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Dependence of the elastic moduli of porous silica gel prepared by the sol–gel method on heat-treatment

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The elastic moduli of silica gel monolith prepared by the sol–gel method from a tetramethoxysilane solution have been measured before and after heat treatment. The elastic moduli showed a drastic change with heat treatment; for example, Young's modulus changed from 0.95 GPa for the gel before heating to 72.5 GPa for the densified product after heating to 1050° C. The change in the Young's modulus of the gel with heating temperature is discussed on the basis of changes of porosity and strength of the silica skeleton.

1. Introduction

The sol–gel method has been extensively applied to the preparation of silica gels and glasses in the form of monoliths (plates and cylinders), fibres and coating films [1]. Silica gels prepared by this method are porous and the micropores contained in the gel change in average size, size distribution, and amount (porosity), depending on the composition of starting solution, mode of fabrication and heat treatment of the gel. Thus, one can obtain a variety of silica gels whose average size of micropores changes over a wide range from several angstroms to micrometres [2, 3]. This gives a potential possibility of using those porous silica gels as supports of catalysts, enzymes and microbials as microfilters, and as starting materials for preparing composite materials. For most of these applications, the elastic moduli are very important, as well as mechanical strength. The elastic moduli are very sensitive to microstructure, and might be useful to obtain knowledge of the structure of the gels.

To date there appears to be only one report published on the elastic moduli of silica gels made by the sol–gel method. Murtagh *et al.* [4] measured the elastic moduli of silica gel bodies prepared from acid-catalysed tetraethoxysilane solution by the pulse-superposition interferometry method. They calculated the elastic modulus of the silica matrix on the basis of a self-consistent scheme approximation [5, 6] by regarding the gel body as a composite of silica matrix and pores. It was concluded that the elastic modulus of the matrix systematically changed with the conditions of hydrolysis of the solution, but it was lower than that of fused silica. It is noticed, however, that their study is limited to gels of relatively lower porosity of less than 36.7%.

In the present study, the elastic moduli of silica gel monolith prepared from a solution containing tetramethoxysilane (TMOS), methanol, water, dimethylformamide (DMF) and NH_4OH have been measured as a function of heating temperature by the cube resonance method described by Goto and Soga [7]. The porosity of the gel covered by this study ranged from 72.6% to 0%. The results of measurements are discussed on the basis of the porosity and stiffness of the silica skeleton which changed with heating temperature. The results on the heated gels which had a relatively small porosity are also discussed on the basis of the relationships so far proposed on the elastic modulus and porosity.

2. Experimental procedure

2.1. Preparation of samples

Most of the present measurements are based on a dried gel monolith prepared by the sol–gel method from a solution of the composition $1\ Si(OCH_3)_4 \cdot 1\ (CH_3)_2NCHO \cdot 2\ CH_3OH \cdot 12\ H_2O \cdot 5 \times 10^{-4}\ NH_4OH$ shown in Table I. 1 mol TMOS, 1 mol DMF and 2 mol methanol were mixed together to make a homogeneous solution. A given amount of water containing ammonia was dropped into the solution at 50° C under stirring over a duration of 20 min followed by another 20 min stirring. The solution was then cooled down to 30° C, placed in a polytetrafluoroethylene (Teflon®) cylinder, 315 mm long and 49 mm i.d. and sealed with an aluminium foil and reacted to gel at 30° C. After gelation, the gel was aged by raising the temperature from 30 to 70° C in 24 h. To dry the wet gel thus prepared, the aluminium foil was perforated with 15 pinholes of 1 mm diameter and the temperature was raised from 70 to 160° C over 9 d and held there for 24 h. The dried gel cylinder was crack-free and opalescent in appearance and had a size 120 mm long and 32 mm diameter.

Heating of the dried gel was carried out in an elec-

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TABLE I Samples used in the measurements

Sample	Description
Gel	Before and after heating the gel prepared from the starting solution: 1 $Si(OCH_3)_4 \cdot 1\ (CH_3)_2NCHO \cdot 2\ CH_3OH \cdot 12\ H_2O \cdot 5 \times 10^{-4}\ NH_4OH$
AM-gel	Gel made from a solution catalysed with NH_3 and without DMF
HC-gel	Gel made from a solution catalysed with HCl and without DMF
FG-1	Foamed glass made by heating at 1050° C for 3 h
FG-2	Foamed glass made by heating at 1050° C for 4 h
Fused silica	Commercial SiO_2 glass (OH content 110 p.p.m.)

