

## Effects of Ultrasonic Irradiation on Physical Properties of Silica/PEG Hybrids

Hwa Young Jung, Ravindra K. Gupta, Sang Ki Lee and Chin Myung Whang<sup>†</sup>

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

(Received January 19, 2002; Accepted January 30, 2002)

### ABSTRACT

The effect of ultrasonic radiation is reported for silica-poly(ethylene glycol) system prepared without the solvent using sol-gel processing by varying various parameters such as ultrasonic irradiation time, PEG content and HCl/TEOS molar ratio. The property of sonogel is compared with classic gel which has been prepared with ethanol as a solvent by traditional sol-gel processing. SEM, BET, DTA-TGA, density and Vickers hardness measurements are carried out for analyzing the samples. The gelation time is found strongly dependent on radiation time, PEG content and pH value, and has been discussed on the basis of existing theories. The SiO<sub>2</sub>-10 & 20 wt% PEG sonogel exhibited superior optical, physical and gel properties as compared to the classic gel, hence, found suitable for device applications. The ultrasonic radiation increased the density and surface area, and also reduced the pore size which is well supported by the shift in the peak of DTA curve. The DTA thermogram was found similar to that of pure silica gel.

**Key words :** *Inorganic-organic hybrid, Sol-gel process, Sonogel, Classic gel, Ultrasonic irradiation, SiO<sub>2</sub>-PEG*

### 1. Introduction

The sol-gel process, originally directed towards the synthesis of purely inorganic materials, is increasingly being extended to the preparation of inorganic-organic hybrid materials, called ORMOSIL or ORMOCER, by using tetraethoxysilane(TEOS) as a raw material, through hydrolysis and condensation reactions.<sup>1-3)</sup> The ORMOSILs have scientific relevance and technological interest because of their application in the field of optics, electronics, mechanics and electrochemistry.<sup>4)</sup> Most of the properties of these materials are related to the synergy between the organic and inorganic parts and to their biphasic nanostructure, providing totally new properties.<sup>3)</sup> These are essentially porous materials and their structures significantly depend on the preparation conditions, such as pH and water/alkoxide molar ratio, solvent composition, amount of polymer, drying as well as aging. When an organic polymer, e.g. poly(acrylic acid) (PAA), poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO), is incorporated into a silica (SiO<sub>2</sub>) system, it produces a physical hybrid and/or composite system with better optical transparency and superior properties.<sup>5,6)</sup> The silica-poly(ethylene glycol) system, an inorganic-organic hybrid system, has wide application as a low-dielectric material, optical material, filter, adsorption material, electrochromic material, high energy density material, etc.<sup>7)</sup>

Ultrasound has recently been used for hydrolyzing TEOS,

getting more homogeneity and reducing the gelation time.<sup>10)</sup> Sonogels, which are prepared in the presence of acid catalyst without solvent, exhibit peculiar ultra-structural properties due to the nature of the preparation method. Thus, unlike the classic gels prepared by the traditional sol-gel method, alkoxide and water reacts in the vapor phase inside the numerous bubbles produced by cavitation provoking the formation of many microgel particles which aggregate later.<sup>8-11)</sup> The cavitation is effective to accelerate the hydrolysis of alkoxides making it possible to obtain a homogeneous liquid, which quickly gels, without using a solvent of the alkoxide-water mixture.<sup>12-15)</sup>

We report in this paper, an effect of ultrasonic irradiation on preparation of silica-poly(ethylene glycol) system. TEOS and PEG were chosen as the inorganic and organic precursors, respectively. The sonogels were prepared without the solvent by varying the processing variables, e.g. ultrasonic radiation time, amount of PEG and HCl/TEOS molar ratio. For direct comparison, classic gels were also prepared by traditional sol-gel process using the ethanol as a solvent under identical condition. SEM, BET, DTA-TGA, density and Vickers hardness measurements were carried out to understand the effect of ultrasonic irradiation on gelation, structure and properties of SiO<sub>2</sub>-PEG sonogel system.

