Journal of Non-Crystalline Solids 147&148 (1992) 56–61
North-Holland

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Map of gel times for three phase region tetraethoxysilane, ethanol and water

S.Y. Chang and T.A. Ring

Laboratoire de Technologie des Poudres, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

The sol-to-gel transition for different starting compositions of tetraethoxysilane (TEOS), ethanol, and water mixtures under acidic catalyzed conditions are reported. According to the physical appearance of the mixtures after mixing, four different types of behavior can be identified. For these systems, opened to an ~70% relative humidity atmosphere, seven regions of the phase diagram have been distinguished according to gelling times. The gelling times are sensitive to the starting composition and have been organized for presentation as functions of the concentration of ethanol [EtOH], the ratio $[H_2O]/[TEOS]$, and [TEOS]/[EtOH]. Gelling time increases with increasing [EtOH]. As $[H_2O]/[TEOS]$ ratio increases, the gelling time first decreases and increases with a minima at the equilibrium concentration.

1. Introduction

The principal synthetic route used by researchers to form silica gels, aerogels or xerogels is through the hydrolysis and condensation polymerization of tetralkoxy silanes, as shown in the following reactions:

$$n\mathrm{Si(OR)_4} + 4n\mathrm{H_2O} = n\mathrm{Si(OH)_4} + 4n\mathrm{ROH} \quad \text{(hydrolysis)}; \qquad (1)$$

$$n\mathrm{Si(OH)_4} = n\mathrm{SiO_2} + 2n\mathrm{H_2O} \quad \text{(condensation polymerization)}; \qquad (2)$$

$$n\mathrm{Si(OR)_4} + 2n\mathrm{H_2O} = n\mathrm{SiO_2} + 4n\mathrm{ROH} \quad \text{(net reaction)}. \qquad (3)$$

The major variables in this reaction sequence include the type of alkoxysilane and its funcionality, catalyst (OH^- or H^+) and its concentration (i.e., pH), the ratio of $[H_2O]/[alkoxide]$, the reaction temperature, and if the system is open or closed to the atmosphere. These variables control the polymerization growth and aggregation of the silica species throughout the transition from the sol to the gel state.

The reactivity of different types of alkoxysilane has been studied by Chen et al. [1]. Systems of alkoxysilane–alcohol–water solutions catalyzed with hydrochloric acid have been studied with different alkoxysilanes which include tetramethoxysilane ($Si(OCH_3)_4$, TMOS), tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS) and tetrabuoxysilane ($Si(OC_4H_9)_4$, TBOS). The hydrolysis rate has been compared for these alkoxysilanes and it decreases with increasing size of the alkoxides, i.e., TMOS > TEOS > TBOS.

Solution pH affects the sol–gel process by modifying the relative rates of the hydrolysis and condensation, controlling the reaction mechanism [2]. The reaction mechanisms [3] and the formed structures are shown in fig. 1. Under acidic conditions, hydrolysis is rapid, producing a rapid increase of Si–OH-containing monomers. These monomers are then slowly polymerized by cluster–cluster growth mechanism into lightly branched polymers which entangle to form a cross-linked gel. This type of gel is usually referred as a polymeric gel [4]. Under basic conditions, the condensation reaction is much faster than hydrolysis reaction. The reactions proceed

by quickly polymerizing the newly generated monomers by a monomer–cluster growth mechanism. Under such conditions, a highly branched structure is produced. Eventually, the highly branched clusters aggregate to become a network. This type of gel is called 'colloidal' [4]. The rates of sol-to-gel transition are different from one system to another. For example, in the TMOS–methanol (MeOH)–water system [5], modified with either HCl of NH_3, the relative gelling times was found to follow the sequence: $t_g(\text{acidic}) > t_g(\text{neutral}) > t_g(\text{basic})$.

The gelling times were also found to be highly dependent on temperature [6]. The reaction rates of both hydrolysis and condensation increase as temperature increases. Colby et al. [7] and Kinouchi Filho et al. [5] have shown that the reaction rates obey an Arrehenius relationship with the apparent activation energy of ~ 10 kcal/mol for TMOS–MeOH–water system. Because of this, the gelling time deceases as the reaction temperature increases.

Reactions performed in open systems and closed systems show great differences in properties. Gelation is much faster in the open system [8]. This difference is due to (1) solvent evaporation and (2) adsorption of moisture from the atmosphere both of which increase the net rate of polymerization. Rheological properties of gels produced in open and closed systems also differ. Open systems with $[H_2O]/[TEOS] < 4$ are Newtonian and closed systems are non-Newtonian either shear thinning or thixotropic.

