

SAXS investigations of the fractal character of additive silica xerogels

Fei He^{a,*}, Xiaodong He^a, Mingwei Li^b and Sumei Zhang^c

^aCenter for Composite Materials, Harbin Institute of Technology, China

^bSchool of Material Science and Engineering, Harbin Institute of Technology, China

^cSchool of Civil Engineering, Harbin Institute of Technology, China

Two-step acid-base catalyzed silica xerogels with different amounts of additives, including TiO₂ powder, silica xerogel powders and short glass fibers, were prepared through a sol-gel route and ambient pressure drying. The fractal dimensions of these additive silica xerogels were investigated by the means of small-angle X-ray scattering (SAXS). Specific surface area and the average chord length were calculated by the Debye method. The changes of the porous structure were compared between the pure silica xerogels and the impure ones. The results show that additive silica xerogels do not possess a surface fractal character. The mass fractal range of silica xerogels decreases and colloid particle size increases with an increase of additives. The adding of excessive silica xerogel powders results in agglomeration of particles which goes beyond the metrical limit of SAXS. The mass fractal dimension and fractal range decrease with the addition of additional short fibers. The shrinkage was restrained in the course of drying by adding short fibers.

Key words: Silica xerogels; Additives; Fractal dimensions; SAXS.

Introduction

Aerogels are low density nano-porous solid materials, and have a continuous random network structure which often exhibits a fractal character. The unique properties of aerogels are related to their nano-size particles and porous distribution, and a striking number of applications have developed for them by scientists [1]. A fractal theory has been widely applied to the study of the porosity of porous materials. Fractal dimension is a quantitative parameter to describe the fractal character from a molecular level, and can be estimated by means of small-angle X-ray scattering (SAXS) [2]. SAXS curves of classical aerogels usually can be divided into five regions approximately (as shown in Fig. 1). Some aerogels perhaps exhibit a fractal character after the Guinier region in accord with the relation of equation (1):

$$I(q) \propto q^{-D} \quad (1)$$

Adding different additives is one method to improve the properties of xerogels, such as the mechanical, thermal and optic properties, etc.[3, 4]. The purpose of this paper is to investigate the effect of the different additives on the fractal character of silica xerogels by the means of SAXS.

Experimental

Two-step acid-base catalyzed silica xerogels were prepared

through a sol-gel route and ambient pressure drying. Sols were prepared by mixing TEOS (tetraethyl orthosilicate), deionized water, absolute ethanol, hydrochloric acid and ammonia with the molar ratios of 1 : 4 : 7 : 7.5 × 10⁻⁴ : 0.0375. At first, TEOS, water and ethanol were mixed. Then according to the proportion needed, silica xerogel powder, TiO₂ powder and short glass fibers were added and were dispersed homogeneously in absolute ethanol by ultrasonic vibration before mixing with TEOS and water. The mixed solution was heated under stirring up to 50 °C, at this moment 0.2 mol/l hydrochloric acid (diluted with absolute ethanol) was added as the acid catalyst. After some time, which was termed the hydrolysis time of acid catalysis, this solution was mixed with the remaining water and ammonia by stirring at 50 °C until gelation. The gels were soaked in an aging solution (70 vol% TEOS/ethanol) for 24 hours [5] at 50 °C in a constant temperature oven. Then the pore solvent was exchanged with cyclohexane three times within 24 hours. The wet gels were dried at ambient pressure at 50 °C. After about 7 or 8 days, silica xerogels were formed. All the dried xerogels were annealed in air at 300 °C for 1 hour to remove organic residues before measuring porosity.

