

Study of R₂-molar ratio effect on the transformation of tetraethylorthosilicat precursor to gels in sol-gel technique

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Abstract

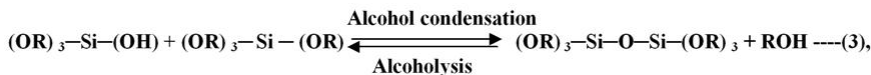
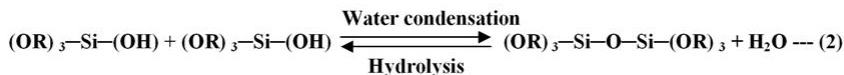
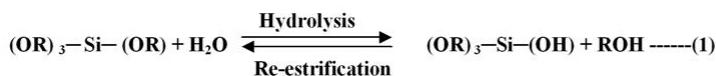
The effect of using different R₂-molar ratio under variable reaction conditions (acidic as well as basic environment and reaction temperature) have been studied. The overall experiments are driven with open and closed systems. The study shows that there is an optimum value for a minimum gelling time at R₂ equal 2. The gelling time for all studied open system found to be shorter than in closed system. In acidic environment and when R₂ value increased from 2 to 10, the gelling time of closed systems has increased four times than open systems at T=30 °C and fourteen times when temperature reaction increased to 60 °C. While in basic environment the influence of increasing R₂ value was limited.

Key words: Sol-Gel, TEOS, R₂-molar ratio

Introduction

The sol-gel process involves the production of a suspension of a solid in liquid, followed by the removal of the liquid, and finally densification of the solid. It has the advantages of low processor temperatures, mixing at the molecular level to produce hybrid systems, and fabrication of novel materials like highly homogenous glasses, ceramics, and composites [1-5].

It is known that two reactions occur during the sol-gel transition: hydrolysis and condensation. Silicate gels are most often synthesized by hydrolyzing monomeric, tetra functional alkoxide precursors such as tetraethylorthosilicat (TEOS), using a mineral acid (e.g.HCl) or a base (e.g. NH₃) as catalyst. The reactions generally used to describe the sol-gel process are [6-8]:



Where; R is an alkyl group such as ethyl reagent (C₂H₅) in TEOS precursor. The formation of the sol (i.e. a colloidal suspension in a liquid of silica particles) occurs from the

hydrolysis reaction of TEOS precursor. While the colloidal particles and condensed silica species linked together to become a 3-D gel network (i.e. a continuous solid structure that

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contains a continuous liquid phase). The reaction from TEOS solution to a solid material is not simple one and many parameters are possible. These parameters involve: \mathcal{R} -molar ratio ($\text{H}_2\text{O}:\text{TEOS}$), and catalyst type which involves pH value of solution, that have major effects on the reactions rate, and subsequently on the characteristics of a silica gel network, reaching the final products. The water content of the silicon alkoxide solution markedly affects the structure and properties of the siloxane particles (Si-O-Si) produced in the sol.

In this study, we will focus on the water content factor (\mathcal{R} -ratio), and its activity on the rate of reactions, gelling time, and the bulk gel nature. Where it was known that the \mathcal{R} values ranging from stoichiometric ratio to high values, depending on the desired polysilicat product.

Materials and Methods

Using sol-gel technique the gel samples were prepared. Firstly two solutions (for each study samples) were prepared: silica solution containing 1ml of (TEOS) (Purity > 98%) supplied by Schuchardt, Hohenbrunn, Germany, and 2ml of ethanol Analytical grade. (Purity

99.9%) supplied by Gainland Chemical Company, U.K. And catalyst solution containing 2 ml of pure ethanol and X ml of Deionized water at pH values: 4, 7, 9; using HCl acid (0.15 M HCl 37%) supplied by Aldrich Co.; and NH_3 base supplied by BDH limited, Poole, England. Where $X = 1.4$ to 10, corresponding to \mathcal{R} -molar ratio: from 1.4 to 10. The catalyst solution was slowly added to the silica solution with magnetic stirring for one hour. The resultant sol was poured into cylindrical glass containers. Immediately after the chemicals are mixed, the recipes were divided into two parts; the first one is kept without any cover while the other one under tightly sealed cover molds, the overall samples kept at fixed reaction temperatures 30°C , 40°C , 60°C for (72 hour) until tetraethylorthosilicat precursor transform to gels. Because of immiscibility of TEOS with water, a mutual solvent such as ethyl alcohol is added. While Formaldehyde, supplied by BDH limited, Poole, England; is added as drying control chemical additive

The following scheme shows the overall process of the recipes which is studied in this work:

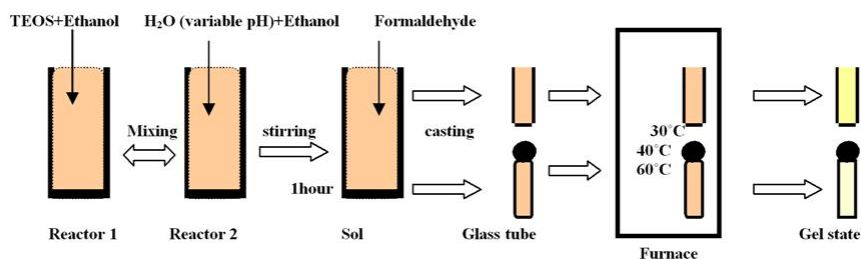
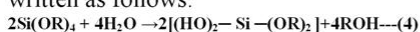


Figure (1): Gelation process of (TEOS- Ethanol-Water) system.

