

Influence of pH and Dye Concentration on the Physical Properties and Microstructure of New Coumarin 4 Doped SiO₂-PDMS ORMOSIL

E. O. Oh, R. K. Gupta, N.-H. Cho, Y.-C. Yoo, W.-S. Cho, and C. M. Whang*

School of Materials Science and Engineering, and Institute of Advanced Materials,
Inha University, 253 Yonghyun-dong, Incheon 402-751, Korea

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Physical properties and microstructure of new coumarin 4 doped SiO₂-PDMS ORMOSILs, synthesized by one-step (*OS*, acid-catalysis) and two-step (*TS*, acid-base catalysis) routes of sol-gel method with varying pH (0.6 to 7) and dye content (5×10^{-4} to 5×10^{-2} mole), are reported. BET, UV-visible spectroscopy and SEM were used for characterizations. The increase in acid or base concentration increased the size of pores and aggregated silica particles. The samples with pH ≤ 2.5 were transparent and attributed to the small size of pores (~ 20 Å) and silica particles. The samples with pH > 2.5 were translucent or opaque due to non-uniform pore system formed by voids and large aggregated silica particles. The surface area was found a key factor controlling the interactions between the gel matrix and the dye. The *OS* samples with the highest dye concentration exhibited the minimal values of pore size, surface area and silica particle size, resulting in the *concentration-quenching* phenomenon.

Key Words : Physical properties, Microstructure, Organic dye, ORMOSIL

Introduction

The organic dye doped ORMOSILs (organically modified silicates) attract widespread interests in recent years due to their wide application as gain media in laser materials, non-linear optical materials, photochemical hole burning, luminescence solar concentrator, chemical sensor, pH sensor, etc.¹⁻³ The organic dyes show the high fluorescent quantum yields, large cross-sections for absorption-emission, low threshold power for laser action, attractive gain characteristics and tunability in the visible region.¹⁻³ The sol-gel derived ORMOSIL network contains a significant amount of organic functionalities, which offers great flexibility with respect to the chemical compatibility of the gel with the organic dye. Further, due to the low processing temperature, excellent homogeneity at molecular level, large flexibility in the control of sol-gel processing variables and high compositional purity, the sol-gel derived organic dye doped ORMOSIL showed several advantageous properties over the organic dye as a solute in a fluid media, *e.g.* elimination of translational freedom by avoiding inter-molecular interaction, immunization of optical properties from high concentration interferences, reduction in rotational relaxation of the excited state of laser dyes, elimination of inherent problems with physical pumping, ease of use and replacement, and fabrication of samples in the desired form and shape.¹ Amongst the several investigated organic dye doped ORMOSILs,⁴⁻¹² the chemical bonded SiO₂-PDMS ORMOSIL is noted as a useful host-matrix for doping a dye. A detailed investigation on the SiO₂-PDMS ORMOSIL has already been carried out in the present laboratory because the tetraethoxysilane (TEOS,

an inorganic precursor for SiO₂) shows a controllable hydrolysis reaction rate and PDMS (poly(dimethylsiloxane)) possesses specific properties like transparency, hydrophobicity, good chemical and thermal stability and similarity of its backbone structure (-Si-O-) to that of TEOS.^{13,14} Recently, we doped coumarin 4 organic dye into the SiO₂-PDMS ORMOSIL using one-step (acid catalysis) and two-step (acid-base catalysis) routes of sol-gel processing with varying acid (HCl), base (NH₄OH) and dye concentrations to synthesize *OS* and *TS* samples, respectively.¹⁵ Coumarin 4 was chosen as a organic dye because of its high fluorescence efficiency, chemical- and photo-stability.⁷⁻⁹ It also exhibits specific molecular species associated with protonation-deprotonation reactions.⁷⁻⁹ It was observed that the increase in the acid or base concentration increased the photo-luminescence peak intensity, which was attributed to an increase in the interaction between the gel matrix and the dye molecules.¹⁵ *Concentration-quenching* phenomenon was also noted with increasing dye concentration due to the deactivation process by the intermolecular energy transfer originating from the collision and aggregation of dye molecules.¹⁵

The present paper, in series, reports the effects of pH and dye concentration on the physical properties and microstructure of new coumarin 4 dye doped SiO₂-PDMS xerogels: *OS* and *TS*. BET and scanning electron microscopy (SEM) were used to characterize the physical properties and microstructure, respectively. The transparency of the samples was monitored by UV-visible spectroscopy.

