A New Coumarin 4 Doped SiO$_2$-PDMS ORMOSIL


Influence of pH and Dye Concentration on the Physical Properties and Microstructure of New Coumarin 4 Doped SiO$_2$-PDMS ORMOSIL


School of Materials Science and Engineering, and Institute of Advanced Materials, Inha University, 253 Yonghyun-dong, Incheon 402-751, Korea
Received September 11, 2002

Physical properties and microstructure of new coumarin 4 doped SiO$_2$-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 ($5 \times 10^{-7}$ to $5 \times 10^{-2}$ 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, nonlinear optical materials, photochemical hole burning, luminescence solar concentrator, chemical sensor, pH sensor, etc. 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. 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. Amongst the several investigated organic dye doped ORMOSILs, the chemical bonded SiO$_2$-PDMS ORMOSIL is noted as a useful host-matrix for doping a dye. A detailed investigation on the SiO$_2$-PDMS ORMOSIL has already been carried out in the present laboratory because the tetraethoxysilane (TEOS, an inorganic precursor for SiO$_2$) 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. Recently, we doped coumarin 4 organic dye into the SiO$_2$-PDMS ORMOSIL using one-step (acid catalysis) and two-step (acid-base catalysis) routes of sol-gel processing with varying acid (HCl), base (NH$_3$OH) and dye concentrations to synthesize OS and TS samples, respectively. Coumarin 4 was chosen as an organic dye because of its high fluorescence efficiency, chemical- and photo-stability. It also exhibits specific molecular species associated with protonation-deprotonation reactions. 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. *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.

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 SiO$_2$-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-
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. 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]ₙ(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 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: OS₄₅, TS₁₀ and OS₀ 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: OSR and TSR prepared without the dye for direct comparison.

---

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

**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

<table>
<thead>
<tr>
<th>Sample name</th>
<th>TEOS (mole)</th>
<th>PDMS (wt%)</th>
<th>THF (mole)</th>
<th>IPA (mole)</th>
<th>H₂O (mole)</th>
<th>HCl (A, mole)</th>
<th>NH₄OH (B, mole)</th>
<th>Coumarin dye (D, mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OS₅</td>
<td>1</td>
<td>10</td>
<td>10</td>
<td>4</td>
<td>8</td>
<td>0.1-1.2</td>
<td>−</td>
<td>5×10⁻³</td>
</tr>
<tr>
<td>TS₁₀</td>
<td>1</td>
<td>10</td>
<td>10</td>
<td>4</td>
<td>8</td>
<td>0.1</td>
<td>0.06-0.25</td>
<td>5×10⁻³</td>
</tr>
<tr>
<td>OS₀</td>
<td>1</td>
<td>10</td>
<td>10</td>
<td>4</td>
<td>8</td>
<td>0.1</td>
<td>−</td>
<td>5×10⁻⁴ - 5×10⁻²</td>
</tr>
<tr>
<td>OSR</td>
<td>1</td>
<td>10</td>
<td>10</td>
<td>4</td>
<td>8</td>
<td>0.8</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>TSR</td>
<td>1</td>
<td>10</td>
<td>10</td>
<td>4</td>
<td>8</td>
<td>0.1</td>
<td>0.06</td>
<td>−</td>
</tr>
</tbody>
</table>
The increase in concentration of acid \((i.e., \text{increase of pH value})\) or base \((i.e., \text{increase of pH value})\) reduced the gelation time, which is a usual sol-gel phenomenon observed in pure SiO\textsubscript{2}, ORMOSIL systems\textsuperscript{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 SiO\textsubscript{2} 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 SiOH\textsubscript{2}\(^+\) (or SiO\textsuperscript{2-}) groups that readily condense. Thus, one can expect faster 3-dimensional silica network formation bonded with PDMS covalently through terminated OH of the TEOS\textsuperscript{2,3,14} In the highly acidic region of sol (pH \(\leq 2.5\)), the silica particulates grow up almost non-linearly, hence, form relatively less dense acid catalyzed OS samples with increased micropore size.\textsuperscript{6,14,19-22} In the acid-base catalyzed (TS) samples prepared with the condition 2.5 \(<\) pH \(\leq 7\), 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.\textsuperscript{14,18,22} This increase in the acid concentration decreased the pore size and surface area resulting in the aggregation of dye molecules.\textsuperscript{15} Figures 2(a), (b) and (c) show the pore size distributions of the coumarin 4 dye doped SiO\textsubscript{2}-PDMS xerogels: OS\textsubscript{A}, TS\textsubscript{B} and OS\textsubscript{D} along with the reference samples without dye.

