent from the wet gel without causing a significant shrinkage, DMF in the gel was firstly exchanged with liquefied carbon dioxide and then carbon dioxide was removed from the gel in the supercritical state. The organic aerogels were stabilized in either air or iodine vapor atmosphere, and these treatments will be called air- and iodine-stabilization, respectively. In the iodine-stabilization, the organic aerogels were exposed to a saturated iodine vapor at 100 °C for various durations as follows: The organic aerogels and ample iodine powder were placed in a separable flask separately. The air in the flask was evacuated using a rotary pump. The flask was put in the furnace pre-heated at 100 °C. After the desired period of stabilization, the flask was cooled down to the room temperature and the stabilized aerogels were taken out of the flask. In the air-stabilization, the organic aerogels were heated in air using the following temperature profile which was found to be suitable for minimizing the mass loss and increasing the pore volume of the carbon aerogels [6]: First, the temperature was kept at 100 °C for 24 h. Then, the temperature was increased by 20 °C and kept at 120 °C for 1 h. Similar increments and holding periods of the temperature were repeated and continued up to 200 °C. The carbon aerogels were obtained by heating the stabilized aerogels up to 1000 °C at a rate of 2 °C min^{-1} under nitrogen gas flow.

The iodine-stabilization put a metallic gloss on the organic aerogels. The cross-section cut from the columnar iodine-stabilized aerogels with a diameter of about 3 mm was uniformly glossy over the entire section even though the stabilization period was as short as 1 h. This suggests that the rate of diffusive transport of iodine in the materials is faster than that of the stabilization reactions and the stabilization proceeds homogeneously in the cross section of the organic aerogels. The iodine-stabilized aerogels did not melt during carbonization regardless of the compositions of the starting mixture and the molecular weights of PVC although cracks were sporadically formed for [PVC] > 5.0 wt%. On the contrary, the air-stabilized aerogels melted during carbonization for [PVC] = 10.0 and 15.0 wt% because of insufficient stabilization in the internal portion of the specimen [6].

It is considered that the thermal stability of the organic aerogels is enhanced during stabilization due to the formation of a cross-linked structure, with which the removal of hydrogen atoms from the dehydrochlorinated PVC molecules is concerned. In the air-stabilization, oxygen uptake is expected to occur in addition to the formation of the cross-linked structure. The infrared (IR) spectra of the PVC powder, the organic aerogel and the air- and iodine-stabilized aerogels, which were measured using a FT-IR spectrometer (MAGNA-IR spectrometer, Nicolet) with a diffuse reflectance spectroscopy method, are compared in Fig. 1. The arrows in the figure indicate absorption bands referred to below. The starting PVC shows the absorption bands characteristic to this polymer at 620, 685, 969, 1252, 1433 and 2916 cm^{-1} [12]. These absorption bands are diminished by dehydrochlorination. The organic aerogel shows a broad absorption band assigned to the stretching of C=C double bonds at around 1600 cm^{-1} [12]. In addition, the organic aerogel exhibits the absorption bands assigned to the C—H out of plane deformation of conjugated trans C=C double bonds and the C—H stretching in unsaturated carbon at 1007 and 3019 cm^{-1}, respectively [12]. These two absorption bands are diminished with air- and iodine-stabilizations. For the air-stabilized aerogel, the oxygen uptake can be detected as the absorption bands assigned to the stretching of the carbonyl and ether groups at 1717 and around 1200 cm^{-1}, respectively. These bands are not observed for the iodine-stabilized aerogel.

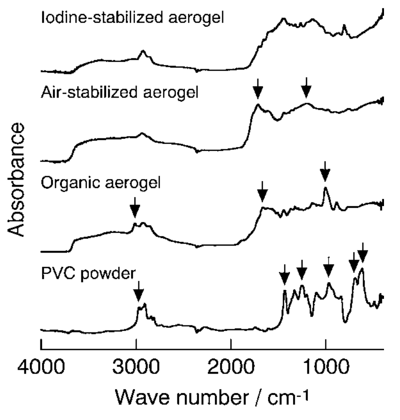

Figure 1 IR spectra for PVC powder with M_n of 22 000, organic aerogel and air-and iodine-stabilized aerogels. DBU/Cl = 2.0, [PVC] = 5.0 wt% and M_n = 22 000. Iodine-stabilization period was 48 h.

