

## INVESTIGATION OF SILICA-PVA XEROGEL MICROSTRUCTURE EVOLUTION DURING THERMAL TREATMENT BY SANS EXPERIMENT

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*The purpose of the study was to investigate the appearance of certain microstructures developing in the SiO<sub>2</sub>/PVA nanocomposite xerogels at different temperatures by small-angle neutron scattering (SANS). The samples were prepared by the alcoxide route of the sol-gel method. The SANS measurements were performed over a  $q$  (scattering vector) range from 0.05 to 3.7 nm<sup>-1</sup>, providing structural information at length scales ( $2\pi/q$ ) between approximately 1 and 100 nm. The measured small-angle scattering intensities of silica and silica/PVA samples aged at 60°C and heat-treated at different temperatures, are presented in log-log plots. It is shown that both the molecular mass of organic and the temperature of thermal treatment have strong influence on transition tendency from mass fractal toward surface fractal structures.*

**KEYWORDS:** Sol-gel; hybrid matrix; nanocomposite; small angle neutron scattering

### INTRODUCTION

Inorganic and hybrid organic-inorganic silica matrices are consistent with nano-structured porous materials which have been intensively studied in the last years. They have many applications, in optics, mechanics, ionoelectronics, catalysis and biology (1). The combination of hardness of an inorganic glass and toughness of an organic polymer makes

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such a system interesting also from the perspective of mechanical behaviour (2). However, non-Euclidean (fractal) nature of such structures could not be easily characterised.

A fractal structure is defined as self-similar structure which remains similar to itself after a change of scale of magnification. It is well known that such random structures can be developed from many growth processes (such as sol-gel), either naturally occurring or generated by computer simulations (3-6). In the real world, fractals are random structures with self-similarity within a certain limited space range. The mass fractal objects are characterized by the fractal dimension  $D_m$  and the relation  $M \propto R^{D_m}$ , where  $R$  and  $M$  are the radius of a sphere and the mass inside this sphere, respectively. For non-fractal objects  $D_m$  equals the dimension of space,  $d=3$ . For a fractal object  $D_m$  is smaller than  $d$  and is generally not an integer. If it is only the external surface which is fractal, then this is a different type of fractal, named surface fractal. The surface fractal objects are characterised by a non-fractal core, but they have fractal behaviour at the surface. The surface area,  $S$ , obeys the relation  $S \propto R^{D_s}$ , where  $D_s$  is the surface fractal dimension (3, 7).

Generally, among other methods of investigations, the scattering techniques provide an appropriate way to study the evolution of inorganic polymer random microstructures obtained by sol-gel route because of averaging in reciprocal space (7-14).

Small angle neutron scattering technique (SANS) is a useful tool to study and evaluate certain microstructure parameters such as, the size and distribution of particles and pores, and the aggregation tendency during aging. Within certain length scale range SANS measurements provide direct information on the type of microstructure fractal behaviour (mass or surface fractal). Both mass and surface fractals exhibit a power law behaviour in the  $q$ -dependence of the SANS intensity. For mass fractals this is  $I(q) \propto q^{-D_m}$  with  $1 \leq D_m \leq 3$ . The scattering from a surface fractal follows the power-law:  $I(q) \propto q^{D_s-2d}$  with  $(d-1) \leq D_s \leq d$  ( $d=3$  is the space dimension). For a dense or homogeneous, non-fractal object, having smooth surface,  $D_s = 2$  and the usual Porod law  $I(q) \propto q^{-4}$  is effective. The log-log plot of the scattering intensity curve  $I(q)$  exhibits a straight line section, whose slope value ( $P$ ) lies between  $-1$  and  $-3$  for mass fractals and between  $-3$  and  $-4$  in case of the surface fractals.