### Table 2: Physical properties of the coumarin 4 doped SiO\textsubscript{2}-PDMS xerogels: OS\textsubscript{A}, TS\textsubscript{B} and OS\textsubscript{D} along with the reference samples without dye

<table>
<thead>
<tr>
<th>Sample name</th>
<th>pH</th>
<th>Gelation time</th>
<th>Pore size (Å)</th>
<th>BET surface area (m(^2) g(^{-1}))</th>
<th>Optical nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>OS\textsubscript{A} (A=0.1)</td>
<td>1.3</td>
<td>21 days</td>
<td>18.8</td>
<td>653.6</td>
<td>Transparent</td>
</tr>
<tr>
<td>OS\textsubscript{A} (A=0.4)</td>
<td>1.0</td>
<td>18 days</td>
<td>19.9</td>
<td>699.1</td>
<td>Transparent</td>
</tr>
<tr>
<td>OS\textsubscript{A} (A=0.8)</td>
<td>0.8</td>
<td>14 days</td>
<td>20.6</td>
<td>833.6</td>
<td>Transparent</td>
</tr>
<tr>
<td>OS\textsubscript{A} (A=1.2)</td>
<td>0.6</td>
<td>12 days</td>
<td>20.8</td>
<td>912.9</td>
<td>Transparent</td>
</tr>
<tr>
<td>TS\textsubscript{B} (B=0.06)</td>
<td>1.5</td>
<td>15 days</td>
<td>18.6</td>
<td>470.2</td>
<td>Transparent</td>
</tr>
<tr>
<td>TS\textsubscript{B} (B=0.14)</td>
<td>2.5</td>
<td>8 days</td>
<td>18.7</td>
<td>493.1</td>
<td>Transparent</td>
</tr>
<tr>
<td>TS\textsubscript{B} (B=0.144)</td>
<td>4.5</td>
<td>1 day</td>
<td>29.7</td>
<td>553.1</td>
<td>Transparent</td>
</tr>
<tr>
<td>TS\textsubscript{B} (B=0.16)</td>
<td>6.2</td>
<td>20 min</td>
<td>33.5</td>
<td>673.1</td>
<td>Transparent</td>
</tr>
<tr>
<td>TS\textsubscript{B} (B=0.25)</td>
<td>7</td>
<td>10 min</td>
<td>37.4</td>
<td>677.1</td>
<td>Transparent</td>
</tr>
<tr>
<td>OS\textsubscript{D} (D=0.25 mole (pH = 7))</td>
<td>1.5</td>
<td>20 days</td>
<td>19.6</td>
<td>582.8</td>
<td>Transparent</td>
</tr>
<tr>
<td>OS\textsubscript{D} (D=1 (\times) 10(^{-3}))</td>
<td>1.5</td>
<td>20 days</td>
<td>18.5</td>
<td>565</td>
<td>Transparent</td>
</tr>
<tr>
<td>OS\textsubscript{D} (D=1 (\times) 10(^{-2}))</td>
<td>1.5</td>
<td>20 days</td>
<td>18.4</td>
<td>520.2</td>
<td>Transparent</td>
</tr>
<tr>
<td>OS\textsubscript{D} (D=5 (\times) 10(^{-2}))</td>
<td>1.5</td>
<td>20 days</td>
<td>18.3</td>
<td>449.8</td>
<td>Transparent</td>
</tr>
<tr>
<td>OSR</td>
<td>0.9</td>
<td>14 days</td>
<td>19.6</td>
<td>751.9</td>
<td>Transparent</td>
</tr>
<tr>
<td>TSR</td>
<td>1.5</td>
<td>16 days</td>
<td>18.5</td>
<td>470.8</td>
<td>Transparent</td>
</tr>
</tbody>
</table>

The porosity of the samples: OS\textsubscript{A}, TS\textsubscript{B} and OS\textsubscript{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 SiO\textsubscript{2} and ORMOSIL systems,\textsuperscript{14,20,21} the isotherms for the OS\textsubscript{A} samples having the sol pH \(\approx 2.5\) 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., \text{the pH was decreased, the isotherms remained Type I, however, vestiges of Type II hysteresis loop, characteristic of mesopore filling, ultimately start to emerge.}\textsuperscript{20,21} A similar variation was also noticed for the TS\textsubscript{B} and OS\textsubscript{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
the voids between the agglomerated silica particles, is higher for the samples with 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: (a) acid (A, HCl), (b) base (B, NH$_4$OH), and (c) dye (D), respectively. OSR & TSR, reference samples without dye.

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 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. 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 (pH = 0.6), can be attributed to almost non-uniform pore system for this composition resulting in a slight light scattering/absorption.
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.\(^{5,6,14,18-22}\)

**Figure 4.** UV-visible spectra 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$_4$OH), and (c) dye ($D$), respectively. $OSR$ & $TSR$, reference samples without dye.

**Figure 5.** Scanning electron micrographs of the coumarin 4 doped SiO$_2$-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 SiO$_2$-PDMS xerogels: $OS_A$, $TS_b$ and
Figure 6. Scanning electron micrographs of the coumarin 4 doped SiO$_2$-PDMS $T_S$ xerogels prepared by varying the base ($B$, NH$_4$OH) 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) $5 \times 10^{-4}$, (b) $1 \times 10^{-3}$, (c) $1 \times 10^{-2}$, and (d) $5 \times 10^{-2}$ mole.
Concentration increased the size of aggregated SiO$_2$ particles

Menon, to the increased the dye agglomeration/collision which gives rise to the increase in dye concentration. Thus, the increase in dye concentration resulted in the translucent or opaque optical behavior. Figure 7 also indicated a decrease in the size of pores and silica particles with increasing dye concentration. This indicates the increase in dye concentration increased the dye agglomeration/collision which gives rise to the concentration-quenching phenomenon.

Conclusions

Coumarin 4 dye doped SiO$_2$-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 (NH$_4$OH) and the 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 $\leq 2.5$ were found transparent in nature due to the smaller size of pores ($\leq 20$ 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.

Acknowledgment. This work was supported by the Korea Research Foundation through Grant, no. KRF-2001-005-E00009.

References