Preparation and Characterization of Hybrid Silica-Poly(ethylene glycol) Sonogel

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An inorganic-organic hybrid system, silica-poly(ethylene glycol) sonogel is reported. This system was prepared *via* sol-gel method by varying various processing variables, *e.g.* ultrasonic radiation time, gelling temperature, PEG content and its molecular weight. Various experimental techniques were employed to analyze the morphological, mechanical and optical properties of the system. The results were discussed in the light of existing theories. The sonogel system exhibited the common features of inorganic-organic hybrids. SiO_2-10 wt% PEG sonogel exhibited the morphological, mechanical and optical properties superior to those reported earlier for the classic gels and found suitable for device applications.

Keywords : Sol-Gel, Sonogel, Ultrasonic irradiation, SiO_2-PEG hybrid, Inorganic-organic hybrid.

Introduction

The inorganic-organic hybrids are a new class of materials which favorably combine the properties of the organic materials to those of the inorganic ones, hence, offer a variety of advantageous properties, such as mechanical, optical, electrical and thermal fulfill the criteria for industrial applications.[1-5] Such a hybrid system is synthesized *via* sol-gel processing by controlled hydrolysis and subsequent condensation of an organic precursor e.g. alkoxysilane in the presence of water, a solvent and a catalyst followed by aging and drying. This process strongly depends on the nature of alkoxy group & the solvent, the concentration of each species in the solvent, the water to alkoxysilane molar ratio, the temperature and the pH value of sol.[1,2] An alkoxysilane derivative is usually used to provide an inorganic (SiO_2) back-bone, generally three-dimensional, onto which organic groups are attached through covalent bands. Tetraethoxysilane (TEOS) is the most common precursor which offers high porosity and large surface area to the system.[5] Acid/base catalyzed SiO_2-PEG hybrid system has recently been studied by various workers due to the following significant features.[6-13] (i) PEG exhibits certain liquid-like properties such as it acts as an immobile solvent for many metallic salts which are found suitable for developing fast ion conductors,[14] (ii) The presence of silica network allows the transparent materials to be obtained with mechanical property superior to pure PEG system,[14] and (iii) It exhibits low dielectric constant.[11]

The samples, prepared by traditional method, exhibit, in general, shrinkage/cracks as well as the longer gelation time.[1-3] Zarzyeki *et al.* and Donatti *et al.* showed separately that the sonocatalysis method can be utilized to avoid the use of solvent and to improve the gelation time, the density, degree of syneresis, elastic and viscoelastic parameters.[15-18]

The ultrasonic energy produces an atomization effect, emulsifying the water-alkoxysilane mixture and provoking a release of alcohol, which, in turn, accelerates the homogenization process. More precisely, on the propagation of ultrasonic wave through the solution, a microcavity is formed in the low pressure phase at a nucleus by a gas bubble. This microcavity expands quasi-isothermally and becomes filled with the vapors of the reactants resulting a high pressure phase. Consequently, due to the high pressure, the microcavity collapses adiabatically and produces high temperature which accelerates the hydrolysis-condensation reaction. Donatti *et al.* showed that the hydrolysis rate is directly proportional to the applied radiation time.[17,18] The SiO_2-PEG hybrid sonogel system has also been reported, in past, in which the effect of drying control chemical additives (DCCA) *e.g.* PEG on SiO_2 was studied with various dose of ultrasonic irradiation.[19] No other studies are found reported in the literatures for the SiO_2-PEG sonogel system.

In the present paper, a detailed investigation of the hybrid SiO_2-PEG sonogel system is reported. This system was synthesized by controlling the processing variables, such as ultrasonic irradiation time, aging temperature, PEG content and its molecular weight. Another hybrid system with 10 wt% of poly(dimethoxysilane) (PDMS) was also prepared under the same conditions for direct comparison. The microstructural, mechanical and optical studies on the bulk samples were carried out using BET, SEM, density & Vicker's hardness measurements and polarizing microscopy. Some novel results are obtained.