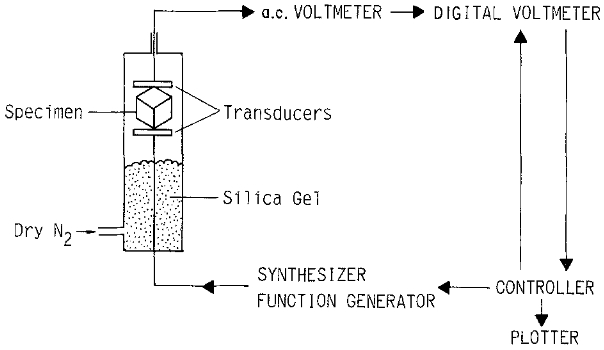

Figure 1 Schematic figure of the system for measuring sound wave velocity.

trical heating furnace with disc-shaped specimens 32 mm diameter and 10 mm thick cut from the 120 mm long cylinder. Gels were heated to given temperatures at a rate of 15° C h^{-1} below 900° C and at a rate of 5° C h^{-1} above 900° C and held for 1 h after their given temperatures were reached. For temperatures below 700° C oxygen gas was passed to burn out organic residues and air was passed above 700° C. The specimen became a transparent silica glass when heated to 1050° C.

Two kinds of foamed glass samples (FG-1 and FG-2) were made by subjecting a transparent glass to further heating at 1050° C for several hours to produce water vapour foams from OH-groups remaining in the transparent glass in amounts of 3700 p.p.m.

A further two types of gel (AM-gel and HC-gel) made from the starting solutions of the composition 1 $Si(OCH_3)_4 \cdot 3.6\ CH_3OH \cdot 10\ H_2O \cdot 5 \times 10^{-4}\ NH_4OH$ and 1 $Si(OCH_3)_4 \cdot 3.6\ CH_3OH \cdot 10\ H_2O \cdot 1 \times 10^{-2}$ HCl, respectively. To prepare AM-gel, a given amount of distilled water containing ammonia was added to a mixture of TMOS and methanol in a beaker under stirring at room temperature (25° C). The solution was poured into a polyethylene container, 50 mm diameter and 70 mm deep, sealed with aluminium foil and placed in an oven at 40° C to convert to gel. A wet gel was dried by perforating the aluminium foil cover with pinholes. HC-gel was prepared by the same procedure described above by replacing ammonia with hydrochloric acid.

Quartz glass was commercially obtained. It was SiO_2 glass containing 110 p.p.m OH-groups. Its bulk density was 2.20 g cm^{-3}.

The samples used for the measurements of elastic modulus are summarized in Table I.

2.2. Characterization of samples

2.2.1. Porosity, pore size and bulk density

The pore size distribution was measured using a Micromeritics Company model AccuSorb 2100E surface measurement meter. The pore-size distribution curve was derived from the adsorption isotherm for nitrogen gas. The porosity, P, was calculated from the Equation

$$P = 1 - \frac{d}{d_0} \qquad (1)$$

where d is the bulk density and d_0 is the density of quartz glass (2.20 g cm^{-3}).

2.2.2. Vickers hardness

The Vickers hardness of the gels was measured using an Akashi Manufacturing Company Type MVK-E microhardness tester. In the measurement, the load was altered between 20 and 100 g with the hardness value and the loading time was kept constant at 10 sec.

2.2.3. Other measurements

For some of the samples, infrared spectra were measured to estimate the water contents. Scanning electron microscopy was also applied for observation of microstructure.

2.3. Measurement of elastic moduli

The elastic moduli of the gels and heated gels were measured using the method based on the resonance of a cubic sample developed by Goto and Soga [7]. The apparatus used is shown in Fig. 1. The samples for elastic modulus measurements were made by cutting a cube of sides 3 to 6 mm from the central portion of the gel disc. The planes of the cube were polished by an emery paper no. 1500 so that the lengths of the sides were identical within the range $\pm 2\,\mu m$. In order to remove water absorbed by the gel, the cube samples were dried in an oven at 120° C, just before measurement.

