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Catalytic activity of acid and base with different concentration on sol–gel kinetics of silica by ultrasonic method

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ABSTRACT

The effects of both acid (acetic acid) and base (ammonia) catalysts in varying on the sol–gel synthesis of SiO_2 nanoparticles using tetra ethyl ortho silicate (TEOS) as a precursor was determined by ultrasonic method. The ultrasonic velocity was received by pulsar receiver. The ultrasonic velocity in the sol and the parameter ΔT (time difference between the original pulse and first back wall echo of the sol) was varied with time of gelation. The graphs of $\ln[\ln 1/\Delta T]$ vs $\ln(t)$, indicate two region – nonlinear region and a linear region. The time corresponds to the point at which the non-linear region change to linear region is considered as gel time for the respective solutions. Gelation time is found to be dependent on the concentration and types of catalyst and is found from the graphs based on Avrami equation. The rate of condensation is found to be faster for base catalyst. The gelation process was also characterized by viscosity measurement. Normal sol–gel process was also carried out along with the ultrasonic one to compare the effectiveness of ultrasonic. The silica gel was calcined and the powdered sample was characterized with scanning electron microscopy, energy dispersive spectra, X-ray diffractogram, and FTIR spectroscopy.

1. Introduction

The sol–gel synthesis, although still difficult to control, has become increasingly more important in the synthesis and fabrication of new materials, such metal and semi-metal oxide glasses and ceramics. The sol–gel process has become the method of choice for many materials because of the high homogeneity in the final products and occurred at ambient temperature. The precursors are metal alkoxides and metal salts which undergo hydrolysis and polycondensation reaction to form a colloid, a system composed of solid particles (size ranging from 1 nm to 1 μm) dispersed in a solvent. The sol evolves with time towards the formation of an inorganic three dimensional network forming another phase gel. The transformation of sol to gel was studied by many methods such as NMR, vibration spectroscopy, small angle X-ray scattering, methods of viscometry etc. [1–7], acoustic resonance technique [8,9]. The determination of gelation time of different types of sol is also performed by other researchers. The study of change in velocity of ultrasonic in the sol was performed by various researchers [8–10] and the gel time was reported. But this change in velocity of ultrasonic is very small at the gel time. In this current study, an alternative method has established to study the sol–gel kinetics and the effects of catalysts on it by using ultrasonic technique. The transition is quite sharp in our process of study than other ultrasonic process so far established [8,10].

The growth of the polymer takes place by the incorporation of the Si—O—Si chains which are normally lamellar. These lamellar structures usually grow linearly with time at a given temperature. This means that the spherulite radius, r, will be related to time 't' through an equation of the form:

$$r = v_g t \tag{1}$$

where 'v_g' is known as the growth rate. This equation is valid until the spherulites become so large that they touch each other. The relation between the total mass of melt (w_0), the mass of melt after forming the polymer network (w_l) and time for formation polymer network have already been well established elsewhere [11] and known as Avrami equation which is:

$$w_l/w_0 = \exp(-zt^n) \tag{2}$$

where 'n' is called the Avrami exponent and 'z' is a constant depending on the number of nuclei formed per unit volume per unit time, density of liquid melt and spherulitic material growth rate 'v_g' [11] etc. Now if the initial and final specimen volume are defined as V_0

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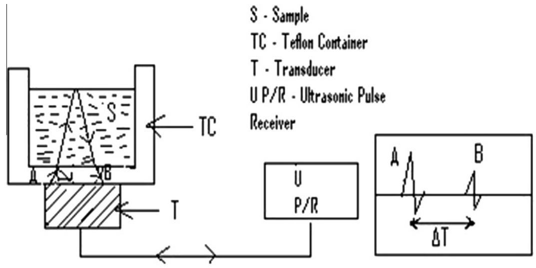

Scheme 1. Schematic diagram of experimental setup.

and V_∞ respectively and the specimen volume at time 't' is given by V_t then it can be written as [11],

$$w_l/w_0 = (V_t - V_\infty)/(V_0 - V_\infty) = \exp(-zt^n) \quad (3)$$

Now taking the specimen in a cylindrical container (having length 'l') this equation is of the form,

$$(V_t - V_\infty)/(V_0 - V_\infty) = (l_t - l_\infty)/(l_0 - l_\infty) = \exp(-zt^n) \quad (4)$$

The Avrami exponent 'n' can be determined from the slope of a plot of $\ln[\ln(l_t - l_\infty)/(l_0 - l_\infty)]$ against $\ln(t)$ and can be inferred about the phase transition and growth rate from the slop of the graph. Now the idea of our work is as follows.