### 2. Experimental

#### 2.1. Gel Preparation

Tetraethoxysilane (Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, TEOS, 98%, Aldrich), a source of silica, and poly(ethylene glycol) (-H(-CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>

<sup>†</sup>Corresponding author : cmwhang@inha.ac.kr

OH-, PEG, Aldrich, Average MW=400 g/mole) were used as precursors. A trace of HCl (37%, Merck) and deionized water were used as catalyst and for hydrolysis, respectively. The molar ratio of TEOS : H<sub>2</sub>O=1 : 4 was held constant for all samples. Sol solutions were prepared following two methods: (A) and (B). In method (A), 20 kHz ultrasonic irradiation was applied to the solution demonstrating phase-separation by a 13 mm diameter probe of Ultrasonic Processor (Sonic & Materials Co., Model 600, USA, 240±5 W) for changing into a transparent mixture without adding any solvent. In method (B), the traditional sol-gel process was used with ethanol as solvent, and reaction was performed under reflux at 75±3°C for 1 h. The molar ratio of ethanol/TEOS was also kept constant at 3.8 in the method (B).

In the both methods (A) and (B), TEOS was mixed with 0, 5, 10, 20, 40 and 60 wt% of PEG. HCl/TEOS molar ratio was also varied from 0.01 to 0.2 in the TEOS-10 wt% PEG solution.

The pH values of sol solutions were measured using a pH/ISE Meter (ISTEX Co., Model-735P). The compositions along with processing condition are listed in Table 1. Also, the route of synthesis for SiO<sub>2</sub>-PEG xerogel is shown schematically in Fig. 1.

The cooled and clear sol was then poured into a container

and covered with a paraffin film. Very small holes were punched into paraffin film to control the rate of evaporation. These containers were kept in 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 left at 50°C for one week for further improvement in the gelation, and then dried at 125°C for 4 days.

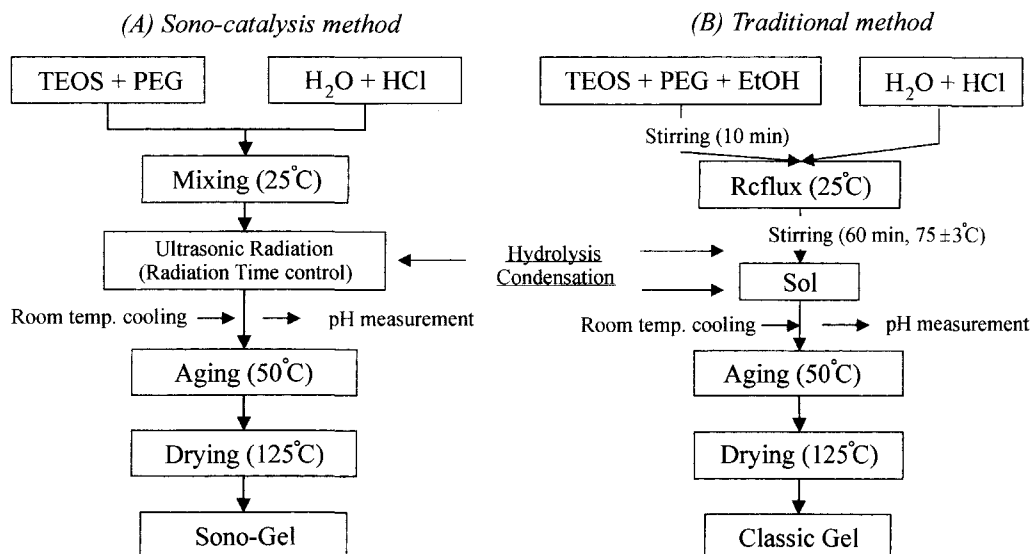
## 2.2. Gel Characterization

Surface area, pore size and pore volume of SiO<sub>2</sub>-PEG xerogels were measured by BET technique using an ASAP 2000 (Micrometrics Co., USA). For these measurements, all samples were outgassed for 1 h at 100°C and then 4 h at 180°C. The density was measured using an Accupye 1330 pycnometer (Micrometrics Co., USA) following the samples were dried at 100°C for 1 h. The Vickers hardness of samples was obtained under the load of 0.245 N (25 g) with dwell time 20 sec. using a Micro-Hardness Tester (Future-Tech. Co., Model FM-7 (HVS-1000)). Microstructures of samples were observed by scanning electron microscopy (SEM) using a S-4200/S-4300 model (Hitachi Co.) with 15.0 kV and ×60,000. The DTA-TGA technique (TA Instrument Co., Model SDT 2960) was used to analyze the thermal behavior of the samples.