Experimental Section

Figure 1 shows the schematic flow chart for synthesizing *OS* and *TS* samples by acid catalysis (one-step) and acid-base catalysis (two-step) routes of sol-gel processing, respec-

*Corresponding author. Fax: +82-32-874-3382, E-mail: cmwhang@inha.ac.kr

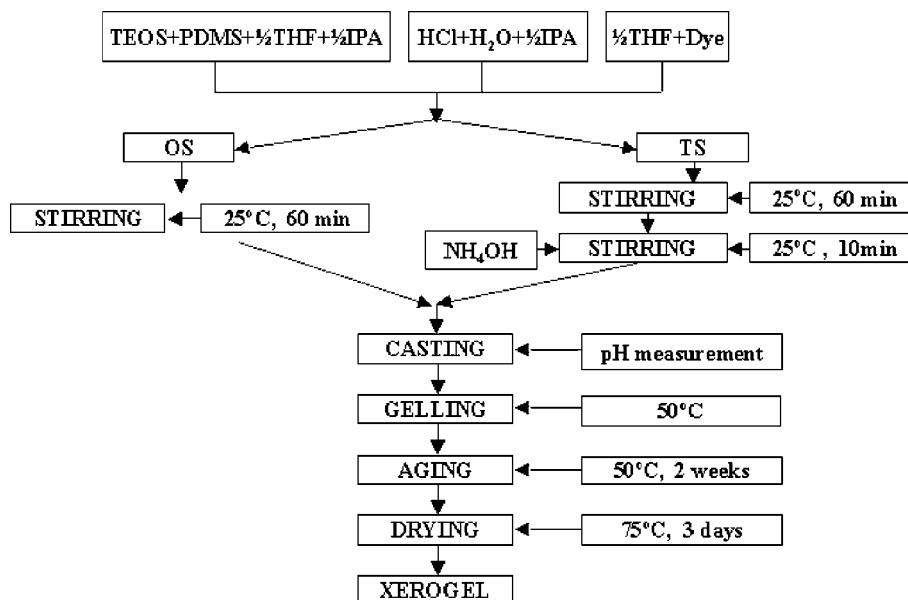


Figure 1. Schematic flowchart of one-step (*OS*) and two-step (*TS*) sol-gel processing for preparing coumarin 4 dye doped SiO₂-PDMS xerogels.

tively. The two-step processing was used in order to get an advantage over the one-step process for getting better controllability over pH by controlling the hydrolysis-condensation reactions at the middle of the stirring.^{13,14} The composition of starting solutions of the *OS* and *TS* xerogels is shown in Table 1. The starting chemicals: TEOS [Si(OC₂H₅)₄, 98%], coumarin 4 [C₁₀H₈O₃, 97%], IPA [2-Propanol, 98%], THF [Tetrahydrofuran, C₄H₈O, 98%] and HCl [Hydrochloric acid, 1M], were bought from the Aldrich (USA), and PDMS [(CH₃)₂SiOH [(CH₃)₂SiO₂]_x (CH₃)₂SiOH, mol. wt.=400-700 g·mol⁻¹] was from the United Chem. Tech. (USA). IPA & THF and HCl & NH₄OH were used as solvents and catalysts, respectively. Clear sol of the *OS* xerogel was obtained by stirring the starting solution at room temperature for 1 h. The base solution (NH₄OH, 1 M) was added into this solution and stirred again for 10 min for getting a clear sol of *TS* xerogel. pH value of the sol was measured by a pH meter (ISTEK, model 735P, Korea). This sol was poured into a mould followed by covering with a paraffin film having small holes for controlling the evaporation rate. The container was kept in an oven at 50 °C to observe gelation time. The gelation time for the bulk solution was determined by simply tilting the container to find out the time at which the fluidity

of the solution was lost. The wet gel was further aged at 50 °C for two weeks and then dried at 75 °C for 3 days. The finished products were found crack-free bulk of diameter 1.5-2 cm and thickness 1-2 mm. The physical parameters, namely surface area, pore size and pore volume of the bulk samples were measured by N₂ (77 K) adsorption BET (Brunauer, Emmet, Teller) isotherm method. For this measurement, all the samples were outgassed for 1h at 50 °C and then for 4h at 75 °C. A UV- visible spectro-fluorophotometer (SHIMADZU, model UV-2401PC, Japan) was used for recording the transmittance of the bulk samples. Microstructure of the bulk samples was observed by a Hitachi S-4300 scanning electron microscope. All these measurements were carried out at the room temperature.

Results and Discussions

Table 2 shows the physical properties of the coumarin 4 dye-doped SiO₂-PDMS xerogels: *OS_A*, *TS_B* and *OS_D* prepared with different concentration of acid (*A*, HCl), base (*B*, NH₄OH) and dye (*D*, coumarin), respectively. This table also depicts the physical parameters of the reference samples: *OS_R* and *TS_R* prepared without the dye for direct comparison.