In this paper silica-polyvinyl alcohol (PVA) nanocomposite materials were prepared using the acid catalysed sol-gel technique. Hybrid xerogels were obtained using tetraethoxysilane (TEOS), and polyvinyl alcohol with two different molecular masses ( $M_1=18000$ g/mol and  $M_2=49000$ g/mol) as inorganic and organic precursors. Pure silica and two hybrid xerogels (differing by molecular weight of PVA) were characterised by SANS. In addition, SANS was used to investigate the microstructure evolution of xerogel containing PVA with higher molecular weight during heating up to  $1000^\circ\text{C}$ .

## EXPERIMENTAL

In the present work, transparent  $\text{SiO}_2$ /PVA sol-gel derived monoliths were obtained. Tetraethoxysilane (Fluka, 98%), polyvinyl alcohol of two molecular mass ( $M_1=18000$  g/mol (Australal, p.a.) and  $M_2=49000$  g/mol (Fluka, p. a.)) were used as precursors. Tetraethoxysilane, was dissolved in ethanol at a mole ratio  $\text{TEOS}/\text{EtOH} = 1:3.85$ . Polyvinyl alcohol was dissolved previously in water. Then, TEOS ethanolic solution was added to PVA and water mixture. In order to promote the hydrolysis reactions and obtain a homogeneous

phase, hydrochloric acid, as catalyst ( $r = \text{HCl}/\text{TEOS} = 0.03$ ) was added. The synthesis parameters are presented in Table 1.

**Table 1.** The synthesis parameters

Symbol	Sample	PVA wt%	Molecular mass of PVA	TEOS:EtOH:H <sub>2</sub> O	Annealing temperature (°C)
S0	SiO <sub>2</sub>	-	-	1:3.85:10	aged at 60°C
V1S10	SiO <sub>2</sub> -PVA	10	18000	1:3.85:10	aged at 60°C
V2S10	SiO <sub>2</sub> -PVA	10	49000	1:3.85:10	aged at 60°C
V2S10 300	SiO <sub>2</sub> -PVA	10	49000	1:3.85:10	300
V2S10 1000	SiO <sub>2</sub> -PVA	10	49000	1:3.85:10	1000

After stirring the precursor mixture for 2 hours, the resulting homogeneous, clear sol was kept in covered vessels at room temperature. The gelation of sols occurred in 2-3 weeks and silica-PVA transparent monolith wet gels have been obtained. Wet gels were dried at 60°C for 48 hours.

Further thermal treatment of hybrid silica/PVA matrix xerogels, (PVA precursor having higher molecular mass  $M_2$ ) was performed in laboratory oven, at 300°C and 1000°C, and kept for 3 hours at each temperature in air.

The SANS measurements on silica and hybrid xerogels and heat treated samples were done at the IBR-2 pulsed reactor, in Dubna, Russia. The  $q$  (scattering vector) range covered in these measurements was  $0.05 - 3.7 \text{ nm}^{-1}$ , providing information at length scales ( $2\pi/q$ ) being approximately between 1 and 100 nm.

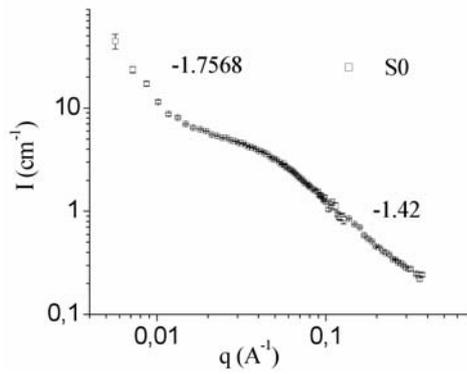
## RESULTS AND DISCUSSIONS

The observed scattered intensities of all samples were monotonously decreasing functions versus  $q$  with no evidence of any peak. The lack of interference peak in the measured  $q$ -range might be due to the larger size of the oxide regions (9).