The ultrasonic velocity through the liquid sample is $v = \sqrt{(K/\rho_0)}$, where 'K' is the bulk modulus and 'ρ_0' is the density of the sample solution. The time difference between the echoes of ultrasonic pulse reflected by back surfaces of the bottom of the container and from the free surface of the liquid sample as shown in Scheme 1, ΔT, actually measures the shrinkage of the solution due to evaporation and condensation when kept in open atmosphere at constant temperature and pressure. If the atmospheric condition is not changed, the evaporation rate is considered to be constant hence ΔT is inversely related to the rate of condensation. Now, the rate of condensation is proportional to the compressibility i.e., reciprocal of bulk modulus. Again bulk modulus of the sample solution is proportional to the ultrasonic velocity passing through the solution or in other words the value of ΔT can be used to measure the change of ultrasonic velocity through the sample. In the present study, the velocity of the ultrasonic wave generated from transducer which is passing through the sample during the experiment was kept constant and was assumed to be constant throughout the path. This assumption is also supported by other [8] where they have reported that the fluctuation may vary within 1.2%. So, by measuring the ΔT value the shrinkage in length of the sample column after formation of the polymeric chain containing metal-oxo or metal-hydroxo polymers due to condensation can be inferred successfully.

In the present study, the time difference between original pulse and the first back wall echo i.e., ΔT which in turn related to ultrasonic velocity change of the sound wave due to presence of different medium, is used to investigate the acid and base catalyzed gelation process of tetramethyl alkoxide in presence of alcohol and further interpretation have made by Avrami equation. Effect of ultrasonic is also studied by comparing the process with normal sol–gel process. Furthermore the nanosilica developed by the process in presence of ultrasonic have been characterized by SEM, EDS, FTIR spectroscopy and viscosity measurement.

2. Experimental

2.1. Materials

Table 1
Composition of reaction mixture with varying concentration of catalyst.

Sample designation	Mole % of reagent		Amount of catalyst added (%, V/V)
	TEOS	C_2H_5OH	
NC	0.8273	3.6788	NIL
A1	0.8273	3.6788	Acetic acid* 5.0
A2	0.8273	3.6788	Acetic acid 10.0
A3	0.8273	3.6788	Acetic acid 15.0
B1	0.8273	3.6788	Ammonia solution 2.5
B2	0.8273	3.6788	Ammonia solution 5.0
B3	0.8273	3.6788	Ammonia solution 10.0

The alkoxides precursors used for this study was tetramethyl orthosilicate (monomeric alkoxides precursor) (TEOS). The precursor was mixed with H_2O, ethanol (C_2H_5OH) and catalyst by varying molar ratio with the help of magnetic stirrer and then poured in a cylindrical Teflon container. TEOS and EtOH were supplied by Merck and the two catalysts acetic acid and ammonium hydroxide were supplied by S.D. Fine Chemical Ltd.

The catalyst concentration for acid is varying as 5%, 10% and 15% whereas for base it is 2.5%, 5% and 10%. This is because for acid catalysis with 2.5 ml the effect is not so pronounced and for base catalysis with 15 ml the process is instantaneous. So the corresponding concentrations are not reported in the result.

The samples of same compositions as shown in Table 1 are prepared without ultrasonics following the same order of addition. The different samples are then stirred separately for one hour at a temperature 60 °C. These samples (40 ml each) are then kept in separate petridish and are allowed to evaporate at open atmosphere. The gelation time of different samples (without ultrasonic method) was noted. Fig. 1 represents the gel sample in petridish.

The samples are then dried for half an hour in hot plate at around 80–100 °C. These are then heat treated at 600 °C through one hour in a muffle furness. The samples are then left to cool in open atmosphere such that it becomes comes to room temperature. Now the samples are then ground by mortar and pastel to get the samples in powder form. The samples are then marked and prepared for testing.

2.2. Testing

2.2.1. Ultrasonic velocity measurement

The ultrasonic velocity measurement was done by pulsar receiver (MBS-8000/SR-9000 DSP MEASUREMENT SYSTEM, MATEC INSTRUMENTS Inc.). The velocity of the ultrasonic in the sol varies with reaction time and measured by the parameter ΔT (time difference between the original pulse and first back wall echo of the sol). The resolution of measurement of ΔT is of the order of 0.01 μs.

2.2.2. Gelation time measurement

The gelation point is determined from the plot of $\ln[\ln(\Delta \mathbf{v})]$ vs $\ln(t)$ which consists of sol and gel region. The gel time is obtained by the intersection point of the graph.

2.2.3. Viscosity measurement

The viscosity measurement was made using a viscometer, BROOKFIELD digital viscometer DVII at 25 °C temperature.

2.2.4. Analysis of morphology of the nanosilica particle

A JEOL scanning electron microscope (JSM 6700S) was used to study the nanosilica powdered samples. Prior to the analysis the samples were sputtered with Au/Pd alloy and stuck on a stub.