Table 1. Composition of starting solutions for preparing dye-doped SiO₂-PDMS xerogels. In the sample name, the notations: *OS* and *TS* stand for one-step and two-step sol-gel processing, respectively. Subscripts: *A*, *B* and *D* correspond to the concentration of acid (HCl), base (NH₄OH) and dye, respectively. *R* → Reference sample

Sample name	TEOS (mole)	PDMS (wt%)	THF (mole)	IPA (mole)	H ₂ O (mole)	HCl (<i>A</i> , mole)	NH ₄ OH (<i>B</i> , mole)	Coumarin dye (<i>D</i> , mole)
<i>OS_A</i>	1	10	10	4	8	0.1-1.2	–	5 × 10 ⁻³
<i>TS_B</i>	1	10	10	4	8	0.1	0.06-0.25	5 × 10 ⁻³
<i>OS_D</i>	1	10	10	4	8	0.1	–	5 × 10 ⁻⁴ - 5 × 10 ⁻²
<i>OS_R</i>	1	10	10	4	8	0.8	–	–
<i>TS_R</i>	1	10	10	4	8	0.1	0.06	–

Table 2. Physical properties of the coumarin 4 doped SiO₂-PDMS xerogels: *OS_A*, *TS_B* and *OS_D* along with the reference samples without dye

Sample name	pH	Gelation time	Pore size (Å)	BET surface area (m ² g ⁻¹)	Optical nature
OS _A (A=0.1)	1.3	21 days	18.8	653.6	Transparent
OS _A (A=0.4)	1.0	18 days	19.9	699.1	Transparent
OS _A (A=0.8)	0.8	14 days	20.6	833.6	Transparent
OS _A (A=1.2)	0.6	12 days	20.8	912.9	Transparent
TS _B (B=0.06)	1.5	15 days	18.6	470.2	Transparent
TS _B (B=0.14)	2.5	8 days	18.7	493.1	Transparent
TS _B (B=0.144)	4.5	1 day	29.7	553.1	Translucent
TS _B (B=0.16)	6.2	20 min	33.5	673.1	Opaque
TS _B (B=0.25)	7	10 min	37.4	677.1	Opaque
OS _D (D=5 × 10 ⁻⁴)	1.5	20 days	19.6	582.8	Transparent
OS _D (D=1 × 10 ⁻³)	1.5	20 days	18.5	565	Transparent
OS _D (D=1 × 10 ⁻²)	1.5	20 days	18.4	520.2	Transparent
OS _D (D=5 × 10 ⁻²)	1.5	20 days	18.3	449.8	Transparent
OSR	0.9	14 days	19.6	751.9	Transparent
TSR	1.5	16 days	18.5	470.8	Transparent

The increase in concentration of acid (*i.e.* decrease of pH value) or base (*i.e.* increase of pH value) reduced the gelation time, which is a usual sol-gel phenomenon observed in pure SiO₂, ORMOSIL systems^{14,16-18} and can be explained with the help of rates of hydrolysis-condensation reactions, as below. Near the point-of-zero-charge (*PZC*, where pH ≈ 2.5 for SiO₂ and its derivative), the condensation becomes rate limiting. This results in randomly branched and relatively linear silicates that form tightly interwoven gels having micropores upon drying. The decrease (or increase) in the pH well below (or above) the *PZC* increases the condensation rate rather than the hydrolysis rate due to the fast protonation (or deprotonation) of silanols to produce SiOH₂⁺ (or SiO⁻) groups that readily condense. Thus, one can expect faster 3-dimensional silica network formation bonded with PDMS covalently through terminated OH of the TEOS.^{2,3,14} In the highly acidic region of sol (pH ≤ 2.5), the silica particulates grow up almost non-linearly, hence, form relatively less dense acid catalyzed *OS* samples with increased micropore size.^{6,14,19-22} In the acid-base catalyzed (*TS*) samples prepared with the condition 2.5 < pH ≤ 7, the silica particles grow up randomly resulting in loosely packed, cluster-like structures having mesopores and large size of silica particles, which can be seen clearly below.^{14,18-22} This resulted in transparent acid-catalyzed *OS* samples (pH ≤ 2.5) and translucent or opaque acid-base catalyzed *TS* samples (pH > 2.5).^{4,6,14,18-22} This phenomenon also results in an increase in the surface area with increasing acid and base concentrations, which is consistent with the earlier reported results.^{6,14,18-20,22} The highest surface area (~913 m²g⁻¹) was obtained for the *OS_A* sample with A = 1.2 mole (pH = 0.6). For the *TS_B* samples, it is ~677 m²g⁻¹ at B = 0.25 mole (pH = 7). Thus, the surface area of the silica particles is also a vital factor to control the interactions between the gel matrix and the dye molecules filled in the pores.^{15, 22} For the *OS_D* samples, the increase in the dye concentration reduced the pore size and surface area resulting in the collision and aggregation of dye molecules.¹⁵