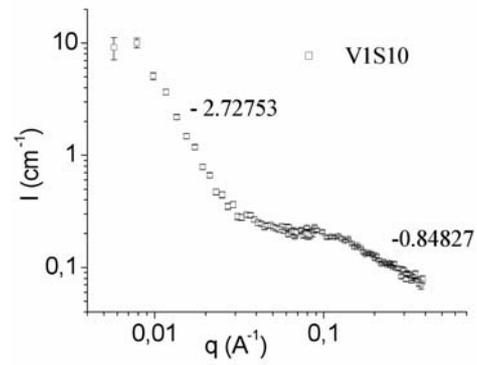
The neutron scattering intensities  $I(q)$  versus  $q$  are shown in Figures 1 to 5 in log-log representation. As can be seen (Figures from 1 to 5), in certain cases the intensity decreases with  $q$  to a value  $q_0$ , denoted as the first cross-over. At this point a plateau begins, extending to the second cross-over at the value  $q_1$ , after which a linear descent is observed. The two linear parts observed in the SANS profile can be interpreted by fractal behavior at two scale sizes.

In small  $q$  range the silica xerogel (S0) sample shows a mass fractal dimension of  $D_m=1.76$  ( $D_m=-P$ , where  $P$  is slope). The observed mass fractal dimension is consistent with those reported in the literature ( $D_m=1.78$  (3)) for open structures formed by diffusion-limited cluster-cluster aggregation (DLCCA), under acidic conditions. At high  $q$  value, the mass fractal dimension is smaller,  $D_m=1.42$ . Lower fractal dimension compared with the classic aggregation model can be explained by tip-to-tip cluster-cluster aggregation process (15), which involves polarisation of the clusters when they approach each other. This process results in more linear structures and consequently a lower fractal dimension occurs. A more general model includes the difference in reactivity of species which have

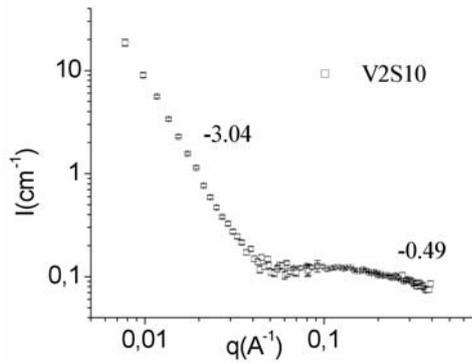
already reacted, which is the reason why a wide variation in fractal dimensions can be obtained.



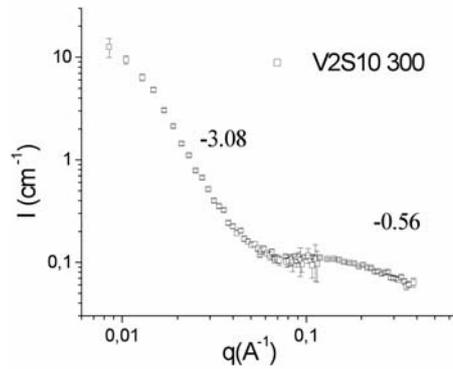
**Fig. 1.** SANS intensity log-log curve of S0 silica xerogel sample



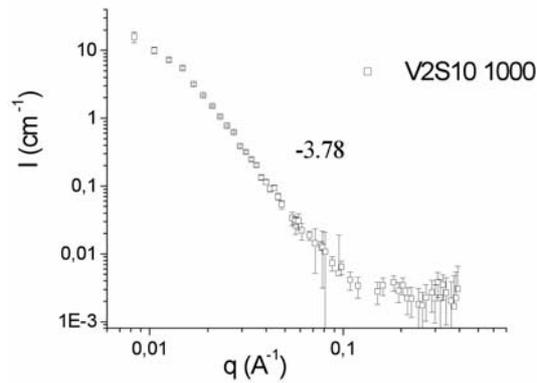
**Fig. 2.** SANS intensity log-log curve of VIS10 silica/PVA hybrid xerogel sample



**Fig. 3.** SANS intensity log-log curve of V2S10 silica/PVA xerogel sample



**Fig. 4.** SANS intensity log-log curve of V2S10 300 silica/PVA hybrid sample



**Fig. 5.** SANS intensity log-log curve of V2S10 1000 silica/PVA sample

In the small  $q$  range, the V1S10 sample shows a mass fractal dimension,  $D_m=2.73$  revealing quite compact silica structures (16). In the high  $q$  region, the curve slope,  $P$ , tends unity, denoting the silica polymer tendency to extend its chains (8). In the small  $q$  range a surface fractal behaviour of V2S10 hybrid xerogel sample with  $D_s \sim 2.96$ , ( $(D_s = 6 - (-P))$ ) was observed. In the high  $q$  range the slope  $P = -0.49$ .