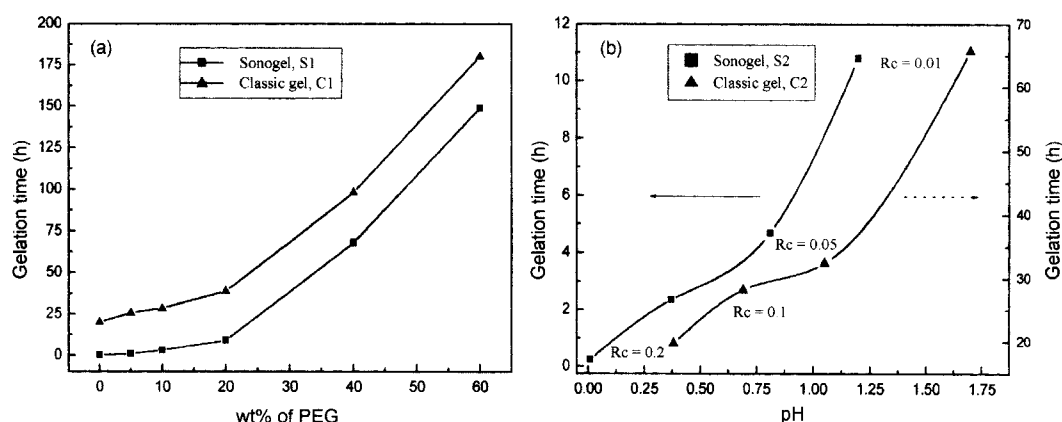
**Table 1.** Composition and Processing Condition for the of Starting Solution

Sample	Experimental method	TEOS (mole)	PEG content (wt%)	Rw*	Rc**	Ultrasonic radiation time (min)	Rs***
S1	A	1	0-60	4	0.1	8	-
S2	A	1	10	4	0.01-0.2	8	-
C1	B	1	0-60	4	0.1	-	3.8
C2	B	1	10	4	0.01-0.2	-	3.8
S3	A	1	10	4	0.1	1-15	-

Notation: \*Rw=H<sub>2</sub>O/TEOS, \*\*Rc=HCl/TEOS, \*\*\*Rs=Ethanol/TEOS molar ratio  
Amount of all sample sol solutions = 60.0 ml (0.1).



**Fig. 1.** Flow chart for the sol-gel process for preparing silica-poly(ethane glycol) sonogels (A) and classic gels (B).



**Fig. 2.** Gelation time as a function of (a) PEG content and (b) pH (by varying HCl/TEOS molar ratio,  $R_c$ ) for the sonogels and classic gels.

### 3. Results and Discussion

#### 3.1. Gelation

Fig. 2 shows the gelation time required for preparing the silica-poly(ethylene glycol) system with different processing variables. Fig. 2(a) corresponds to gelation time-PEG content variations for the sonogel, S1 and the classic gel, C1. It is obvious from the plot that the gelation time was increased linearly with increasing PEG content up to 10 wt% then increased rapidly. This variation can be explained on the basis of percolation and DLVO models, suggested for the gelation phenomenon.<sup>16</sup> According to these theories, gel structure is formed of different units containing electrical-double layers. In the percolation models, either a bond is established or a site is occupied with a probability, 'p' in a completely random fashion throughout a geometrical silica network. After a percolation threshold ' $p_c$ ', an infinite cluster of bonds or site exists. The percolation threshold corresponds to the gel point where gelation occurs. The aggregation of silica particles carrying a surface charge can also be modeled by DLVO theory.<sup>17</sup> In this theory, the activation barrier to aggregation increases linearly with the size of two equal particles. Hence, the rate of aggregate decreases exponentially with their size. However, the