Figures 2(a), (b) and (c) show the pore size distributions of the coumarin 4 dye doped SiO₂-PDMS xerogels: *OS_A*, *TS_B* and *OS_D* prepared with different concentration of acid (A), base (B) and dye (D), respectively. The pore size distributions for the *OSR* and *TSR* samples without the dye are also included for direct comparison. Consistent with the earlier reports^{14,20,21} and also depicted in the Table 2, the increase in A for the *OS_A* samples shifted the pore size distribution towards the larger pore size indicating an increase in the pore size. A similar behavior is also noticed for the pore size distributions of *TS_B* samples having broad distribution curves as compared to the *OS_A* samples. This is most probably due to the fast co-condensation of TEOS and PDMS with increasing pH resulting in highly branched clusters in the *TS_B* samples. As observed earlier and also indicated by down shift of pore size distributions for the *OS_D* samples, the increase in the dye concentration decreased the pore size.

The porosity of the samples: *OS_A*, *TS_B* and *OS_D* and the reference samples: *OSR* and *TSR* are illustrated in Figures 3(a), (b) and (c), respectively, by nitrogen adsorption-desorption isotherms. As observed earlier for pure SiO₂ and ORMOSIL systems,^{14,20,21} the isotherms for the *OS_A* samples having the sol pH ~2.5 are clearly of BET-Type I with no indication of a hysteresis loop suggesting the existence of micropores having almost equal size of openings leading into them. However, as the acid concentration was increased *i.e.* the pH was decreased, the isotherms remained Type I, however, vestiges of Type II hysteresis loop, characteristic of mesopore filling, ultimately start to emerge.^{20,21} A similar variation was also noticed for the *TS_B* and *OS_D* samples with increasing base concentration (B) and decreasing dye concentration (D), respectively. These trends have already been shown in the Table 2, where the size of pores was slightly increased with increasing acid and decreasing dye concentrations. The increase in base concentration largely increased the pore size. The SEM micrographs, discussed below, well revealed that the uniformity in the pore system formed by

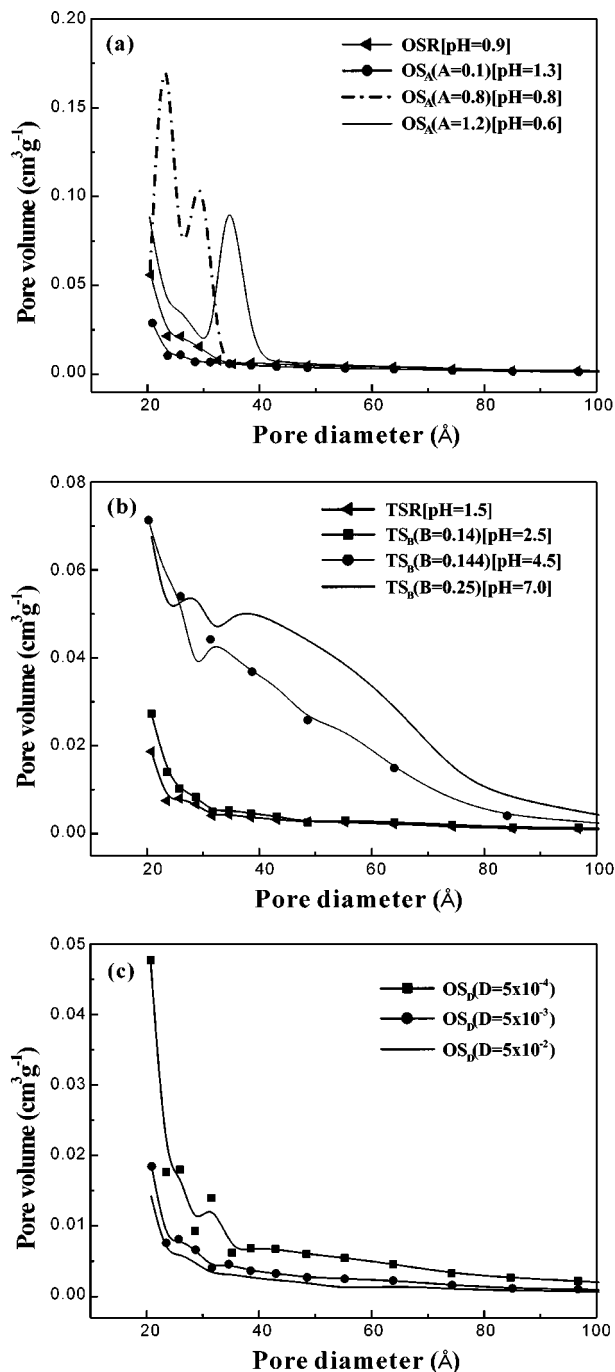


Figure 2. Pore distribution of the coumarin 4 doped SiO_2 -PDMS xerogels: OS_A , TS_B and OS_D prepared with different concentration of: (a) acid (A , HCl), (b) base (B , NH_4OH), and (c) dye (D), respectively. OSR & TSR , reference samples without dye.

the voids between the agglomerated silica particles, is higher for the samples with $\text{pH} < 2.5$.