Experimental Section

Preparation. Organic precursors: tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS, Aldrich, 98%) as a source of silica, poly(ethylene glycol) (-H(-CH$_2$CH$_2$O)$_n$OH-, PEG, Aldrich, Average molecular weight = 400 g/mole, 4600 g/mole) and poly(dimethylsiloxane) ($(CH_3)_2SiOH$-$((CH_3)_2SiO_2)_x(CH_3)_2$-SiOH, PDMS, U.C.T., Average molecular weight = 450 g/

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Table 1. Composition of the stock solutions and processing conditions

Sample	Added Polymer			TEOS (mole)	H₂O/TEOS molar ratio	HCl/TEOS molar ratio	Ultrasonic irradiation time (min)	Gelation temperature (°C)
	Polymer	Average molecular weight (g/mol)	Content (wt%)					
S1	PEG	400	0-60	1	4	0.1	8	50
S2	PEG	400	10	1	4	0.1	1-15	50
S3	PEG	400	0-60	1	4	0.1	8	25
S4	PEG	400	10	1	4	0.1	1-15	25
S5	PEG	4600	10	1	4	0.1	8	50
S6	PDMS	450	10	1	4	0.1	8	50

mole) as polymer constituents, were used as supplied. Trace of HCl (Merck, 37%) was used as catalyst and deionized water was used for hydrolysis. The composition of stock solutions and processing conditions are summarized in Table 1. An SiO₂-10 wt% PDMS hybrid system was also prepared in the identical manner for direct comparison. All solutions were phase separated before being subjected to 20 kHz ultrasonic irradiation, which was applied by a 13 mm diameter probe of Ultrasonic Processor (Sonic & Materials Co., model 600, USA, Power 240 ± 5W). The change in temperature of the solution during the ultrasonic irradiation was measured using a thermometer until it leveled off. The clear sol was left to cool for a few minutes at the room temperature, and, subsequently, poured into a polypropylene based container.. Then, it was covered by a paraffin film having small holes in order to control the evaporation rate. The container was kept in oven at either ~25 °C or ~50 °C to observe gelation time. After gelation, the wet gel was further aged at 50 °C for one week, and dried at 125 °C for 4 days. The other wet gel was aged at 25 °C for one week, and dried at 125 °C for 5 days.

Characterization. The morphological parameters, *viz.* surface area, pore size and pore volume of SiO₂-PEG sonogels were measured by BET technique (Micrometrics Co., ASAP 2000 model). For these measurements, all the bulk samples were outgassed for 1 hour at 100 °C and then 4 hours at 180 °C. The bulk density was measured by a Pycnometer (Micrometrics Co., Accupye 1330, USA) after drying the samples at 100 °C for 1 hour. Microstructure of the bulk samples was analyzed by a SEM (Hitachi, model S-4300). The Vicker's hardness of bulk sample was measured using a Micro-Hardness Tester (Future-Tech. Co., FM-7 (HVS-1000) model) under the load of 0.245 N (25 g) and dwell time of 20 sec. The transparency of bulk samples was observed by a Polarizing Microscope (Nikon, model OPTIPHOT, Japan).

Results and Discussion

Gelation. Figure 1 shows the change in the temperature of the SiO₂-10 wt% PEG stock solution (S2) during the ultrasound irradiation. The temperature of stock solution increased abruptly to ~78 °C within ~1 min. and then it leveled off at ~75 °C. A similar variation has also been
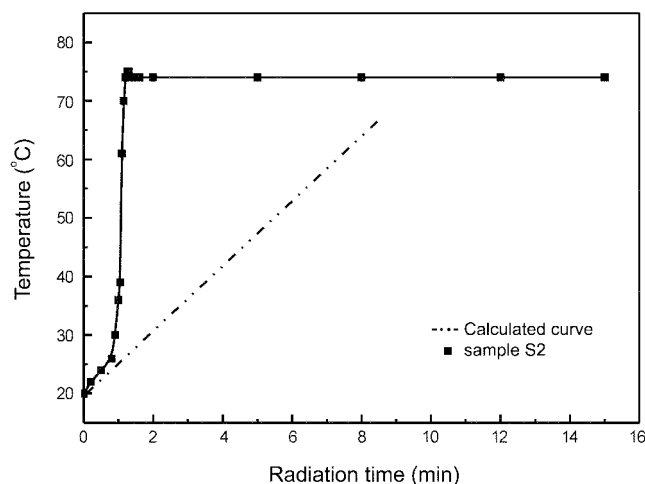

Figure 1. The change in temperature of the stock solution (SiO₂-10 wt% PEG, S2) during sonogel reaction. The dotted line corresponds to the calculated change in temperature for solutions of constituents.

reported for SiO₂-10 wt% PDMS sonogel system.[20] This variation can be explained on the basis of ultrasonic effect, discussed earlier in the Introduction Section.[15-18] The temperature ~78 °C corresponds to the boiling temperature of the ethanol which is produced during the hydrolysis of TEOS. Further, this increase in temperature was much higher than that of calculated value of increased temperature of individual components during ultrasonic irradiation, indicating that this excess heat is generated due to the exothermic hydrolysis-condensation reaction of TEOS.