During measurement the sample was put in a container which contained silica gel and flowing dry nitrogen gas for drying. A sample cube was inserted between two sheets of $BaTiO_3$ transducers. A vibration was generated in one of the transducers by a synthesizer, and another transducer served to detect the resonance of the cubic sample. The resonance was magnified by an amplifier and recorded.

In the estimation of elastic moduli, Poisson's ratio was calculated. For this purpose, dimensionless frequencies, a_n, were obtained for respective vibration modes from the relative values of respective observed resonance peaks relative to the lowest resonance frequency, EV-1. Then, the experimental a_n values for vibration modes EF-2, OS-2, OD-2 and OD-3 were fitted to the relationship between a_n and Poisson's ratio, calculated beforehand for a cubic, isotropic elastic body. Poisson's ratios thus obtained were used

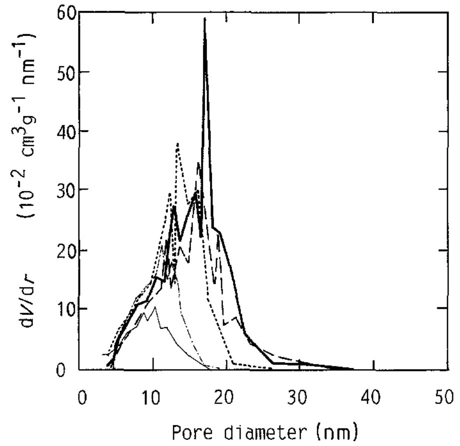

Figure 2 Change in pore size distribution of gels heated at different temperatures. (——) Dried gel, (- - -) 700° C, (----) 900° C, (---) 1000° C, (——) 1020° C.

to estimate elastic moduli. The velocity of the transverse wave, v_s, is calculated using the EV-1 mode resonance of which the non-dimensional frequency is independent of Poisson's ratio. The velocity of the longitudinal wave, v_l, is calculated using the formula

$$v_l = [2(1 - \mu)/(1 - 2\mu)]^{1/2} v_s \tag{2}$$

The modulus of rigidity, G, Young's modulus, E, and bulk modulus, K, are calculated from μ, v_s, v_l and d (bulk density) using Equations 3, 4 and 5, respectively.

$$G = dv_s^2 \tag{3}$$

$$E = 2G(1 + \mu) \tag{4}$$

$$K = d(v_l^2 - \tfrac{4}{3}v_s^2) \tag{5}$$

3. Results

3.1. Changes of pore size distribution, bulk density and Vickers hardness of the gel with heat treatment

Pore size distributions of the gel heated to different temperatures between 700 and 1020° C are shown in Fig. 2. No appreciable change is observed up to 700° C. It is seen that the most probable pore size and the overall distribution curve shift to lower pore sizes, and the distribution curve becomes small, indicating that above 700° C appreciable shrinkage of the pores takes place and some of the pores disappear.

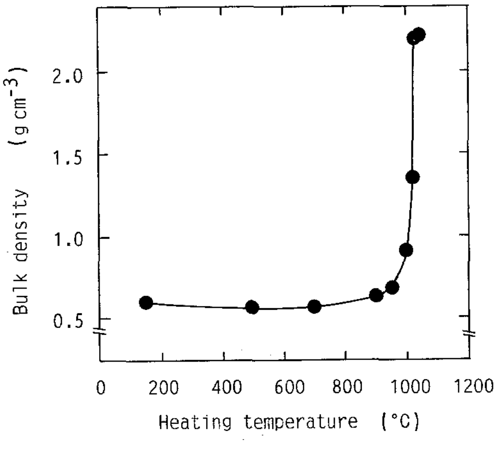

Figure 3 Change in bulk density of the dry gel with heating temperature.