Figures 4(a), (b) and (c) show the UV-visible transmittance spectra of the coumarin 4 dye-doped SiO_2 -PDMS xerogels: OS_A , TS_B and OS_D prepared with different concentration of acid (A), base (B) and dye (D), respectively. Transmittance spectra of the reference samples: OSR and TSR are also included for direct comparison. One can note that the transmittance of OS xerogels is as good as that of reference

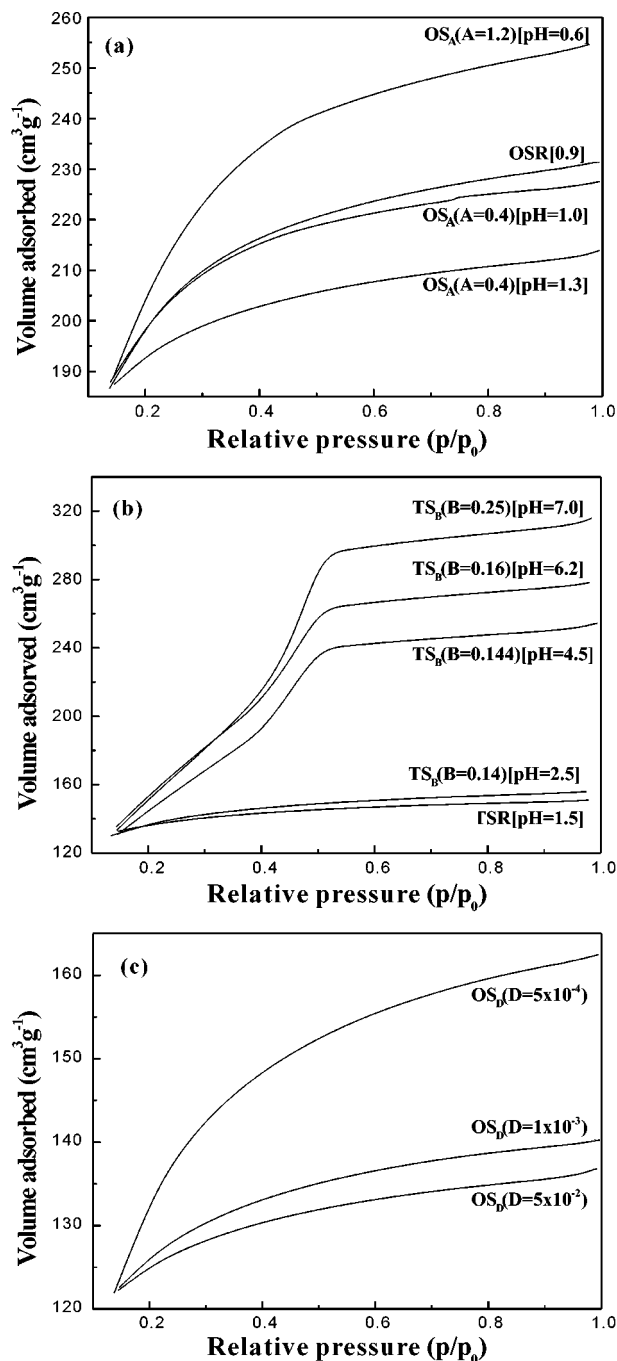


Figure 3. BET isotherms of the coumarin 4 doped SiO_2 -PDMS xerogels: OS_A , TS_B and OS_D prepared with different concentration of: (a) acid (A , HCl), (b) base (B , NH_4OH), and (c) dye (D), respectively. OSR & TSR , reference samples without dye.

sample, OSR . Transmittance 94-90% in the visible region (500-700 nm) was observed for the OS samples and can be attributed to the pore size smaller than the visible wavelength.^{4,6,14,18-22} As indicated by the SEM study, discussed below, these samples possessed very small size of uniformly distributed silica particles. The lowest transmittance (90%), observed for the OS_A sample with $A = 1.2$ mole ($\text{pH} = 0.6$), can be attributed to almost non-uniform pore system for this composition resulting in a slight light scattering/absorption