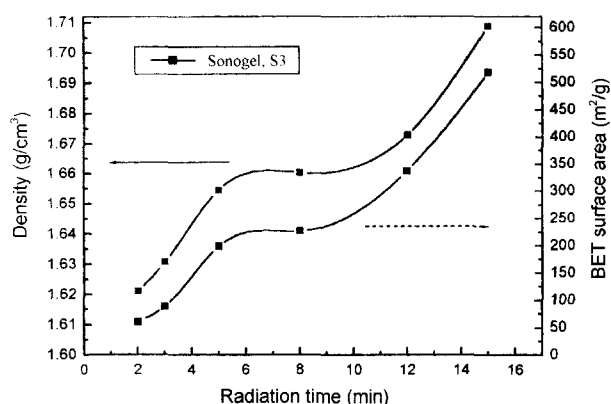
smaller particles aggregate with larger ones at a much higher rate. Thus, for  $p < p_c$ , where PEG content is very less than the  $\text{SiO}_2$  oligomers, the aggregation takes place linearly resulting in slow linear increase in the gelation time with increasing PEG content.<sup>18</sup> While, for  $p > p_c$ , a ramified aggregation forms which slows down the gelation and increases the gelation time rapidly. One can also note from the plot that the gelation time was always less than ~24 hours for the sonogels, compared to those obtained for the classic gels, which is due to the preparation route adopted. The sonocatalysis method provides the energy to accelerate hydrolysis reaction resulting in a better homogeneity and hence a reduced gelation time.<sup>10</sup> The observation on physical appearance of gels and their properties, mentioned in Table 2, well supports these results.

Since, the gelation time strongly depends on the pH value of the sol solution, gelation time-pH study has also been carried out on the sonogel, S2 & classic gel, C2 with 10 wt% of PEG, which is shown in Fig. 2(b). The gelation time is measured below the point-of-zero-charge (PZC) of  $\text{SiO}_2$  (pH=2.5) for avoiding the redissolution process occurs between pH=3 and 8. In general, the gelation time reaches to a maximum at the PZC. At pH ~2, near to the PZC of silica, gelation time shows a maximum.<sup>19</sup> As the HCl/TEOS molar ratio

**Table 2.** Properties of Sample S1 (sonogels) and C1 (classic gels) with Various PEG Content

Sample	PEG content (wt%)	Appearance of Gels*	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Average pore diameter (nm)	Bulk density ( $\text{g}/\text{cm}^3$ )	Vickers hardness ( $\text{Kg}/\text{mm}^2$ )
S1	0	C(Tp)	975.87	0.1343	1.997	1.6749	71.76
	5	C(Tp)	371.89	0.0732	1.842	1.7010	86.44
	10	B(Tp)	226.67	0.0387	1.889	1.6604	89.96
	20	B(Tp)	43.00	0.0012	2.545	1.5585	19.48
	40	B(Tp)	0.175	-	3.086	1.4221	7.84
	60	B(Ts)	-	-	-	1.2215	-
C1	0	F(Tp)	750.17	0.2006	2.196	1.6445	76.16
	5	C(Tp)	345.96	0.0937	2.018	1.6518	83.68
	10	B(Tp)	217.46	0.0750	2.128	1.6325	68.3
	20	B(Tp)	39.01	0.0414	2.945	1.5417	9.27
	40	B(Ts)	0.077	-	3.814	1.3983	2.68
	60	B(Ts)	-	-	-	1.2088	-

\*C-Crack, F-Fragment, B-Bulk, Tp-Transparent, Ts- Translucent



**Fig. 3.** Density and BET surface area of sonogel, S3 with different ultrasonic radiation time.

(Rc) of the sols was increased from 0.01 to 0.2, pH of the sols was decreased from 1.2 to 0.01 for S2 and from 1.73 to 0.35 for C2, which is a well-known phenomenon occurred due to dilution effect of HCl. Here, the pH of classic gel was higher than that of sonogel because of the presence of solvent.