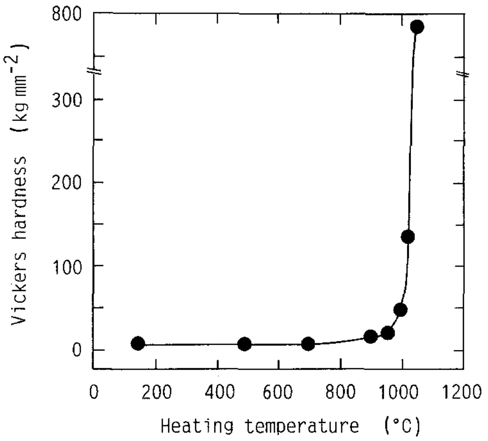

Figure 4 Change in Vickers hardness of the dry gel with heating temperature.

Fig. 3 shows the bulk density as a function of heating temperature. The bulk density of the gel decreases slightly when the gel is heated at 500 and 700° C. This decrease in bulk density is attributed to the decrease in weight due to burning of residual organic matter and dehydration due to the progress of the polycondensation reaction without appreciable shrinkage of the gel. Above 900° C, the bulk density gradually, and then rapidly, increases with heating temperature, agreeing with the change in the pore size distributions shown in Fig. 2.

Fig. 4 shows the change in Vickers hardness with heating temperature. The Vickers hardness remains very small at 4 to 8 kg mm^{-2} below 700° C, and above 700° C, it increases quite markedly and reaches a value shown by quartz glass.

The bulk densities, porosities and the most probable pore sizes are shown in Table II. The results of measurements on other samples used for comparison are also shown in Table II, as are the elastic moduli.

3.2. Elastic moduli

The results of measurements on the elastic and related properties such as sound velocity, Poisson's ratio, Young's modulus, bulk modulus and shear modulus, are summarized in Table II.

Fig. 5 shows the change in Young's modulus of the dry gel as a function of heating temperature. It is seen from Fig. 5 and Table II that the Young's modulus of

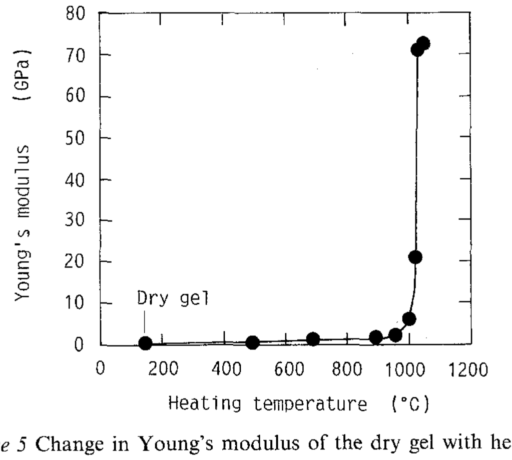

Figure 5 Change in Young's modulus of the dry gel with heating temperature.

TABLE II Bulk density, porosity, the most probable pore size, sound velocity, Poisson's ratio, Young's modulus, bulk modulus and shear modulus of the porous silica

Specimen	Bulk density ($g\,cm^{-3}$)	Porosity (%)	Most probable pore size (nm)	Young's modulus (GPa)	Bulk modulus (GPa)	Shear modulus (GPa)	Poisson's ratio	Sound velocity ($km\,sec^{-1}$)
gel	0.604	72.55	16	0.95	0.40	0.50	0.186	0.81
500° C	0.57	74.1	–	1.11	0.47	0.58	0.183	0.91
700° C	0.57	74.1	16	1.40	0.59	0.74	0.186	1.02
900° C	0.64	71.0	14	2.14	0.91	1.11	0.178	1.19
950° C	0.68	69.1	–	2.67	1.13	1.40	0.181	1.29
1000° C	0.91	58.6	11	6.55	2.76	3.49	0.187	1.74
1020° C	1.35	38.9	10	21.2	9.00	10.7	0.171	2.59
1030° C	2.18	0.8	–	71.7	31.0	34.9	0.157	3.77
1050° C	2.20	0	–	72.5	31.3	35.4	0.159	3.77
AM-gel*	0.76	65.5	–	1.85	0.77	1.02	0.193	1.01
HC-gel†	1.50	31.6	–	7.74	3.24	4.25	0.220	1.44
FG-1	1.13	48.5	–	21.3	8.85	12.1	0.205	2.79
FG-2	1.76	20.1	–	47.3	19.8	25.9	0.196	3.35
Fused silica	2.20	0	–	76.4	32.5	39.4	0.177	3.86

*Ammonia catalysed gel (without DMF).
†Hydrochloric acid catalysed gel (without DMF).

the dry gel before and after heating to temperatures lower than 900° C is very small at 0.40 to 0.91 GPa compared with 72.5 GPa for the non-porous glass obtained by heating the gel up to 1050° C. Young's modulus of the dry gel increases slightly with increasing heating temperature up to 900° C and increases sharply at higher temperatures, reaching a value similar to that for the fused quartz.