As mentioned earlier, the gelation phenomenon strongly depends on the processing variables such as ultrasonic irradiation time, H₂O/TEOS mole ratio, gelation temperature, polymer content and molecular weight of the polymer, etc., hence, the effect of these parameters are discussed below.

Figure 2(a) shows the 'gelation time versus irradiation time' variations for the SiO₂-10 wt% PEG sonogels aged at 50 °C (sample S2) and 25 °C (sample S4). One can note that the gelation time decreased linearly with increasing irradiation time for both samples showing an inversely proportional relation. Morita *et al.* have also reported a similar result for SiO₂-10 wt% PDMS sonogel system.[20] It seems legitimate also because the rate of hydrolysis is directly
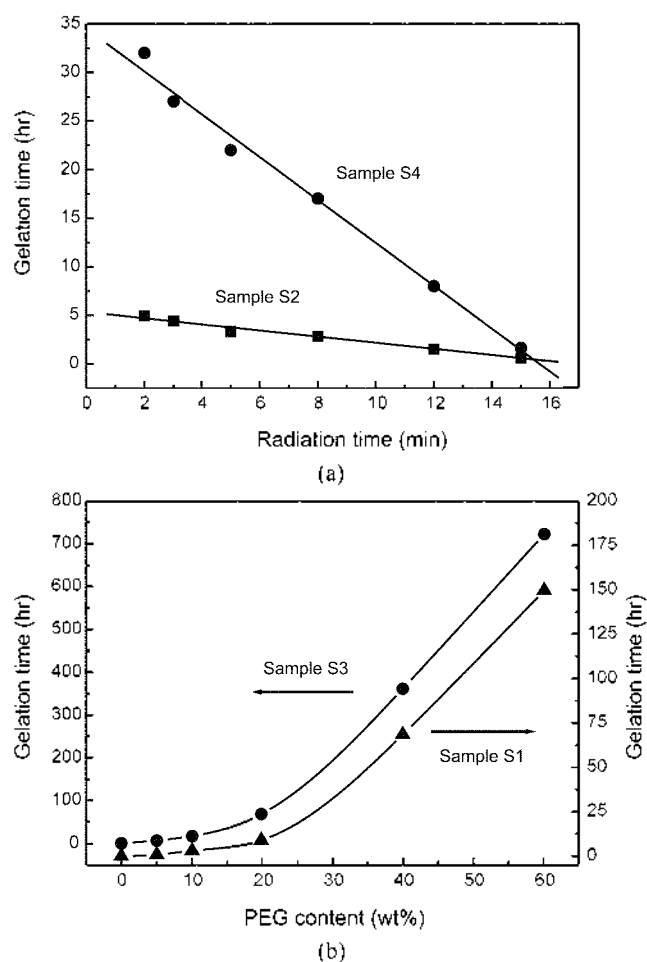
Figure 2. Gelation time as a function of (a) ultrasonic radiation time for SiO_2-10 wt% PEG sonogels: S2 & S4, and (b) PEG content for SiO_2-10 wt% PEG sonogels: S1 & S3.

proportional to the irradiation time. However, logarithm of gelation time was also found inversely proportional for several sonogel systems.[19,20] Further, the higher aging temperature resulted in the lower gelation time indicating that thermal energy, similar to ultrasonic energy, is also a factor controlling the gelation phenomenon. A similar variation has already been noted for TEOS-H_2O sonogel system.[16]

In Figure 2(b), the effect of PEG content on the gelation time for the SiO_2-PEG samples, S1 & S3 is shown. The increase in the PEG content up to 10 wt% resulted in slow increase in the gelation time and, thereafter, a non-linear fast increase in gelation time is observed. This is a well-known phenomenon and can be explained in the light of theoretical models, *e.g.* Percolation and DLVO.[1,2,21-24] These models assumed that the gel structure consists of different units containing electrical double-layers. The common feature for the Percolation models is the existence of bond or occupation of sites with a probability, 'P', in a completely random fashion throughout a geometrical silica network.[21,22] After a percolation threshold, 'Pc', where the gelation occurs, an infinite cluster of bonds or site exists. Thus, for