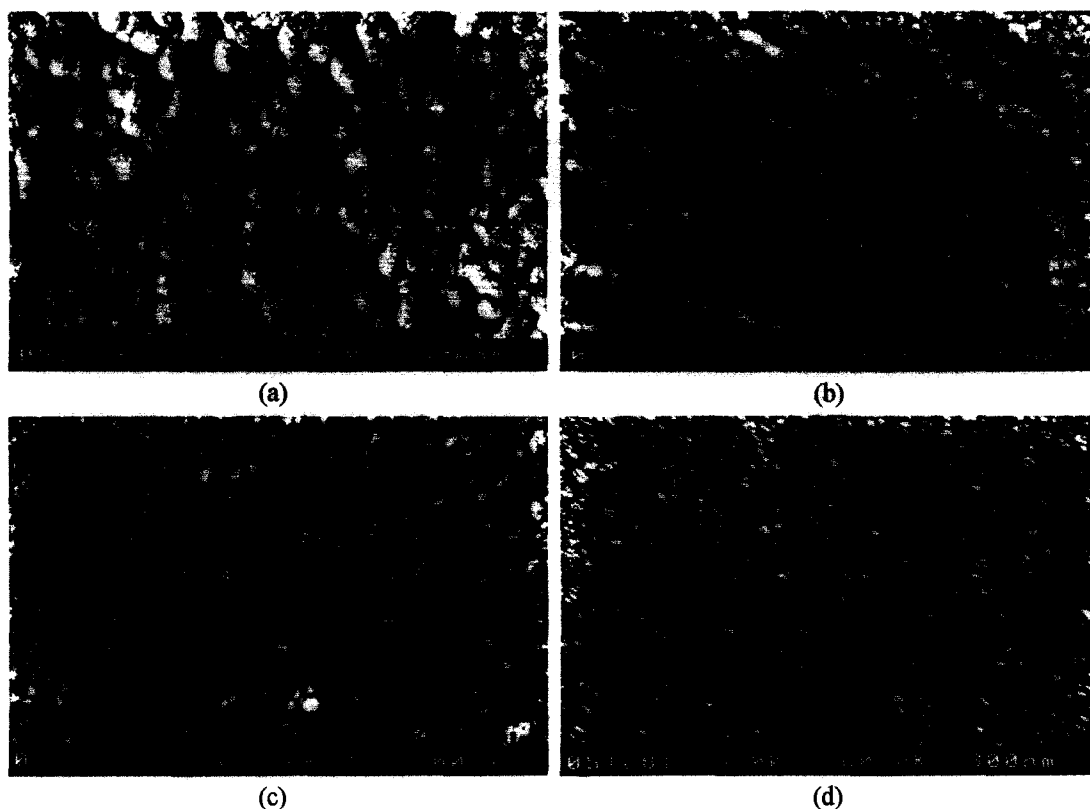
The decrease in the pH of the sols showed a decreased trend in the gelation time, and hence the sols gelled very rapidly. Similar variations have also been observed during the hydrolysis of TEOS at the presence of HCl, TSA and  $\text{HNO}_3$  catalysts respectively.<sup>2)</sup> This is attributed to the increased rate of condensation due to the fast protonation of silanols for producing  $\text{SiOH}_2^+$  groups.<sup>19)</sup> Since, silica particles become to have positive ions under PZC, as adding of anionic polyelectrolyte such as poly(acrylic acid), PAA, the gelation and the growth of gel particles accelerate due to electrostatic interaction between silica sol particles and polyions, but uncharged PEG does not have interaction with silica sol particles.<sup>7)</sup>

### 3.2. Gel Properties

Fig. 3 shows the density and BET surface area for the sonogel, S3 with different ultrasonic radiation time. The values of density and surface area were increased from 1.61 to 1.71  $\text{g/cm}^3$  and from 55 to 520  $\text{m}^2/\text{g}$ , respectively. Further, both the variations of density and surface area with radiation time are almost similar. An analogous 'density-radiation time' variation for the 'TEOS-glycerol' system has already been reported and these two regimes were explained on the basis of predominant hydrolysis and polycondensation stages, respectively.<sup>13)</sup> At the highest irradiation time, a reesterification mechanism could also be operating. These studies have clearly shown that the irradiation time constitutes an additional parameter that can be used to control the textures of the resulting gels.<sup>13)</sup>