Fig. 6 shows Young's modulus plotted against the fractional porosity for sol-derived dry gels prepared from different starting solutions and foamed glasses. In Fig. 6, two curves are drawn by dashed lines: one corresponding to gels and the other to foamed glasses. It is seen that at given porosities Young's modulus of the gels is much lower than that of foamed glasses.

Fig. 7 shows the plot of the sound velocity against porosity for the gels before and after heat treatment. It is seen that the plot for the porous silicas obtained by heating at temperatures between 700 and 1020° C is expressed by a straight line. It is also seen that the gel before and after heating at 500° C shows smaller sound velocities than the above straight line.

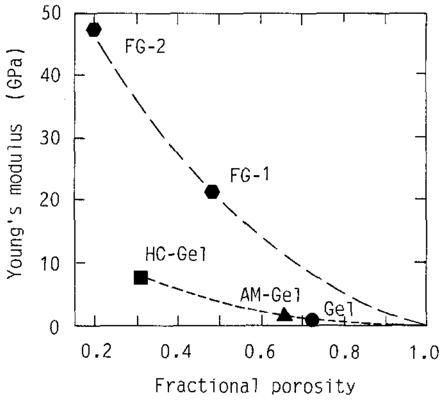

Figure 6 Relationship between Young's modulus and fractional porosity for various gels and foamed glasses. FG-1 and FG-2, foamed glasses. HC-gel, gel prepared by acid catalysis without DMF. AM-gel, gel prepared by ammonia catalysis without DMF. Gel, gel made with DMF.

Fig. 8 shows the plot of fractional Young's modulus against porosity for the samples obtained by heating the dry gel between 700 and 1050° C. It is seen that the plots can be expressed by a smooth curve combining the point of porosity, zero, and fractional Young's modulus, one, and the point of porosity, one, and fractional Young's modulus, zero.

4. Discussion

4.1. The change in elastic moduli with heating temperature

The measurements of Young's moduli of the dried and heated gels (Fig. 5) indicated that Young's modulus of gels is quite low and increases slightly with heating temperature at heating temperatures lower than 900° C and sharply at heating temperatures higher than 900° C. This change in Young's modulus of the gel with heating temperature is quite similar to that for the Vickers hardness shown in Fig. 4. This suggests that the changes with heating temperature of Young's modulus and Vickers hardness are determined by the same factor.

It is natural to assume that the porosity of the gel and the strength of the skeleton consisting of silica

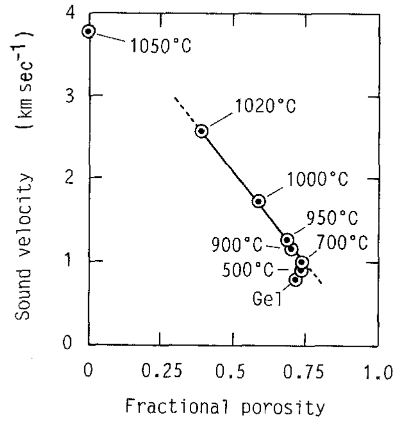

Figure 7 Relationship between sound velocity and porosity for the gel before and after heating to various temperatures.

particles are the main factors affecting Young's modulus. The role of these two factors will be discussed below.

Fig. 6 indicates that the Young's moduli of gels in which the skeleton is assumed to be weaker than that of the glass are lower than those of foamed glasses, suggesting that the strength of the skeleton largely affects Young's modulus of the porous silica. Fig. 7 shows that the sound velocity is related to the porosity by a straight line for the gels heated at temperatures of 700 and 1020° C and that the gels before and after heating at 500° C have lower values of sound velocity than is expressed by the straight line. This indicates that the porous silica samples obtained by heating the silica gel at higher temperatures than 700° C can be regarded as having skeletons of similarly high strength and, therefore, their Young's moduli can be approximately expressed as a function of porosity only.