'P' < 'Pc', where amount of PEG is much smaller than the SiO_2 oligomers, a slow & linear aggregation takes place. For the higher PEG content lying in the region where P > Pc, a ramified aggregation takes place and slows down the gelation and increases the gelation time rapidly. The DLVO model well considered attractive Van der Waals and repulsive electrostatic interactions between near neighbor particles and expressed the total interaction energy (Φ) as a function of separation distance (x) between two particles as: $\Phi = \Phi_A + \Phi_R$.[23,24] The attractive term, Φ_A dominates at small and large value of 'x' and approximately equal to -Ar/12x. While, the repulsive term, Φ_R [=$2\pi\varepsilon$ ε_0 r Ψ_0^2 exp(-κx)] dominates only in some instances, which strongly depends on the pH and double layer thickness [κ^{-1}, = ($2e^2$ n(∞) $z^2/\varepsilon\varepsilon_0$ k_b T)$^{-1/2}$] at intermediate value of 'x'. The notations used are: A, Hamaker constant; r, radius of particle; ε, relative dielectric constant of the liquid medium; ε_0, the dielectric permittivity of the vacuum; k_b, Boltzmann constant; e, the electronic charge; n(∞), concentration of the ions having charge 'z' and Ψ_0 [= 2.303 k_b T((pzc)-pH)/e], the electric potential at the surface of the charged particles. Thus, the DLVO theory well accounted almost all the factors, such as particle size, pH, separation distance between particles, concentration of ions & its charge, temperature etc. for explaining the gel texture. This theory can be applied to the present system in the following way. A silica particle has point of zero charge (pzc) at pH ~2.5. Above this value, its surface has a negative electric charge and otherwise it has a positive charge. Therefore, it was expected that addition of polymer might affect the sol particle growth and/or gelation process due to the electrostatic interaction between the polymers and the silica sol. However, uncharged polymer PEG does not interact with silica sol particles, so that, PEG chains and silanol oligomers coexist in the solution without specific interaction, with the progress of the hydrolysis and condensation of alkoxysilane. The interaction between PEG chains and silanol takes place only after silanol oligomerizes to the size of the several nanometers due to the different dependence of Φ_A & Φ_R on the radius of silica particle. The disentangled PEG chain and the silica oligomers possibly attract each other to form an aggregated complex through hydrogen bonds between silanols on silica and -OH or -O on PEG. However, the number of free silanol sites should become less leading to less branched silica network. Since silica gel has highly open structure, PEG chains are supported in the silica network in a quasi-interpenetrating manner. Therefore, as the amount of polymer is increased, the gelation time of the sol solution is also increased.

Morphology. The various morphological parameters, such as specific surface area, pore diameter and pore volume for the SiO_2-PEG sonogels, S1 & S3, are listed in Table 2 in which the variations for surface area and pore volume with PEG content are almost similar. A non-linear decrease in the values of surface area and pore volume was obtained with increasing PEG content. For the higher PEG content, 40 wt% and more, the values of the surface area and pore volume became zero. While, the pore diameter decreased a

Table 2. Morphological parameters and physical appearance of bulk samples: S1 & S3

Sample	PEG content (wt%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	Appearance of Gels
S1	0	975.87	0.1343	1.997	crack (transparent)
	5	371.89	0.0732	1.842	crack (transparent)
	10	226.67	0.0387	1.889	bulk (transparent)
	20	43.00	0.0012	2.545	bulk (transparent)
	40	0.175	–	3.086	bulk (transparent)
	60	–	–	–	bulk (translucent)
S3	0	938.17	0.1706	1.863	fragment (transparent)
	5	750.96	0.0735	1.908	crack (transparent)
	10	337.46	0.0501	1.928	bulk (transparent)
	20	60.36	0.0114	2.735	bulk (transparent)
	40	0.677	–	3.324	bulk (translucent)
	60	–	–	–	bulk (translucent)
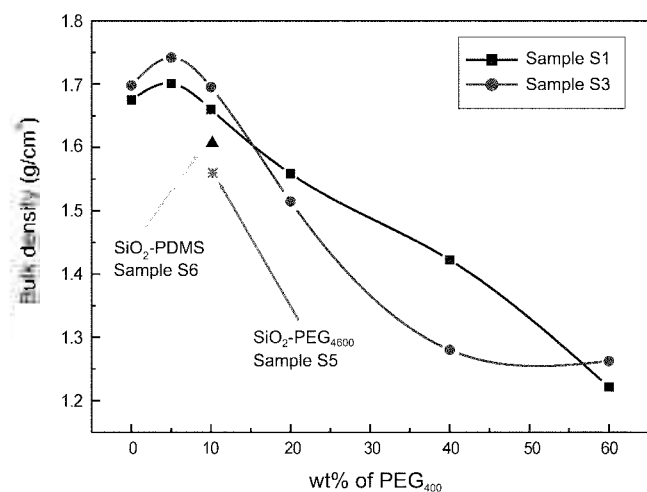
Figure 3. 'Bulk density versus PEG content' plots for SiO_2-PEG sonogels, S1 & S3.