Results and discussion

The precursor solutions which are prepared at molar ratio $R=2$ for all pH values and reaction temperatures, takes minimum time to reach a gel state (i.e. gelling time), as shown in figure (2) and subsequently figures (3 a-d). In order to explain this behavior, it was known that R value of 2 is theoretically sufficient for complete hydrolysis and condensation reactions [8-10]. Equation (1) at $R=2$ can be written as follows:



Here we have an equivalent numbers of (OH) and (OR) groups on the silicon atom in each monomer, producing a partially hydrolyzed molecules and needing a half time for hydrolysis reaction. Thus alcohol producing condensation here is favored. This equivalence between the two types of groups (i.e. OH and OR on Si atom) will be accelerated the formation and aggregation of the condensed species. So the speed of cross-linking of siloxane particles will be increased. Therefore, we have equilibrium in the rate of hydrolysis and condensation reactions, which yield minimum gelling time [11].

While at stoichiometric ratio ($R=1.4$), the gelation process of the prepared solutions have gelling time longer than at in the case of ($R=2$) as shown in figures (2, 3). This may be attributed to the slow hydrolysis rate, where the monomers of TEOS precursor have not chemically equivalent amount of water molecules required to complete the hydrolysis

reaction, and leads to delay the condensation process.

However, in excess water recipes ($R=10$), the hydrolysis reaction will promote by increasing the number of sites to be hydrolyzed. Therefore, the water producing condensation will be favored here. Although, since water is the by-product of condensation reaction (Eq. 2). So it retards the condensation reactions and caused more completion to the hydrolysis of monomers before significant condensation occurs (reverse of Eq 2) [12]. The high excess in water ratio will reduce the probability of primary aggregation between the silanol groups Si (OH), resulting in a long gelling time as shown in figures (2, 3).

Open and closed systems effect

However alcohol is more evaporate than water at the studied temperatures in open system. So that the probability of re-esterification reaction (reverse of eq.(1)) will be decreased leading to enhanced the hydrolysis rate. On the other hand, the quantity of alcohol and water remain approximately constant under tightly sealed molds. The closed system prevents the evaporation of alcohol and water. Therefore the reverse reaction of Eq. (1) is prompt and the hydrolysis rate will be decreases and subsequently the condensation rate. So the gelling time for all the closed system recipes at all pH values and reaction temperatures are longer than its value for open system recipes as shown in figs. (3-a, c) and figs. (3- b, d).

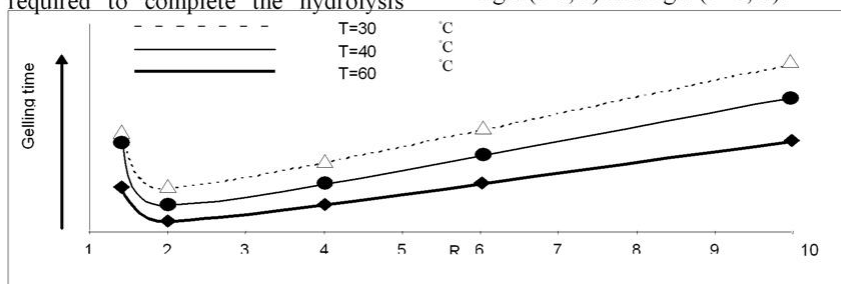


Figure (2): Gelling time as a function of R-ratio at three temperatures.

The present study shows that there is a noticeable effect of the reaction temperature on the gelling time when R -ratio increased from 2 to 10. This affection is obviously clear in acidic solutions (i.e. pH 4), and little in basic solutions (i.e. pH 9).

Assuming that (δ_τ) is the ratio of the gelling time at ($R=10$) to its value at ($R=2$). In the case for acidic solution; the results of open system recipes show that $(\delta_\tau=4)$ at $T=30^\circ\text{C}$, and $(\delta_\tau=14)$ at $T=60^\circ\text{C}$. This means that the gelling time is increased four times at $T=30^\circ\text{C}$ and fourteen times when temperature reaction increased to 60°C as shown in figures (3: a, b). These results may be explained as follows:

Iler [11] confirmed that an increasing in temperature reaction leads to further growth of silica particles in size, and therefore decreases in number. Also when the

reaction temperature increased the particles kinetic energy will be increases too. Thus the probability of collision (aggregation and cross-linking) will be increased resulting in short gelling time.