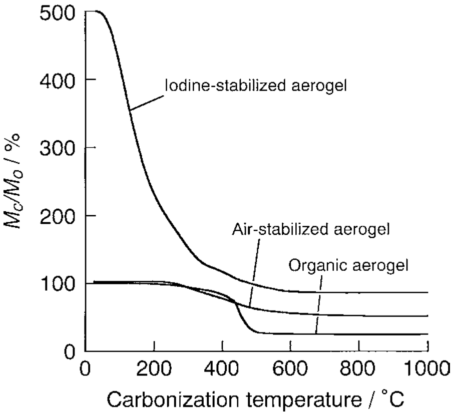

Figure 2 Ratio of mass of carbon aerogel against that of organic aerogel (M_c/M_o) versus carbonization temperature for organic aerogel and air- and iodine-stabilized aerogels. DBU/Cl = 2.0, [PVC] = 5.0 wt% and M_n = 22 000. Iodine-stabilization period was 48 h.

During the iodine-stabilization, the aerogels gained mass considerably due to the iodine uptake. The mass of the iodine-stabilized aerogels steeply increased with increasing the stabilization period up to 12 h and the ratio of mass of the iodine-stabilized aerogel against that of the organic aerogel reached about 500% at 48 h stabilization.

During the carbonization, the aerogels lost mass. Fig. 2 shows the thermogravimetric (TG) curves of the organic aerogel and the air- and iodine-stabilized aerogels, which were measured using a TG analyzer (TGA-50, Shimadzu) with a heating rate of 10 °C min^{-1} under nitrogen gas flow. The ordinate of this figure shows the ratio of the mass of the carbon aerogel (M_c) against that of the organic aerogel (M_o). When the organic aerogels are carbonized without applying stabilization, an intensive decomposition takes place in the range of 400–500 °C and M_c/M_o decreases to 21% at 1000 °C. During decomposition, the organic aerogels melt and the porous structure developed in the organic aerogels is collapsed. The air-stabilization makes the organic aerogels infusible and the total mass loss during stabilization and carbonization is effectively suppressed, while M_c/M_o at 1000 °C remains at 51%. The oxygen atoms taken up during the air-stabilization are released during carbonization as the decomposition gases containing carbon atoms, and M_c/M_o is invariably lower than the mass fraction of carbon atoms in the organic aerogels. In contrast, the total mass loss through stabilization and carbonization is significantly reduced with the iodine-stabilization, and M_c/M_o at 1000 °C reaches 80%. The elemental analysis using elemental analyzers (CHN corder MT-5, Yanaco and SX-Elements micro analyzer YS-10, Yanaco) revealed that the carbon aerogel obtained by carbonizing the iodine-stabilized aerogel at 1000 °C included non-carbon atoms by the mass fraction of 13%. By considering this value and M_c/M_o = 80%, the rate of the mass of carbon atoms in this carbon aerogel against

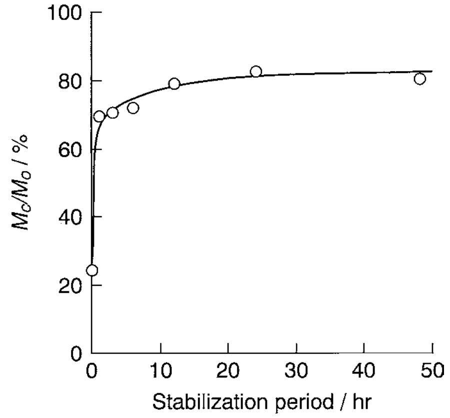

Figure 3 Ratio of mass of carbon aerogel against that of organic aerogel (M_c/M_o) versus iodine-stabilization period. DBU/Cl = 2.0, [PVC] = 5.0 wt% and M_n = 22 000. Carbonization temperature was 1000 °C.

that of the organic aerogel is estimated to be 70%. This value is close to the mass fraction of carbon atoms in the organic aerogel, 71%. This suggests that the removal of iodine atoms during carbonization scarcely causes loss of carbon atoms. Thus, the iodine-stabilization is superior for minimizing overall loss of carbon atoms during preparation of the carbon aerogels.

In the air-stabilization, it is required to raise the temperature gradually up to 200 °C. This is because if the maximum temperature is below 200 °C, the thermal stability of the organic aerogels is insufficient [6] and if the temperature is rapidly raised, the organic aerogels are burned out during stabilization due to the storage of the heat evolved with the exothermal reactions. Thus, the air-stabilization is a lengthy process. The relation between the iodine-stabilization period and M_c/M_o is presented in Fig. 3. It is found that a high thermal stability of the organic aerogels is achieved even with the stabilization for 1 h. Thus, the iodine-stabilization is advantageous for shortening the production process of the carbon aerogels.