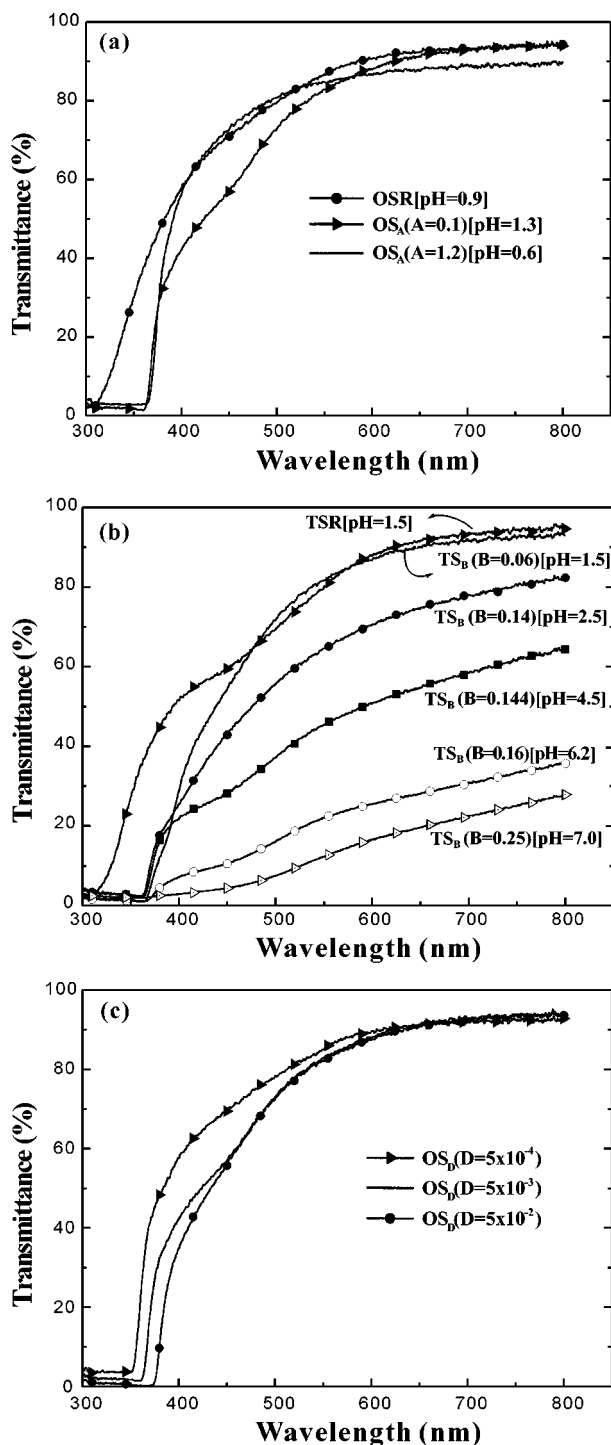


Figure 4. UV-visible spectra of the coumarin 4 doped SiO₂-PDMS xerogels: OS_A , TS_B and OS_D prepared with different concentration of: (a) acid (A , HCl), (b) base (B , NH₄OH), and (c) dye (D), respectively. OSR & TSR , reference samples without dye.

phenomenon.^{4,6,14,18-22} The TS_B xerogels prepared with the $pH \leq 2.5$ also exhibited the transmittance in the range: 93-82%. Further increase in the base concentration (B) largely decreased the transmittance to 27% (opaque nature), which may be due to the formation of non-uniform pore system by the large size of pores and aggregated silica particles resulting in a large light scattering/ absorption phenomenon.