little for sonogel S1 with 5 wt% of PEG (~1.8 nm), then, it increased abruptly for higher PEG content. This is also an usual phenomenon reported for several systems and explained on the basis of theoretical models, such as Percolation & DLVO, discussed earlier.[1,5,7,10,21-24] It is also obvious from the table that the values of morphological parameters for samples aged at 50 °C are mostly lower than those of the samples aged at 25 °C. A similar result has already been reported for SiO_2-PEG classic gel system.[11] These results are well supported by our density, BET, SEM and mechanical & optical property studies, which are discussed below.

Figure 3 shows the compositional variation of bulk density for SiO_2-PEG sonogels, aged at 50 °C (sample S1) and 25 °C (sample S3). The density increased a little from pure SiO_2 system to 5 wt% of PEG and then decreased for higher values of PEG, which is due to the fact that small amount of PEG polymer was sufficient to create PEG polymer chains around silica particles in a way similar to adsorption of polymer inside the pores of a silicate network without volume expansion. As a result, the highest close packed
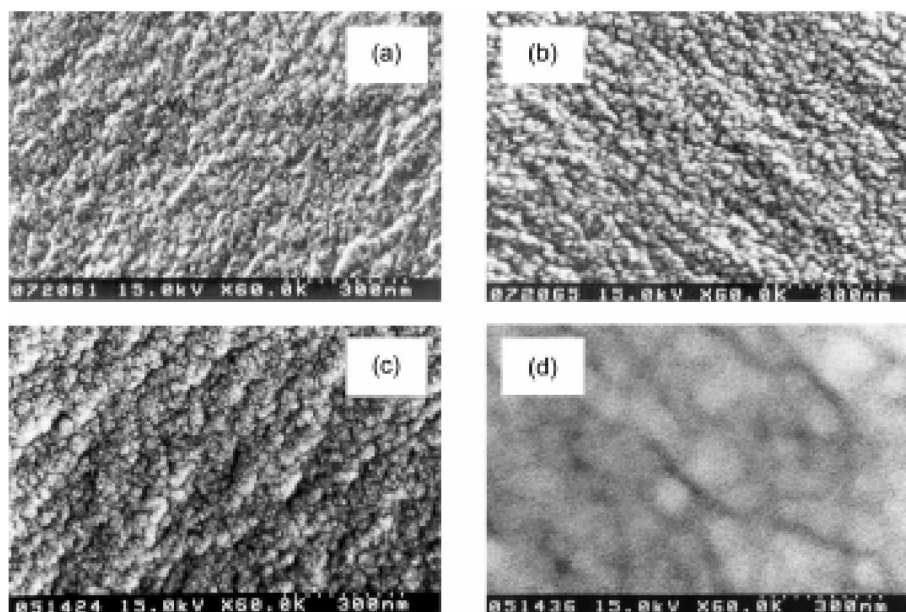
Figure 4. SEM micrographs for the SiO_2-PEG sonogel, S1 with different PEG content. (a) 5 wt%, (b) 10 wt%, (c) 20 wt%, (d) 40 wt%.
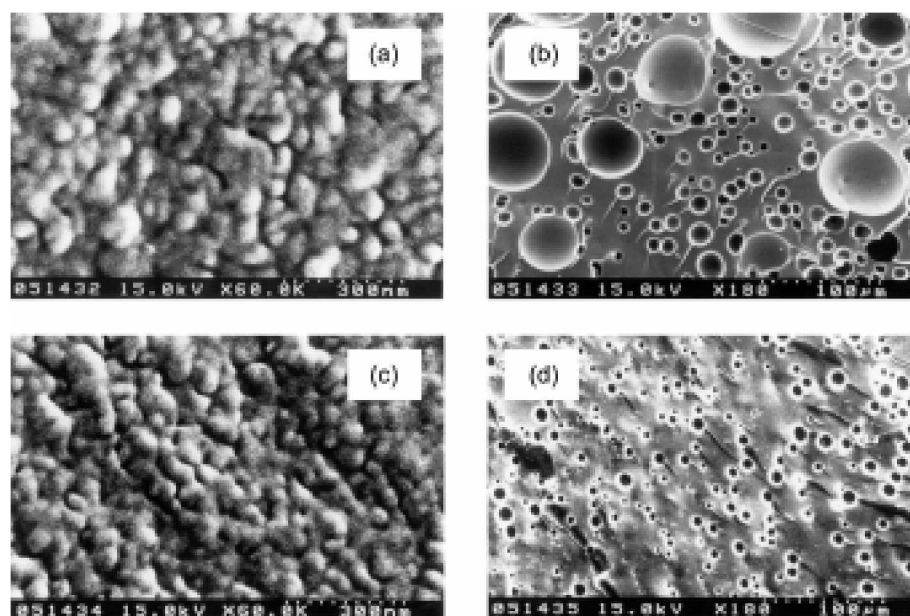
Figure 5. SEM micrographs at the magnifications (a) × 60,000 and (b) × 180 for the SiO$_2$-10 wt% PEG$_{4600}$ sonogel, S5 and at (c) × 60,000 and (d) × 180 for the SiO$_2$-10 wt% PDMS sonogel, S6.