Table 2 summarizes the properties of some sonogel, S1 and classic gel, C1 with various PEG content. A transparent bulk was observed for all the samples except for 60 wt% of PEG in S1 and 40 & 60 wt% in C1 those are showing translucent optical property. Hydrogen bonding between the silanols on the silica polymer and the carbonyl groups on the

PEG, is the principal factor controlling transparency in the physical hybrid, which prevents macroscopic phase separation. Phase separation, if any, occurred on such a small scale, that transparent materials were formed, without the need for covalent bonding.<sup>5,20)</sup> Hence, with increasing PEG content, hydrogen bonding decreased and finally became negligible for the higher PEG content in the  $\text{SiO}_2$ -PEG system. Moreover, the pure  $\text{SiO}_2$  bulks were found either cracked or fragmented. The 10-20 wt% PEG produced a good quality samples, while the higher PEG content exhibited rubber-like elastic property which is due to the presence of a large amount of PEG into the silica network. It is also obvious from the table that pure silica sample (S1) prepared by sonocatalysis method exhibits larger surface area and low pore volume as compared to that of sample (C1) prepared by traditional sol-gel method. The increase in the PEG content led to decrease in the specific surface area and pore volume for both S1 & C1 samples. While, it resulted in first decreased in the pore diameter till 5 wt% of PEG and then increased for both the samples, S1 & C1. These results have also got further support from the bulk density measurement, which is shown in the Table 2. The values of bulk density for both the samples, S1 & C1 increased upto 5 wt% of PEG and then decreased. A decrease in the surface area/pore volume/bulk density with increasing PEG content which also well accompanied with an increase in the pore diameter is an usual phenomenon and can be explained on the basis of Percolation and DLVO theories, discussed earlier.<sup>16,17)</sup> The 5 wt% of PEG for both the sonogel and classic gel exhibited the highest bulk density and the lowest pore diameter, which is due to the low amount of PEG embedded homogeneously in pores of the silica matrices without volume expansion of the silica network. In other words, the highest close packed structure between chain molecular  $[-(\text{O}-\text{CH}_2-\text{CH}_2)-]$  of PEG polymer and 3-dimensional silica network was achieved for 5 wt% of PEG. The higher amount of PEG leads to the volume expansion resulting in less bulk density but large pore diameter. The Vickers hardness was also measured as a function of PEG content for S1 & C1 samples. In both the samples, hardness was decreased with increasing PEG content except for the 10 wt% of PEG in the S1 sample and 5 wt% of PEG in the C1 sample. Further, the value of hardness for S1 samples was always higher than that obtained for the C1 samples showing more densification of sonogels. The sonogels are more reticulated than the classic gels, during hydrolysis and condensation reactions by ultrasonic irradiation. Further, no solvent was used during the preparation of sonogel, which play a vital role in the gel structure during aging and drying of sample. These results are well supported our previous results mentioned in Section 3.1 as well as well agreed with the physical and mechanical properties of sonogels reported by Esquivias<sup>10)</sup> and Zarzycki.<sup>13)</sup> Hence, it is obvious from these studies that sonocatalysis method resulted into a superior gel system as compared to the traditional sol-gel method. Further,  $\text{SiO}_2$ -10 wt% PEG xerogels exhibited the superior physical and