Table II indicates that Young's modulus of non-porous silica glass which is prepared by heating the gel to 1050° C is 72.5 GPa and slightly lower than that for the fused silica (76.4 GPa). This may be caused by higher water content of the gel-derived silica glass. As reported previously, this glass retains 3700 p.p.m. OH, which is higher than the OH content (100 to 300 p.p.m.) of the commercial fused quartz glass.

4.2. Relationship between elastic modulus and porosity

Young's moduli of gel-derived porous silica, which can be expressed approximately as a function of porosity only, will be discussed on the basis of the reported *E–P* relationships. The elastic moduli of ceramic porous bodies consisting of a brittle matrix decrease with increasing porosity. The following formulae have been proposed as equations expressing the relation between Young's modulus and porosity.

$$E = E_0(1 - aP) \qquad P < 0.1 \qquad [10] \tag{6}$$

$$E = E_0(1 - P)^{\alpha} \qquad [11] \tag{7}$$

$$E = E_0(1 - aP)^{n} \qquad [12] \tag{8}$$

$$E = E_0(1 - bP + cP^2) \qquad [13, 14] \tag{9}$$

$$E = E_0\left[1 + \frac{AP}{1 - (A + 1)P}\right] \qquad [15, 16] \tag{10}$$

$$E = E_0 \exp(-dP) \qquad [17, 18] \tag{11}$$

$$E = E_0 \exp[-(eP + fP^2)] \qquad [19] \tag{12}$$

where P is the porosity, E_0 the Young's modulus at $P = 0$, a, b, c, d, e, f, n and α are positive constants and A is a negative constant. Most of the above equations are purely empirical or semi-empirical.

It was confirmed by Hasselman [10] that Equation 6 expresses the Young's modulus–porosity relation of fired alumina bodies within the porosity range below 0.1. McAdam [11] showed that Equation 7 is valid for Young's modulus of porous iron alloys. Equation 8 has been derived semi-empirically by Phani and Niyogi [12]. They state that unlike other formulae, this equation satisfies the boundary condition that Young's modulus becomes zero at the porosity equaling one and is capable of treating both closed pores and interconnected pores. Equation 9 is a formula which has been derived by Mackenzie [13] from Equation 6 by raising the degree of approximation to the quadratic formula. Coble and Kingery [14] showed that this equation continued to be valid for higher porosities than that obeyed by Equation 6. Equation 10 was derived by Hashin [15] from an approximate method based on the variational theorems of the theory of elasticity and on a concentric-spheres model. It was shown by Hasselman [16] that this formula expresses the Young's modulus–porosity relationship for sintered alumina. Equation 11 was derived by Spriggs [17] in 1961 and has been regarded as typical formula for the *E–P* relation. Knudsen [18] showed that this formula is valid for various porous bodies. Equation 12 has been derived theoretically by Wang [19] and shown to be valid for porous alumina over a wide range of porosities between 0 and 0.38.

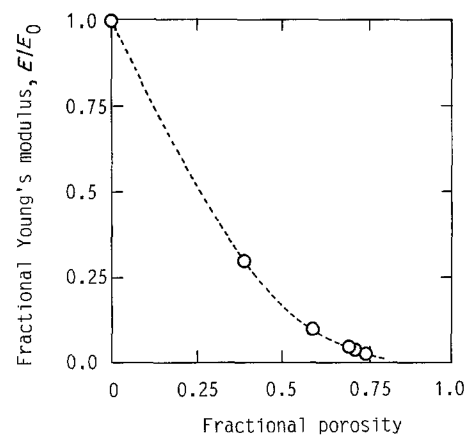

Figure 8 The relation between the fractional Young's modulus and porosity for the samples prepared by heating dried gels at temperatures higher than 700° C.