While for closed system recipes, also in acidic solutions, where $(\delta_\tau=1.3)$ at $T=30^\circ\text{C}$, and $(\delta_\tau=4.8)$ at $T=60^\circ\text{C}$, comparing with there values of open system recipes, the value of δ_τ will be decreased, in general, three times of its values in open system. This may be attributed to the same reasons mentioned before (i.e. the evaporation of water as well as alcohol which increase the probability of collision). Then the evaporation prevention in close system can act as the essential factor in reducing (δ_τ) from 4 to 1.3 at $T=30^\circ\text{C}$ and from 14 to 4.8 at $T=60^\circ\text{C}$ in open system. This may enhance the explanation of evaporation factor.

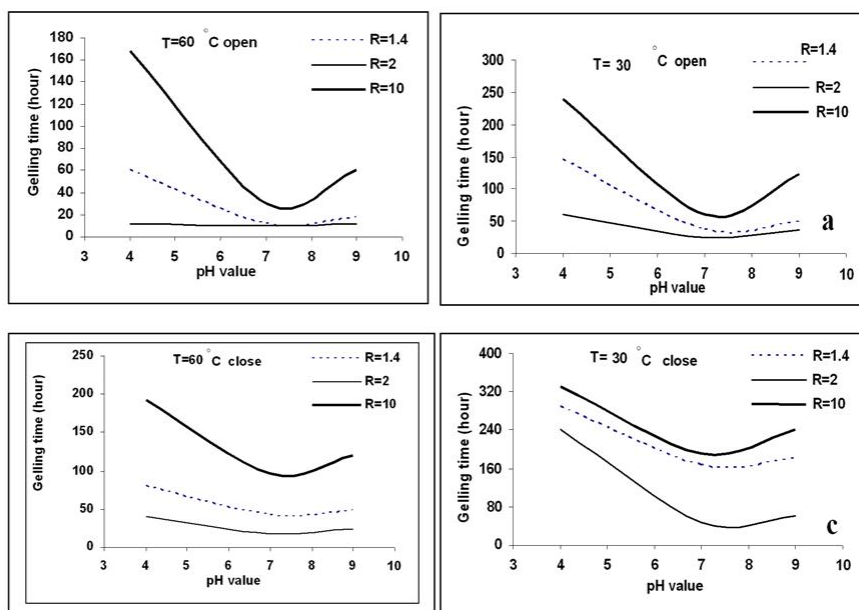


Figure (3): Gelling time as a function of pH at three R-ratio values; a. T=30°C open, b. T=30°C close, c. T=60°C open, d. T=60°C close.

Regarding to the figures (3-a, c) and figures (3-b, d), the effect of removing the sealed cover from the mold of the recipes driven at $R=2$ and $T=30^{\circ}\text{C}$ is very clear compared with the case of $T=60^{\circ}\text{C}$. However alcohol is co-solvent in sol-gel process (i.e. does not chemically react with the precursor in hydrolyses and condensation) [1], but its excess amount will prevent the particles collision leading to retardation of the cross-linking and gelation process. At $T=30^{\circ}\text{C}$; the rate of water evaporation is very little and can be negligible compared with alcohol evaporation. In this case the sol in the open system will suffer from alcohol evaporation only, resulting in faster gelling time. While at $T=60^{\circ}\text{C}$ the effect of primary growth of particles with temperature dominates.

Conclusion

Regardless of increasing the reaction temperature, which enhances the gelation process, and starting from stoichiometric R ratio, for both open and closed systems, the gelation process is promoted and then the gelling time is reduced reaching a minimum value at R equal 2. Then the gelling time increases monotonically with further increase of R value. In acidic environment, as R ratio increases more than 2 the gelling time will increase dramatically, while there are little influences in basic environment.

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دراسة تأثير النسبة المولارية R على تحول محلول مادة التتراثيل اورثو سيلكات الى حالة الجيل في تقانة السول – جيل

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الخلاصة

تم في هذا البحث دراسة تأثير تغيير النسبة المولارية R تحت ظروف تفاعل مختلفة وفي اوساط حامضية وقاعدية. وقد اجريت التجارب عند عدة درجات حرارية. لقد حضرت النماذج في انظمة تحضير مفتوحة الاغطية ومغلقة. اظهرت الدراسة ان اقل زمن لازم للوصول الى حالة الجل يكون عند $R = 2$, وان هذا الزمن يكون اقل عند التحضير في انظمة التحضير المفتوحة, ولكل النماذج, مقارنة مع مثيلاتها في الانظمة المغلقة. وجد عند زيادة قيمة R من 2 الى 10 وفي الاوساط الحامضية يزداد زمن الوصول الى حالة الجل في النظام المغلق الى اربعة اضعافه لكل النماذج عندما تكون درجة حرارة التفاعل 30°C , اما اذا زادت درجة حرارة التفاعل الى 60°C فان زيادة الزمن تكون اربعة عشر ضعفاً. أما في الاوساط القاعدية فان تأثير تغيير قيمة R على الزمن اللازم للوصول الى حالة الجل يكون محدوداً.