Two-step acid-base catalyzed silica xerogels were prepared through a sol-gel route and ambient pressure drying. In the process of forming the sol, the different additives were added into the silica solution, including 10 wt% TiO₂ xerogel powder (T1), 10 wt% TiO₂ powder and 3 wt% short glass fibers (T2), 20 wt% TiO₂ powder and 3 wt% short glass fibers (T3), 30 wt% TiO₂ powder and 3 wt% short glass fibers (T4), 5 wt% SiO₂ xerogel powder (S1), 10 wt% SiO₂ xerogel powder (S2), 15 wt%

*Corresponding author:
Tel : +86-451-86402928
Fax: +86-451-86402323
E-mail: he_fei@126.com

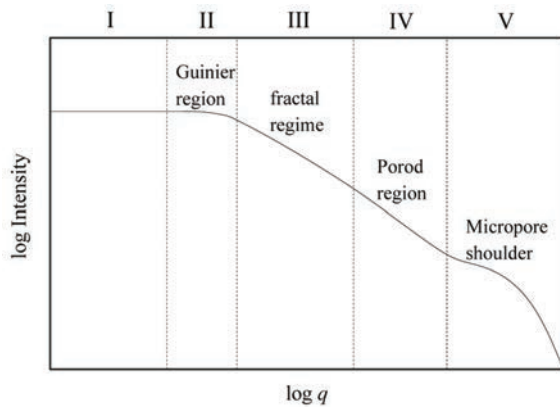


Fig. 1. General SAXS pattern for aerogels.

SiO₂ xerogel powder and 3 wt% short glass fibers (S3) and 3 wt% short glass fibers only (F1) before gelation and non-supercritical drying.

Their porous structures were compared with pure silica xerogel (S0) by means of SAXS. SAXS experiments were operated at 298 K by means of a Kratky compact small-angle system equipped with a position sensitive detector (OED 50 M from Mbraun, Graz, Austria) containing 1024 channels of a width 54 mm. The range of scattering angle was chosen from $h = 0.0005$ to 0.06 nm^{-1} , where the magnitude of the scattering vector $h = 2\pi \sin \theta / \lambda$, 2θ and λ being, respectively, the scattering angle and incident X-ray wavelength of 0.1542 nm. The distance from sample to detector was 27.7 cm and the exposure time was 1000 s for each sample.

Results and Discussion

The fractal structure of aerogels analyzed by means of SAXS generally exhibits three characters, that is the mean size of the clusters (ξ) which are connected to form the network, the mean size of the primary particles (a) which stick together to build the cluster and the fractal dimension (D) which expresses the clusters compactness [6]. From Fig. 1, we can see that there is a fractal region between the Guinier region and the Porod region for aerogels. When the scatter vector from the Guinier region to the fractal one is defined by q_G , the fractal clusters ξ equals to $2\pi/q_G$, which shows that aerogels exhibit obvious nonuniformity. When the initial position of the scatter vector from the fractal region to the Porod one is defined by q_p , the size of the elementary particles a is $2\pi/q_p$.

According to the exponential relations of aerogels, SAXS slit collimation data can be illustrated in $\ln\text{-}\ln$ plots of $I(q)/q$ versus q , and the slope of the line $-\alpha$ is called attenuation index. When $1 < \alpha < 3$, scatterers take on a mass fractal, and its dimension (D_m) equals to α . D_m is a parameter to reflect the mass distribution. The higher D_m is, the more compact is the structure of the aerogel is and the larger mass is in the unit volume. When $3 < \alpha < 4$, scatterers are surface fractals and their dimension (D_s) is $6 - \alpha$. A surface fractal dimension indicates degree

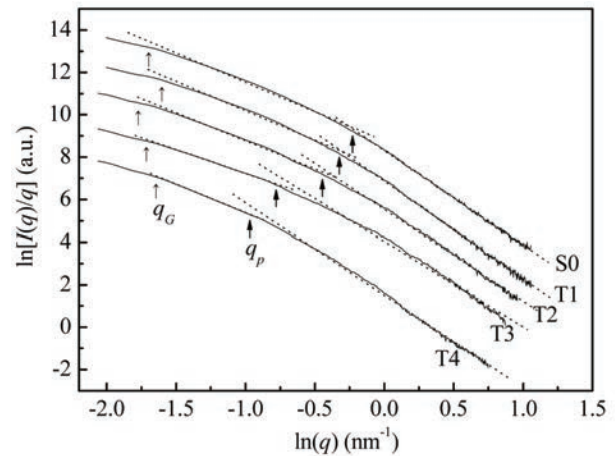


Fig. 2. Fractal fitting isotherms of SiO₂ xerogels by adding different amounts of TiO₂ powder and short fibers.