structure was obtained between chain molecule [-(O-CH$_2$-CH$_2$)-] of PEG polymer and three-dimensional silica network. On comparing this variation with those obtained for surface area and pore volume, one can conclude that the decrease in density with increasing PEG content is due to the decrease in surface area & pore volume, resulting in an increase in pore size with increasing PEG as also obvious from the Table 2. It is also a well-known fact that the polymer with higher molecular weight results less dense samples with low surface area and high pore size.[1-5] Hence, to observe the effect of high molecular weight/similar molecular weight but of different material on the density, the density was also measured for SiO$_2$-10 wt% PEG$_{4600}$ (molecular weight 4600 g/mol), S5 and SiO$_2$-10 wt% PDMS (molecular weight 450 g/mol), S6, which are shown in the Figure 4 obeying the usual phenomenon. It is also noteworthy that the density obtained for samples S1 and S3 are almost equal. The SEM and hardness studies, which have been discussed below, well entrenched these results. A similar result for SiO$_2$-10 wt% PDMS sonogel has already been reported in the literature.[20]

Figure 4(a-d) shows the SEM micrographs for the SiO$_2$-PEG sonogel, S1 with increasing PEG content. One can note from the picture that increase in PEG content resulted in an increase in the grain size, which is spread homogeneously, due to aggregation of PEG into silica network. It is also obvious from the picture that the morphology of sonogel has a fine micro-structural PEG back-bone at 5 wt% of PEG. As the PEG content increased, an increase in the particle size and pore diameter observed. This is considered to be due to the occurrence of micro-phase separation related to volume of PEG polymer trapped homogeneously, which was incorporated in sites such as macro-pores and voids of silica matrix by ultrasonic irradiation. Also, particle size for the

samples with over 20 wt% PEG content increased due to the fact that PEG polymer penetrates into and distends the silica network. These results are in accordance with the Percolation and DLVO theories, discussed earlier and also in good agreement with the BET & density results, discussed earlier as well as the results of hardness and transparency studies.

Figure 5(a & b) shows SEM micrographs for the SiO$_2$-10 wt% PEG$_{4600}$ (molecular weight 4600 g/mol) sonogel, S5 at magnifications: × 60,000 and × 180, respectively, showing an effect of high molecular weight on the microstructure. While, Figure 5(c & d) corresponds to the SEM micrographs for SiO$_2$-10 wt% PDMS (molecular weight ~450 g/mol) sonogel, S6 at the same magnifications: × 60,000 and × 180, respectively, showing an effect of similar molecular weight but of different material. On comparing the micrograph of Figure 5(a) with Figure 4(b) having the same weight percent of PEG but different molecular weight, it is clear that PEG with the higher molecular weight results in a large grain/pore-sized sample. Further, at the same weight percent, the grain size of sonogel, S6 with PDMS (Figure 5c) was comparatively larger than that of sonogel, S5 with PEG$_{4600}$ polymer (Figure 5a). The PEG polymer largely forms physical bond which do not affect the grain growth as it mixes well with silica sol particles, though, it depends on the volume of interpenetrated amount of PEG in the silica network. It is also a well-known fact that the grain growth is affected by chemical bond between terminal -OH of PDMS polymer and silica sol particles.[11,25] In both samples, S5 & S6, a macro-pore of size: 20-100 μm, was observed. It is a well-known fact that a sample having large pores-size exhibits translucent optical property due to the scattering and dispersion of light by macro-pores. This phenomenon has also been observed for the samples, S5 & S6, which has

been discussed below.