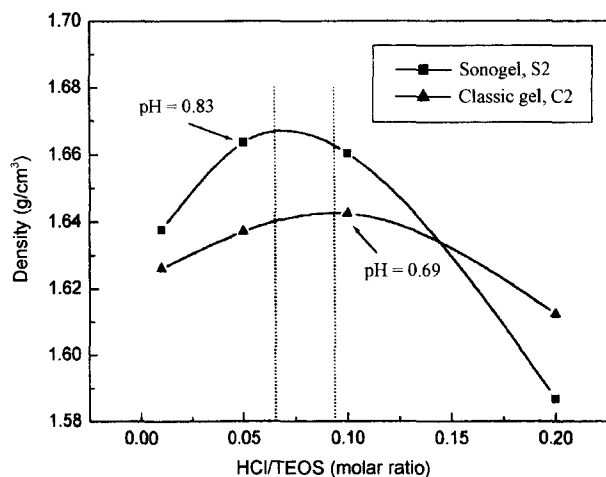
**Fig. 4.** SEM micrograph of  $\text{SiO}_2$ -PEG sonogels (sample S3) prepared with various ultrasonic irradiation time (a) 2 min, (b) 5 min, (c) 8 min and (d) 15 min.

gel properties, and found suitable for device applications.

Fig. 4(a-d) shows the morphology of  $\text{SiO}_2$ -PEG sonogel, S3 prepared with different ultrasonic radiation time: 2, 5, 8 and 15 min. The grain size and pore diameter were decreased with increasing radiation time due to resolve aggregation of PEG into silica network, i.e. the ultrasonic phenomenon mentioned earlier in Section 1.<sup>8-15</sup> For the 2 min of radiation time, the sample had quite large PEG particulates in the silica cluster, and simultaneously, had the

large pore diameter ( $\sim 2.8$  nm). The pore size was decreased to 1.9 nm for the 8 min. radiation time. This result is in accordance with our earlier BET and pore diameter data shown earlier in the Fig. 3 and Table 2 respectively.

Fig. 5 shows the density with different HCl/TEOS ratio ( $R_c$ ) for the samples, S2 and C2. One can note that the increase in the HCl content in the  $\text{SiO}_2$ -10 wt% PEG system increases the density very little for  $R_c=0.05-0.1$  and start to decrease. This  $R_c$  ratio is at pH  $\sim 0.7$  well below the PZC. This phenomenon can be explained on the basis of theory proposed by Brinker *et al.*<sup>21</sup> Further, the density of sonogel was higher than that of the classic gel, which is due to the well-known ultrasonic effect. Our BET & SEM results also support this phenomenon.



**Fig. 5.** Density as a function of HCl/TEOS molar ratio ( $R_c$ ) for samples S2 and C2.

### 3.3. Thermal Properties

Fig. 6 shows the DTA and TGA plots for sonogel, S1 with and without 20 wt% of PEG. The DTA and TGA curves for pure silica sonogel system is identical with the system reported by Brinker *et al.*<sup>2)</sup> and Ota *et al.*<sup>22)</sup> The DTA and TGA plots for the sonogel, S1 are also similar to those obtained for the pure silica system with some modification in temperature and weight loss at 195-270°C and 270-320°C. Hence, on the lines of argument used by Brinker *et al.*<sup>2)</sup> and Ota *et al.*<sup>22)</sup> to explain the thermal behavior of their system, the endothermic peak between 60 and 120°C corresponds to the evaporation of adsorbed water. The exother-

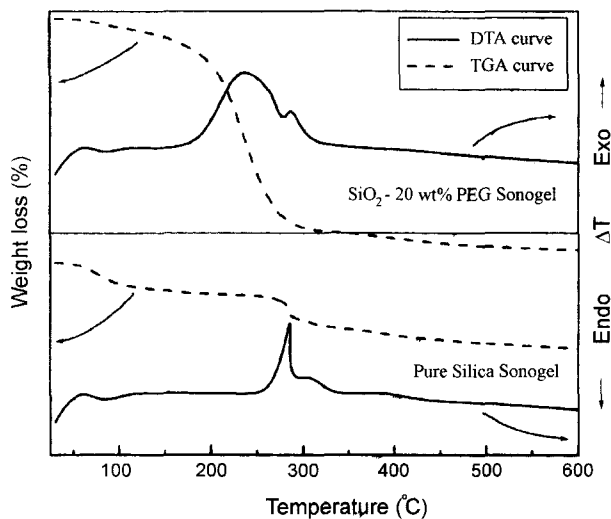


Fig. 6. DTA and TG curves for the sonogel, S1 with and without 20 wt% of PEG.