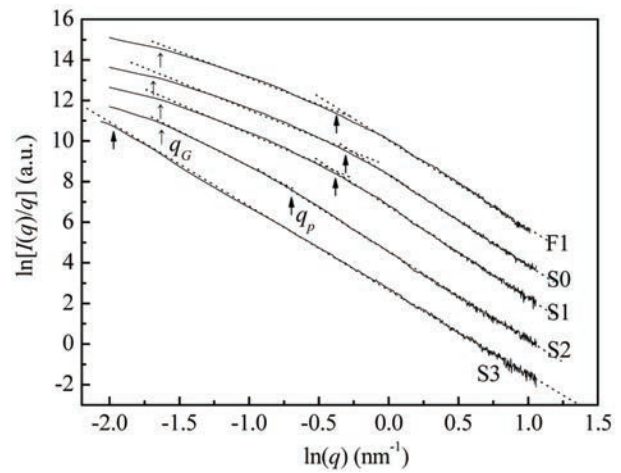


Fig. 3. Fractal fitting isotherms of SiO₂ xerogels by adding different amounts of SiO₂ xerogel powder and short fibers.

of coarseness of the surface. When the surface fractal dimension is closer to 3, the surface is coarser, otherwise it is slicker.

The exponent (D) is estimated by plotting $\ln I(q)/q$ versus $\ln q$ can be related to either the mass fractal dimension (D_m) or the surface fractal dimension (D_s) [7]. Fractal fitting curves of SiO₂ xerogels with different amounts of TiO₂ powder, SiO₂ powder and short fibers are shown in Fig. 2 and Fig. 3. Arrowheads in the figures are q_G and q_p respectively. To separate these curves in Fig. 2 and Fig. 3, they are moved appropriately vertically. The fitting fractal and porous structure parameters by SAXS analysis are listed in table 1. l_p and S_m are the average pore chord length and specific surface area calculated by the Debye method [8].

The scattering intensity took on some obvious changes at low wave vectors by adding different amounts of additives into the silica xerogels. The changes from strong to weak of these two groups samples are S0→T4→T1→T2→T3 and S2→S3→S1→S0→F1 respectively. Adding the large size TiO₂ powder reduces the scattering intensity, whereas

Table 1. The fitting fractal and porous structure parameters by SAXS analysis

No.	$q_G \text{ nm}^{-1}$	$\xi \text{ nm}$	$q_P \text{ nm}^{-1}$	$a \text{ nm}$	ξ/a	D_m	D_s	$l_p \text{ nm}$	$S_m \text{ m}^2/\text{g}$
S0	0.183	34.39	0.802	7.83	4.39	2.767	4.443	29.336	585.38
T1	0.207	30.42	0.723	8.69	3.50	2.770	4.581	12.426	457.12
T2	0.191	32.99	0.635	9.89	3.33	2.653	4.312	10.840	510.87
T3	0.183	34.37	0.477	13.18	2.61	2.246	4.023	7.653	591.02
T4	0.199	31.64	0.398	15.79	2.00	2.672	4.354	14.817	271.18
S1	0.199	31.64	0.683	9.20	3.44	2.946	4.503	20.308	413.53
S2	0.199	31.64	0.469	13.40	2.36	3.464	4.345	32.706	247.09
S3	-	-	0.143	43.94	-	-	4.139	-	-
F1	0.199	31.64	0.683	9.20	3.44	2.598	4.320	12.243	615.83

adding the small size SiO_2 xerogels powder enlarges it. Adding short fibers corresponds to adding large particles, thus it also reduces the scattering intensity. The different additives produce on different porous structures. Micropores and comparable size particles are complementary systems and make the same contributions to the scattering intensity. The change of scattering intensity is the result of the effects of additions and pores together for the samples with additives.

From table 1, the average size of colloid particles (a) increases with an increase in the amount added. For the addition of TiO_2 powder, large size TiO_2 powder brings an increase of a . The conglomeration of nano-size SiO_2 powder and enwrapping colloid particles formed in the sol-gel results in an increase of a by the addition of SiO_2 xerogel powder.