Mechanical and Optical Properties. Table 2 listed the physical appearance and optical nature of SiO_2-PEG sonogel systems, S1 & S3. Pure SiO_2 bulk samples are found either cracked or fragmented but they were quite transparent. For 5 wt% of PEG, the transparent bulk systems were still found cracked. The bulk samples having the PEG content higher than 10 wt% exhibit lower transparency, which are shown in Figure 6 for the SiO_2-PEG sonogel system, S1. Finally, the bulk samples became translucent with 40 and/or 60 wt% of PEG depending up on the aging temperature. In this compositional region, the samples exhibited rubber-like property. It is also noticed that sonogels with 10 wt% PDMS (S6) prepared with the identical experimental condition, exhibited cracks, several times, in the wet gel and the dried gel became fragmented and opaque. Sonogels prepared at higher gelation temperature (>50 °C) were also found, many times, cracked during the gelation process, irrespective of the amount of PEG. Gels with no PEG were transparent and felt rigid when touched. With increasing amount of PEG, the sonogels became more opaque and elastic. The sample with 5 wt% of PEG fragmented into small pieces while drying. This is an usual phenomenon and can be explained on the basis of Percolation & DLVO theories as well as the morphological parameters, which have already been discussed earlier. As the PEG content was increased from 20 to 60 wt%, PEG polymer interpenetrates and distorts the silica network, and consequently, bulk density started to decrease and approached the PEG density (1.12 g/cm³) and the prepared sonogels exhibited elastic property of organic polymer. The optical nature of the samples can be explained on the basis of nature of bonding between PEG and silanol group of SiO_2 network. In general, physical hybrids depend on the polymerization of TEOS in the presence of the polymer dissolved in the solution. In the SiO_2-PEG system, the interactions between the polymer and the silica network are largely through hydrogen bonding between ethereal-oxygen in PEG and silanols in silica. Hydrogen bonding
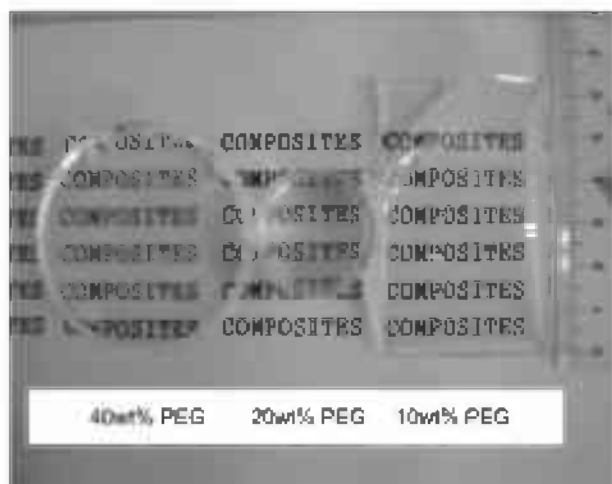
prevented macroscopic phase separation and was principal factor in controlling transparency.[25] Takahashi's results[26] showed that the scale of the phase separation depends strongly on the amount of polymer, the molecular weight of the polymer, the solvent composition and the pH. The gel morphologies are the result of a competition between the phase separation and gelation. In the present study, if any phase separation occurred on such a small scale, transparent composites will be obtained due to the very low pore diameter.[25] Increasing PEG content leads to a decrease in the specific surface area and pore volume from 975.87 to 0.17 m^2/g and from 0.1343 to 0.0012 cm^3/g, respectively, but increase in average pore diameter from 1.997 to 3.86 nm. Therefore, obtained sonogels are transparent with homogeneous nano-pores.