With all this work, however, there is no consistent map of the gel times place on a ternary phase diagram. For this reason, in this work, we report on the sol-to-gel transition times for the ternary system of TEOS–EtOH–H_2O catalyzed by HCl with different starting compositions

2. Experimental materials and methods

Materials TEOS (Merck, 98% pure), ethanol (Fluka, 99.8% pure), and filtered deionized water (thru Milli-Q, Millipore) were used. The catalyst was HCl at a fixed mole ratio of 0.025 to TEOS for all experiments. A two-step procedure was adopted. The first step is to mix TEOS, ethanol and water containing the HCl that has a mole ratio of TEOS to H_2O of 1 in a beaker under vigorous stirring. The temperature was maintained at 50 ± 0.2°C. After 1 h, the rest of water or TEOS was added into the bath. The solution was kept in a beaker either open or close to the atmosphere until gelation occurred. The average

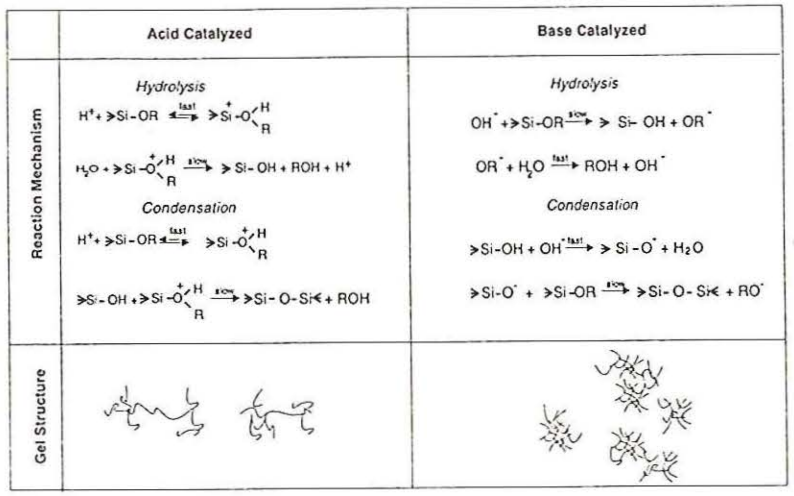

Fig. 1. Schematic diagram of reaction mechanism and gel structure under acidic and basic conditions.

ison
The
than
anol
here,
aker.
and
asti-
sys-
than
eme
osed
dif-
erent
0, 30
are

me for

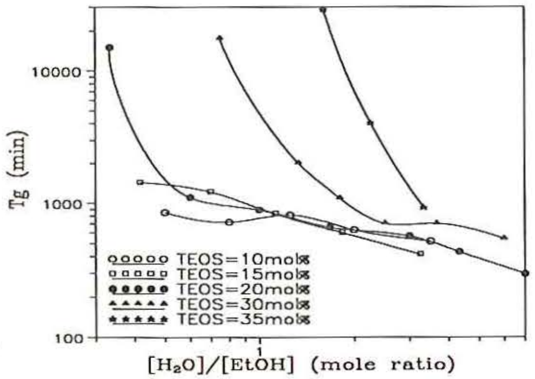

Fig. 7. Effect of $[H_2O]/[EtOH]$ ratio on the gelling time for different TEOS concentrations.

observed at $[H_2O]/[TEOS] \sim 4$. Theoretically, increasing $[H_2O]$ will increase the hydrolysis rate. However, Le Chatelier's principle states that the reaction rate slows down after $[H_2O]$ concentration exceeds the equilibrium value since water is also the product of the condensation reaction. Thus as $[H_2O]$ increases, the gelling time will first decrease and then increase with a minima at the equilibrium concentration, as shown in fig. 6. Figure 7 gives the results of these compensating effects of $[H_2O]$ and $[EtOH]$ on the t_g for different [TEOS]. For all TEOS concentrations, the gel time increases with decreasing $[H_2O]/[EtOH]$ ratio. This increase becomes abrupt at a particular $[H_2O]/[EtOH]$ ratio for 35 mol%, 30 mol% and 20 mol% TEOS. These points of diversion correspond to the points where there is insufficient H_2O for the amount of TEOS in the system. Figure 8 is a plot of gelling time versus [TEOS]/[EtOH] ratio for different $[H_2O]$. Since increases in the [TEOS] diminishes the ratio of $[H_2O]/[TEOS]$, the gelling time is thus increased. This figure shows that t_g increases as [TEOS]/[EtOH] ratio increases for $[TEOS]/[H_2O]$ ratios less than the equilibrium value of 0.25 and that t_g decreases as [TEOS]/[EtOH] ratio increases for $[TEOS]/[H_2O]$ more than the equilibrium value of 0.25.