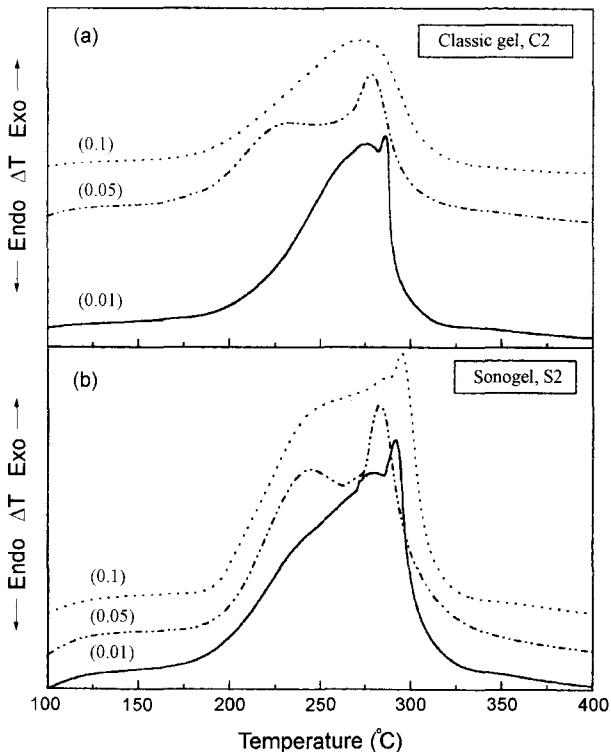


Fig. 7. DTA exothermic peaks for: (a) classic gel, C2 and (b) sonogel, S2 with different HCl/TEOS molar ratio ( $R_c$ ), marked in the parenthesis.

mic peaks at temperature regions: 195-270°C and 270-320°C, can be ascribed to the combustion of  $-C_2H_5$  groups or related to burn out reaction of PEG polymer constituents respectively.<sup>10</sup> In the above TG-curve at the same region, about 35% weight loss was observed which is due to decomposition of organic (PEG) compound.

Since, a small change in the pore size directly indicates a shift in the peak of thermogram,<sup>23</sup> we carried out DTA stud-

ies for the sonogel S2 and classic gel C2 with different HCl/TEOS ratio ( $R_c$ ) at the temperature region: 100-400°C, which are shown in Fig. 7. The thermograms for both the samples are almost similar to that shown earlier in Fig. 6. A shift in the peaks towards lower temperature was observed in all three thermograms for classic gels. A similar behavior was also observed at  $R_c=0.01$  & 0.05 for sonogels, however, it reshifted to the original temperature value for  $R_c=0.1$ . These results well support our previous one (cf. Table 2) obtained from the pore size, density and pH measurements.

#### 4. Conclusion

$SiO_2$ -PEG xerogel system is investigated. The system is prepared via sol-gel processing by varying various processing parameters, e.g. ultrasonic irradiation time, HCl/TEOS molar ratio and PEG content. The property of sonogel, obtained by various studies, such as SEM, BET, DTA-TGA, density and Vickers hardness is compared with that obtained for the classic gel. The following significant conclusions may be drawn from the investigation.

The irradiation of ultrasonic during the sample preparation reduced the gelation time of xerogel system without the presence of solvent. The sonogel systems exhibited larger surface area, lower pore volume/diameter and higher bulk density compared with that of the classic gel systems. The increase in the irradiation time resulted in higher density with large surface area sonogels. It is also noticed that the PEG content strongly affects the physical properties and transparency of sonogels and classic gels. 10-20 wt% of PEG resulted a transparent, nano-structured, crack-free and hard bulk and found suitable for device applications. The pore diameter for this composition is ~1.8-2.5 nm as obtained by BET and SEM techniques. The HCl/TEOS ratio is found a vital factor controlling the density/pore size and pH of the samples giving a shift towards the low temperature in the DTA-TGA thermograms. These results are well discussed on the basis existing theories.

#### Acknowledgment

This work was supported by grant No. R04-2000-00076 from the Korea Science & Engineering Foundation.

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