The Young's modulus–porosity data shown in Fig. 8 are fitted to Equations 6 to 12, and the most suitable values of parameters are listed in Table III, together with the sum of squares of the derivatives from the measured values. Fig. 9 shows the fitted curves. It is

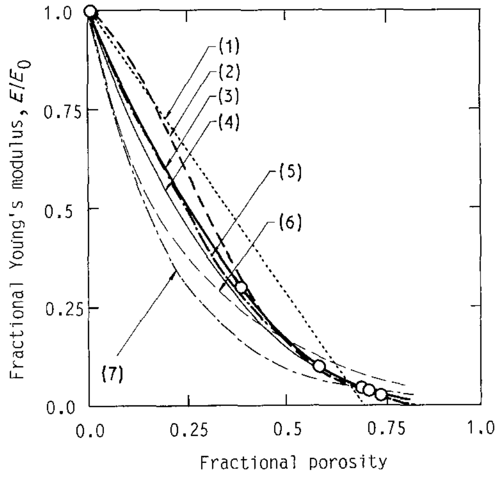

Figure 9 Fitting of various Young's modulus–porosity relationships to the present samples obtained by heating gels between 700 and 1050° C. Equations (1), 6, (2) 12, (3) 9, (4) 7, (5) 8, (6) 10, (7) 11.

TABLE III Summary of parameters for porous silica heated at temperatures between 700 and 1050° C

Equation	Parameters	Sum of squares of deviations from the measured values
(6) $E = E_0(1 - aP)$	$a = 1.43$	2.69
(7) $E = E_0(1 - P)^{\alpha}$	$\alpha = 2.83$	3.78
(8) $E = E_0(1 - aP)^n$	$a = 1.13$ $n = 2.20$	0.192
(9) $E = E_0(1 - bP + cP^2)$	$b = 2.38$ $c = 1.43$	5.58×10^{-3}
(10) $E = E_0\left[1 + \frac{AP}{1 - (A + 1)P}\right]$	$A = -5.20$	0.786
(11) $E = E_0 \exp(-dP)$	$d = 4.74$	1.41
(12) $E = E_0 \exp[-(eP + fP^2)]$	$e = 0.577$ $f = 6.22$	4.20×10^{-2}

seen that Equations 8, 9 and 12 fit well the experimental data. The following experimental equations are obtained from fitting to Equations 8, 9 and 12, respectively.

$$E = E_0(1 - 1.13P)^{2.20} \qquad (13)$$

$$E = E_0(1 - 2.38P + 1.43P^2) \qquad (14)$$

$$E = E_0 \exp[-(0.577P + 6.22P^2)] \qquad (15)$$

It should be noted that Equations 8, 9 and 12 are assumed to be applied to the porous systems in which pores are isolated and the porosity is limited. It is interesting to see that those equations are valid for the present porous silica bodies which have high porosities reaching more than 0.7.

5. Conclusions

Silica monoliths with a wide range of porosity from 0 to 0.726 have been prepared from an $Si(OCH_3)_4$–$(CH_3)_2NCHO$–CH_3OH–H_2O–NH_4OH solution by sol–gel method and heating them to different temperatures up to 1050° C, and their elastic moduli have been measured. The following results have been obtained.

1. The silica monoliths with elastic modulus ranging from 0.95 to 72.5 GPa have been obtained depending on the temperature of heat treatment.

2. The dependence of Young's modulus of the porous silica on the heating temperature is similar to that of the Vickers hardness, indicating that both properties are generated by the same factors.

3. Young's modulus of the porous silica slightly increases with increasing temperature up to 700° C, probably due to the strengthening of the skeleton consisting of silica particles, and above 700° C it increases sharply with increasing heating temperature due to the decrease in porosity.

4. Young's modulus of silica monoliths heated at temperatures between 900 and 1050° C, where the porosity changes from 0.726 to zero, could be expressed as a function of the porosity by Phani and Niyogi's formula $E = E_0(1 - 1.13P)^{2.20}$, Coble's formula $E = E_0(1 - 2.38P + 1.43P^2)$ or Wang's formula $E = E_0 \exp[-(0.588 + 6.22P^2)]$, where E_0 is the Young's modulus at $P = 0$, i.e. 72.5 GPa and P is the fractional porosity.

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