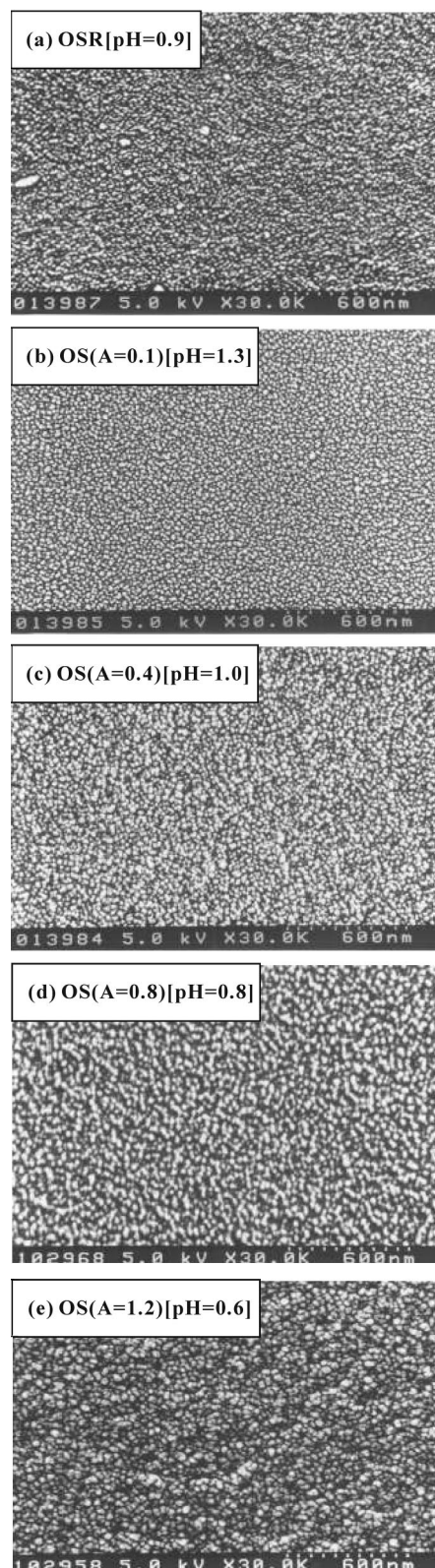


Figure 5. Scanning electron micrographs of the coumarin 4 doped SiO₂-PDMS OS_A xerogels prepared by varying the acid (A , HCl) concentration. (a) OSR , reference sample without dye, (b) 0.1, (c) 0.4, (d) 0.8, and (e) 1.2 mole.

Figures 5, 6 and 7 show the SEM micrographs of the coumarin 4 dye doped SiO₂-PDMS xerogels: OS_A , TS_B and

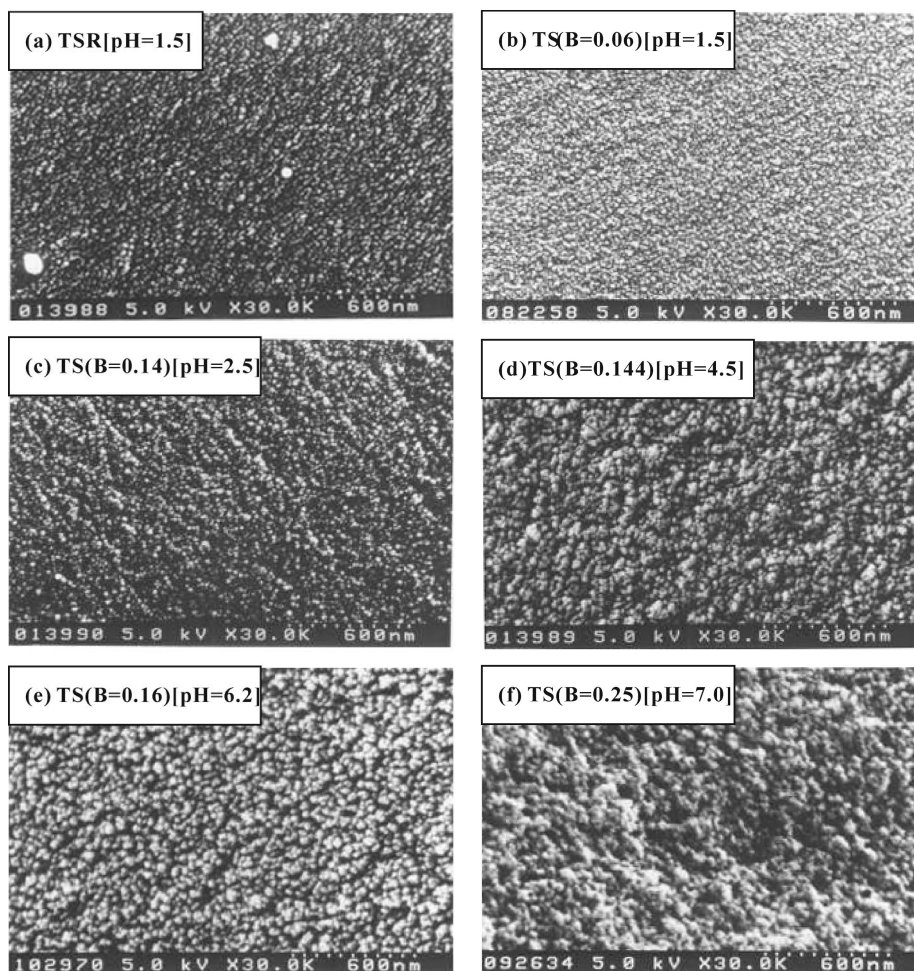


Figure 6. Scanning electron micrographs of the coumarin 4 doped SiO_2 -PDMS TS_B xerogels prepared by varying the base (B , NH_4OH) concentration. (a) TSR , reference sample without dye, (b) 0.06, (c) 0.14, (d) 0.144, (e) 0.16, and (f) 0.25 mole.