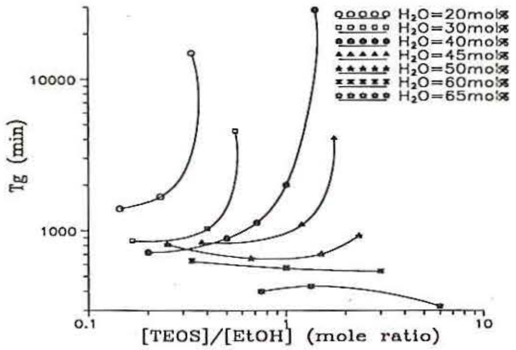

Fig. 8. Effects of [TEOS]/[EtOH] ratio on the gelling time for different water concentrations.

4. Discussion

Sakka and co-workers have reported a great difference in the properties of the sols prepared from opened and closed vessels [11,12]. The sols prepared in the open system with composition of $[H_2O]/[TEOS]$ ratio less than 4 show an unique characteristic of spinnability. The rheological properties of the sol are different for open and close systems. In the open system, the solutions have the Newtonian behavior up to a viscosity of 2.3 Poise and exhibit spinnability [11] in the range 10–100 Poise. In the closed system, the solution becomes non-Newtonian at high viscosities and shows non-spinnable. Shear thinning as well as thixotropy characteristics can also be found at still higher viscosities in the closed system [12]. We have also observed this spinnability of sols in our preparations with compositions of $[H_2O]/[TEOS] < 4$. In addition, with small $[H_2O]/[TEOS]$ ratio near to 1, the resulting gels are strong and they did not crack when exposed to air for months. These compositions fall in group 1 of fig. 3 but close to the boundary with group 2 are non-cracking (e.g., sols with [TEOS] = 20 mol%, [EtOH] = 60 mol%, $[H_2O]$ = 20 mol%, [TEOS] = 35 mol%, [EtOH] = 25 mol%, $[H_2O]$ = 40 mol%, [TEOS] = 35 mol%, [EtOH] = 20 mol%, $[H_2O]$ = 45 mol%; and [TEOS] = 30 mol%, $[H_2O]$ = 40 mol%, etc.)

5. Conclusions

This work reports the sol–gel transition for different starting compositions of TEOS, ethanol, and water mixtures under acidic catalyzed conditions. Physical appearance of the mixtures and the gelation times were observed. According to the physical appearance of the mixtures after mixing, four different types of behavior can be classified. For these systems opened to a ~ 70% relative humidity atmosphere, seven regions of the phase diagram have been distinguished according to gelling times. The gelling times are sensitive to the starting composition and can be explained by the Le Chatelier principle and dilution effects (i.e., gelling time increases with increasing [EtOH]). As $[H_2O]/[TEOS]$ ratio increases, the gelling time first decreases and increases with a minima at the equilibrium concentration.

Those solutions with compositions of low water contents result in the long gelling times and form strong gels which did not crack even when exposed to the air for months.

This work was financed by the Suisse Fonds National, NPF 19.

References

[1] K.C. Chen, T. Tsuchiya and J.D. Mackenzie, J. Non-Cryst. Solids 81 (1986) 227.
[2] E.J.A. Pope and J.D. Mackenzie, J. Non-Cryst. Solids 87 (1986) 185.
[3] R.J.P. Corriu, D. Leclerco, A. Vioux, M. Pauthe and J. Phalippou, Mater. Res.Soc. Symp. Proc. 121 (1988) 113.
[4] C.J. Brinker and G.W. Scherer, J. Non-Cryst. Solids 70 (1985) 221.
[5] O. Kinouchi Filho and M.A. Aegerter, J. Non-Cryst. Solids 105 (1988) 191.
[6] M.F. Bechtold, W. Mahler and R.A. Schunn, J. Polym. Sci., Polym. Chem. Ed. 18 (1980) 2823.
[7] M.W. Colby, A. Osaka and J.D. Mackenzie, J. Non-Cryst. Solids 82 (1986) 37.
[8] H. Kozuka, H. Kuroki and S.J. Sakka, J. Non-Cryst. Solids 100 (1988) 226.
[9] M. Prassas and L.L. Hench in: Ultrastructure Processing Ceramics, Glasses and Composites, ed. L.L. Hench and D.R. Ulrich, (Wiley, New York, 1984).
[10] R.W. Jones, Fundamental Principles of Sol–Gel Technology (Institute of Metals, London, 1989) p. 53.
[11] S. Sakka and K. Kamiya in: Emergent Process Chods for High Technology Ceramics, Mater. Sci. Res. Vol. 17, ed. R.F. Davis et al. (Plenum, New York, 1984) p. 83.
[12] H. Kozuka, H. Kuroki and S. Sakka, J. Non-Cryst. Solids 101 (1988), 120.