Figure 7(a) shows the Vickers hardness as a function of PEG content for the SiO_2-PEG sonogel systems, S1 & S3. The hardness for both systems increased with increasing PEG content. However, it started to decrease rapidly thereupon. Further, on comparison with morphological parameters, it is obvious that the compositional variation of density is almost similar to the 'Vicker's hardness-PEG content' variation. It seems logical also. The increase in PEG content up to 10 wt% led to fragmentation of PEG polymer into small enough (-CH_2-CH_2-O-) units to interpenetrate into pores of silica network by ultrasonic radiation resulting in high dense system. The further increase in PEG content, *i.e.* after crossing the percolation threshold (of the Percolation models), 'Pc', the density decreased very rapidly. In addi-
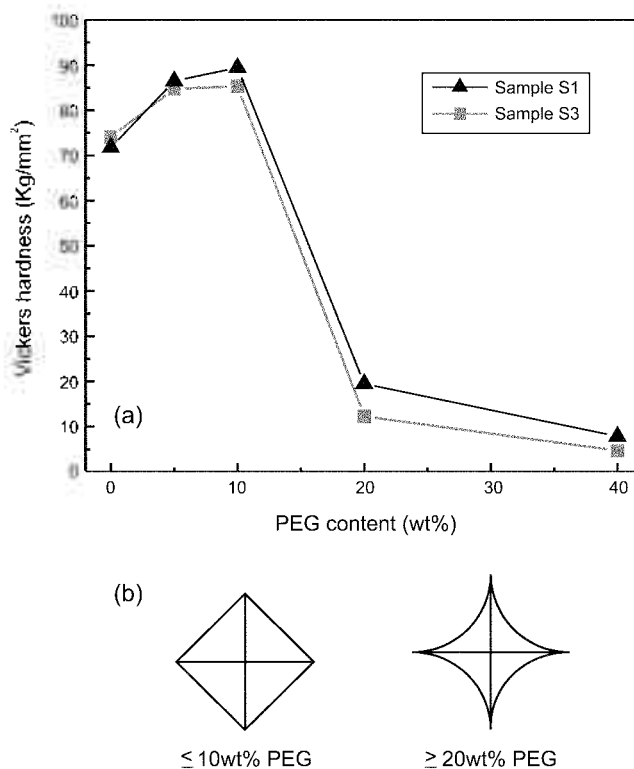

Figure 6. Photograph of SiO_2-PEG sonogel, S1 showing transparency for different PEG$_{content}$.

Figure 7. (a) 'Vicker's hardness versus PEG content' curves for the SiO_2-PEG sonogels, S1 & S3. (b) A schematic diagram of indents which were recovered after removal of 0.245N (25g) load.

tion, it is believed that higher Vicker's hardness of the sonogels after aging at 50 °C than at 25 °C is due to the more densification in gels.

Some of the gels with high PEG content (about 20 wt% PEG) exhibited an indent recovery which indicates an elastic property in the gel. This can also be seen in schematic diagrams [Figure 7(b)] of indents which were recovered after removal of the load. Indent recovery was observed over 20 wt% PEG samples, but not under 10 wt% PEG sample. It was found that indent recovery of gel occurred to compression strain, and rubber-like elastic property may appear by addition of the polymer.[13,25] These results are supported by our BET and density results, discussed earlier.

Conclusions

Silica-poly(ethylene glycol) sonogel system is prepared via sol-gel method by varying various processing variables. The gelation time was monitored with ultrasonic radiation time, gelling temperature and PEG content, which were also used as a parameter for analyzing the morphology, mechanical and optical properties of the samples. Various techniques were used for this purpose and the results were discussed in the light of existing theories and earlier studies. This system showed all the features reported earlier for classic gels, with several superior properties and found suitable for device applications/investigating a new system e.g. ORMOLYTEs. Some novel results are summarized below.

The gelation time was found strongly dependent on ultrasonic radiation time, gelling temperature and PEG content. The gelation time decreased with increasing radiation time/ gelling temperature, which was explained on the basis of ultrasonic-/thermal- energy effect resulting in increased hydrolysis-condensation reaction. An increased value of gelation time was found for increasing PEG content, well supporting the Percolation and DLVO theories. These theories well supported the study on compositional variation of morphological parameters exhibiting the usual phenomena. Surface area and pore volume decreased non-linearly with increasing PEG content, while pore diameter increased non-linearly. The SiO_2-5 and 10 wt% PEG sonogel exhibited maximum density and Vickers hardness along with superior optical and physical properties. The replacement of PEG by higher molecular weight of same material or by almost similar molecular weight but of different material resulted in an translucent, cracked/fragmented, low density and macro poresized hybrid as observed by density/SEM studies.

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