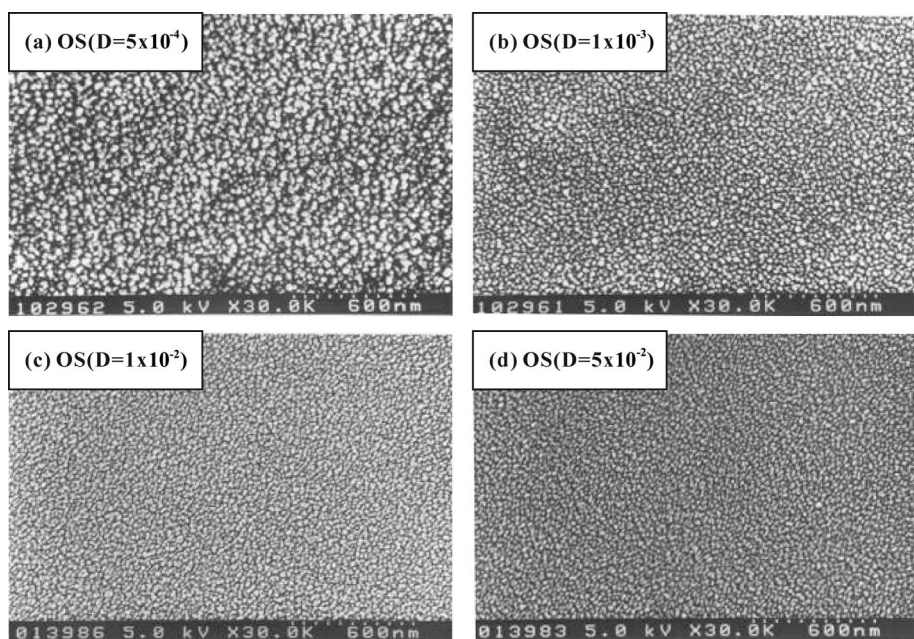


Figure 7. Scanning electron micrographs of the coumarin 4 doped SiO_2 -PDMS OS_D xerogels prepared by varying the dye (coumarin 4) concentration. (a) 5×10^{-4} , (b) 1×10^{-3} , (c) 1×10^{-2} , and (d) 5×10^{-2} mole.

OS_D prepared with different concentrations of acid (*A*), base (*B*) and dye (*D*), respectively. The micrographs for the reference samples: *OSR* and *TSR* without the dye are also shown for direct comparison. As observed earlier for a number of silica and ORMOSIL systems, the average size of silica particles and pores are strongly dependent on the pH condition.^{6,14,18-21} The *OS* samples prepared with pH ≤ 2.5 exhibited relatively small size of SiO₂ particles and pores than those obtained for *TS* samples prepared with the sol condition 2.5 < pH ≤ 7. Further, the increase in acid or base concentration increased the size of aggregated SiO₂ particles and pores. Moreover, a globular morphology was obtained for the *OS_A* sample with pH = 0.6, which might be resulted into the highest surface area, a major cause for the highest interactions between the silanols of gel matrix and the dye residing into the relatively large pores. Further, the increase in size of silica particles and pores increased the light scattering phenomenon diminishing the transparency of the *OS_A* samples with increasing acid content. The size of silica particles and pores are quite large in the *TS_B* samples prepared with sol condition 2.5 < pH ≤ 7 resulting in translucent or opaque optical behavior. Figure 7 also indicated a decrease in the size of pores and silica particles with increasing dye concentration. Thus, the increase in dye concentration increased the dye agglomeration/ collision which gives rise to the *concentration-quenching* phenomenon.¹⁵

Conclusions

Coumarin 4 dye doped SiO₂-PDMS xerogels: *OS_A*, *TS_B* and *OS_D* were synthesized using one-step (*OS*, acid catalysis) and two-step (*TS*, acid-base catalysis) routes of sol-gel processing as a function of acid (HCl), base (NH₄OH) and dye (coumarin 4) concentration, respectively. A usual phenomenon, *i.e.*, the decrease in gelation time with increasing acid or base concentration was noted and explained with help of rates of hydrolysis-condensation reactions. The samples possessing pH ≤ 2.5 were found transparent in nature due to the smaller size of pores (≤ 20 Å) and agglomerated silica particles as suggested by BET, SEM and UV-visible spectroscopy studies. The pH higher than 2.5 resulted in the translucent or opaque samples due to non-uniform pore system formed by voids and large aggregated silica particles. The surface area was found the highest for the *OS_A* samples with pH = 0.6 (acid content = 1.2 mole) resulted in the highest interactions between the gel matrix

and the dye. The morphological parameters were also noted as crucial factors controlling the *concentration-quenching* phenomenon, observed for the *OS* samples with high dye concentration.

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