The D_s s of all samples are larger than 4 according to the results of fractal fitting, which indicates these samples do not possess a surface fractal character. The mass fractal range (ξ/a) of silica xerogels decreases and colloid particle increases with an increase of amount of TiO_2 powder added. The fractal network scale (ξ/a) is between 30 nm and 34 nm approximately. Sample T3 has the least D_m presenting the least mass in a unit volume and an incompact system structure. The mass fractal range (ξ/a) also decreases and colloid particle increases by adding SiO_2 xerogel powder. But D_m of sample S2 exceeds 3 and also does not take on a mass fractal character.

The mass fractal characters of samples are related to their porous structure whose parameters are the specific surface area and the average pore diameter. The smaller the colloid particles unit is, the higher corresponding surface areas of a unit mass is. The change of a porous structure has an obvious regularity when short fibers and TiO_2 powder are added into the silica xerogel by comparing S0 with T1-T4. The average pore diameter becomes larger by adding TiO_2 powder and reduces with an increase of the amount added. For T1 and T2 which have the same content of TiO_2 powder, adding additional short fibers is propitious to enhance the specific surface area and retain the pore diameter distribution. When the amount of TiO_2 powder is beyond 20 wt%, the average pore diameter becomes large again. The reason

is perhaps that the interaction between short fibers and the TiO_2 powder restrains the shrinkage of the xerogel and maintains almost the same porous structure of the gel, however, adding excessive TiO_2 powder reduces the specific surface area because of the SiO_2 colloid particles enwrap the TiO_2 powder and fill the opening pores.

For samples of S0, S1 and S2, the average pore diameters were also enlarged by adding SiO_2 xerogel powder. The curve of sample S3 enlarges the Porod region in longer range, i.e. almost beeline, which goes beyond the metrical limit of SAXS. The reason is perhaps that an aggregation in the process of the sol-gel process results in larger particles with an average size of 44 nm. More detailed information can be detected by ultra-small-angle X-ray scattering (USXAS) [9]. The mass fractal dimension and fractal range are reduced with the adding of additional short fibers by comparing S0 and F1, with T1 and T2, i.e. the mass is lower per unit volume than the case of no additives, which indicates fibers can confine the shrinkage of xerogels to a certain extent.

Conclusions

Two-step acid-base catalyzed silica xerogels with different amounts of additives were prepared through a sol-gel route and ambient pressure drying. These adulterated silica xerogels do not possess a surface fractal character as determined by means of SAXS. The mass fractal region decreases with an increase of TiO_2 powder content and colloid particle size increases with an increase of additives. The samples with added SiO_2 xerogel powder also give the same fractal results. The fitting curve for S3 exhibits a large range Porod region in large range, which indicates the particles present give a collective phenomenon. The mass fractal dimension and fractal range decrease with the addition short fibers.

Acknowledgements

The author would like to acknowledge the project supported by "Natural Scientific Research Innovation Foundation in Harbin Institute of Technology (HIT.NSRIF.2008.39)".

References

1. L.W. Hrubesh, J. Non-Cryst. Solids. 225 (1998) 335-342.
2. W.C. Zhuang, X. Chen, J.K. Zhao and L.Y. Wang, Progress in Chemistry. 17[5] (2005) 881-888.
3. C.J. Ctepaniny, G. Gould and R. Bega, Chinese Patent 1592651A. (2005).
4. X.Y. Ni, Y.D. Huang and Y.B. Chen, Chinese Patent 200310109280.1. (2004).
5. M.A. Einarsrud, M.B. Kirkedelen, E. Nilsen, K. Mortensen and J. Samseth, J. Non-Cryst. Solids. 231 (1998) 10-16.
6. C. Marlière, T. Woignier and P. Dieudonné, J. Primera, M. Lamy and J. Phalippou, J. Non-Cryst. Solids. 285 (2001) 175-180.
7. Ph. Dieudonné, P. Delord and J. Phalippou, J. Non-Cryst. Solids. 225 (1998) 220-225.
8. D.R. Vollet, D.A. Donatti and A.I. Ruiz, J. Non-Cryst. Solids. 332 (2003) 73-79.
9. J. Shen, J. Wang and X. Wu, Journal of Tongji University. 24[1] (1996) 76-81.