The characteristics of the porous structure in the carbon aerogels derived by carbonizing the iodine-stabilized aerogels are summarized in Table I. These values were obtained as follows: The bulk density (ρ_{bulk}) was obtained as mass/(bulk volume) where the bulk volume was calculated from the specimen dimensions. The apparent density (ρ_{app}) was obtained from the weights of the specimen under a reduced pressure and that soaked in propylene carbonate. The total pore volume (V_{den}) was obtained as $(1/\rho_{\text{bulk}}) - (1/\rho_{\text{app}})$. The nitrogen gas adsorption-desorption isotherms were measured at −196 °C with an automatic gas adsorption apparatus (BELSORP-28SA, BEL Japan) using the specimens degassed under a reduced pressure at 200 °C. The volume of the pores denoted as V_{ad} was obtained from the mass of the nitrogen adsorbed at a relative pressure of 0.99 and the density of liquefied nitrogen at −196 °C, 808 kg m^{-3}. The difference of the pore volumes, $V_{\text{den}} - V_{\text{ad}}$ corresponds to the macropore volume. The distribution of the mesopore sizes as represented by the mesopore volume (V_{meso}) in various regions of the mesopore radius (R_{meso}) was obtained by analyzing the nitrogen gas desorption isotherms following the Dollimore-Heal method [13]. The mesopore radius at the distribution maximum was denoted as R^*_{meso}. The micropore volume (V_{micro}) was obtained by analyzing the adsorption isotherms in the relative pressure range below 0.10 following the Dubinin-Radushkevich method [14]. The BET surface area (S_{BET}) was obtained from the adsorption isotherms in the relative pressure range of 0.05–0.30.

Fig. 4 shows the distributions of the mesopore radius of the organic and the carbon aerogels derived using the air- and iodine-stabilizations. It can be seen that mesopores in the organic aerogels reduces their size and volume during stabilization and carbonization. This is because the framework structure composing the walls of mesopores in the organic aerogels contracts due to the mass loss and the densification of the material. The smaller mass loss for the iodine-stabilization as compared to the air-stabilization leads to the smaller reduction in size and volume of mesopores. By adopting the iodine-stabilization, the controllable range of pore size in the PVC-based carbon aerogels was extended up to several tens nanometers. Such a large mesopore will not lose contact with the external surface even when a coating is applied for functionalizing the carbon aerogels. The present authors are examining the application of the carbon aerogels coated with electrochemically

TABLE I Preparation conditions and characteristics of pores in carbon aerogels

Specimens	DBU/Cl	[PVC] (wt%)	M_n ($\cdot 10^4$)	ρ_{bulk} (10^3 kg/m^3)	ρ_{app} (10^3 kg/m^3)	V_{den} (10^6 mm^3/kg)	V_{ad} (10^6 mm^3/kg)	V_{micro} (10^6 mm^3/kg)	S_{BET} (10^5 m^2/kg)	R^*_{meso} (nm)
A	1.0	2.5	4.7	0.51	1.70	1.34	1.16	0.13	2.80	15.3
B	1.0	2.5	8.2	0.51	1.72	1.37	1.25	0.19	4.25	15.3
C	1.0	5.0	2.2	0.74	1.66	0.74	0.80	0.18	3.84	8.1
D[a,b]	1.0	5.0	4.7		1.53					
E[a,b]	1.0	5.0	8.2		1.49					
J	2.0	2.5	2.2	0.31	1.61	2.60	2.02	0.16	3.32	20.0
K	2.0	2.5	4.7	0.58	1.66	1.11	0.91	0.20	4.08	20.0
L	2.0	2.5	8.2	0.77	1.62	0.67	0.75	0.16	3.40	8.1
M	2.0	5.0	2.2	0.75	1.65	0.72	0.79	0.18	3.62	8.1
N[a]	2.0	5.0	4.7		1.56		0.25	0.05	1.08	5.5
O[a]	2.0	5.0	8.2		1.53		0.17	0.03	0.81	5.0

[a] Specimens were cracked or broken into fragments during carbonization.
[b] Specimens did not adsorb detectable amount of nitrogen.

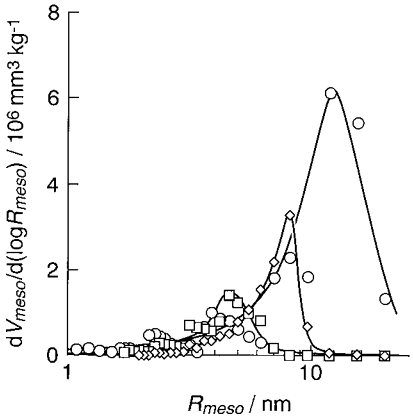

Figure 4 Distributions of mesopore radius (R_{meso}) for (○) organic aerogel and carbon aerogels derived with (□) air- and (◊) iodine-stabilizations. DBU/Cl = 2.0, [PVC] = 5.0 wt% and $M_n = 22\,000$. Iodine-stabilization period was 48 h and carbonization temperature was 1000 °C.

active materials to the electrodes of the electrochemical capacitors.

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