The increased mass fractal dimension, observed for V1S10 sample, compared to  $D_m$  of silica matrix,  $S_0$ , (17) can be attributed to the steric restriction, to the growth of the siloxane structure exerted by the rigid organic moiety (8). The surface fractal behaviour, implied by higher molecular mass of PVA in V2S10 sample can be the expression of more effective steric influence due to the extended chains of organic polymer. In the meantime, if their physical dimensions fit, the polyvinyl alcohol oligomers, as other guests (18), may fill the silica polymeric network pores (19).

At high  $q$  values, the plot of the V2S10 (higher  $M$ ) sample is almost flat, probably indicating the absence of inhomogeneous structure at the length scale shorter than 5 nm.

The  $D_s=2.92$  characteristic value for V2S10 300 sample, (Figure 4), is not essentially different comparing with that of xerogel, indicating however a slightly smoother surface, probably due to temperature influence. It can be attributed to the elimination of the organics, shrinkage of the gel backbone without a significant pores collapse (20).

More dramatic changes, caused by the higher ignition temperature ( $1000^\circ\text{C}$ ) are obvious in the case of V2S10 1000 sample. The observed slope,  $P \sim -3.77$ , resulted in a value of surface fractal dimension of  $D_s \sim 2.23$ , obviously diminished comparing to those corresponding to the xerogel or samples treated at  $300^\circ\text{C}$ . This indicates that the particles are almost well defined, exhibiting the tendency to have smoother surfaces with increasing the temperature of thermal treatment. The surface fractal dimensions ranging from 2.23 ( $1000^\circ\text{C}$ ), to 2.92 ( $300^\circ\text{C}$ ) and 2.96 (hybrid xerogel) show without doubt that the temperature below  $300^\circ\text{C}$  did not drastically damage the porosity. As a general rule, it can be said that the higher is the temperature of thermal treatment the smoother is the particle surface.

## CONCLUSION

The silica-polyvinyl alcohol hybrid xerogels were obtained by sol-gel processing. Their sample microstructure evolution during the thermal treatment at  $300^\circ\text{C}$ , and  $1000^\circ\text{C}$  was qualitatively evaluated by small angle neutron scattering (SANS) technique. All the synthesized samples present mass or surface fractal characteristics, most of them in both (long and short) length scale range. A significant conclusion is that both molecular mass and increase of thermal treatment temperature cause a dramatic change in microstructure fractal behaviour from mass fractal to surface fractal and even to nonfractal appearance. The sample treated at  $1000^\circ\text{C}$  showed the smoothest surface.

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### **ИСПИТИВАЊЕ РАЗВОЈА МИКРОСТРУКТУРЕ СИЛИКА-PVA КСЕРОГЕЛА У ТОКУ ТЕРМИЧКЕ ОБРАДЕ ПРИМЕНОМ SANS МЕТОДЕ**

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Циљ овог рада је испитивање развоја микроструктуре SiO<sub>2</sub>/PVA нанокомпозитног ксерогела на различитим температурама, применом методе расејавања неутрона под малим углом (SANS). Узорци су припремани сол-гел методом полазећи од алкоксида. SANS мерења су извршена преко вектора расејавања,  $q$ , у интервалу од 0.05 до 3.7 nm<sup>-1</sup>, чиме је омогућено добијање структурних информација на скали ( $2\pi/q$ ) приближно између 1 и 100 nm. Измерени интензитети расејавања под малим углом узорака силике и композита силика/PVA, после старења на 60°C и термичке обраде на различитим температурама, су представљени у log-log дијаграмима. Показано је да и молекулска маса и температура термичке обраде имају велики утицај на тенденцију преласка од масених фракталних облика према површински фракталним облицима.

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