# Middle East Technical University

## Department of Metallurgical and Material Engineering

### Mete215 – Materials Processing Laboratory

**Experiment 3:** Sol-Gel Processing

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## ABSTRACT

In this experiment Sol-gel process step were used and the effects of ph change with the reaction time was observed. As an acid catalyst HCl and as a base catalyst NaOH were used. Sample 1 had a Ph value of 0-1 sample 2, 4-5 and sample 3 ‘s Ph value was estimated to be around 10. For the gelification to happen the hydrolysis and the condensation reactions were done in Ph value ranges where the reaction rates were high but the possibility of the reactions happening in negative conditions were also tested. The Ph value was changed with the above mentioned acid and base catalysts. The viscosity and the color changes were also observed that changed from the effect of hydrolysation and condensation reactions.


## INTRODUCTION

Normally, to make glass high temperatures are needed therefore scientist looked for ways to synthesize glass at relatively low temperatures. One method that has been found is the sol-gel process. It is a process done in a bottom up fashion. It can be done in low temperatures. The process usually starts with a liquid source containing metal oxides for example silicon alkoxide to get oxides in the reactions. The source also contains water needed for hydrolysation, Alcohol to act as the solvent as well as acids and bases to speed up the process (Sakka, 2013). The hydrolysation and the condensation reactions can happen in the room temperature to create the sol allowing the process to be non-melting process different from the usual way of making glasses. After the hydrolysation and the condensation, the sol becomes an integrated network of particles and it called gel (Roberto Nistico, 2017). After this the drying and sintering stages must be done in order to get an end result of glass material.

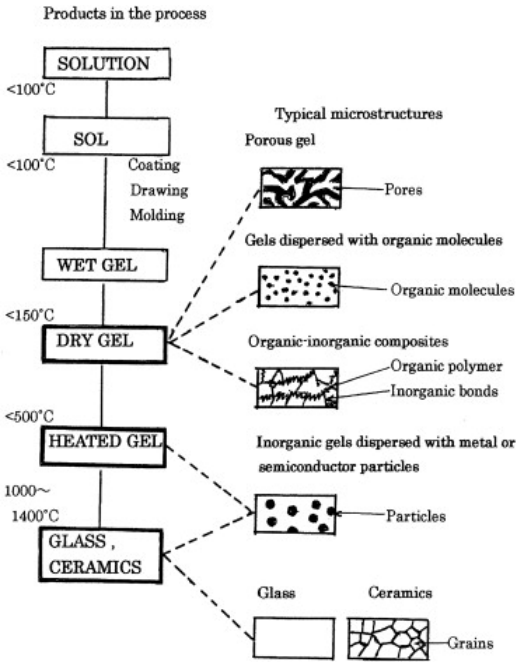


**Figure 1.** The steps of the sol-gel process (Sakka, 2013)

These steps can be seen as such in figure 1.

To talk about the advantages of the Sol-gel process, the synthetization at low temperature has already been discussed, to add to this the high purity of the resulting product is also an important advantage of the sol-gel process as the high purity can be correlated with the production cost as well as better performance of the finished product (Roberto Nistico, 2017). Also by using the sol-gel process glasses that are hard to be produced in classical ways can be synthesized because "it has the potential to increase the concentration of dopants, expand the compositional range, and construct tailored photo-and mag-netoactive centers" (Kajihara, 2013). However, the process also includes disadvantages. One problem is that in the making of the silica glasses in the drying stage extreme shrinkage occurs from the evaporation of the solvent (Kajihara, 2013). Figure 1 also shows the difference between that of a wet gel dried gel and glass made from 25 mmol tetraethoxysilane (TEOS).

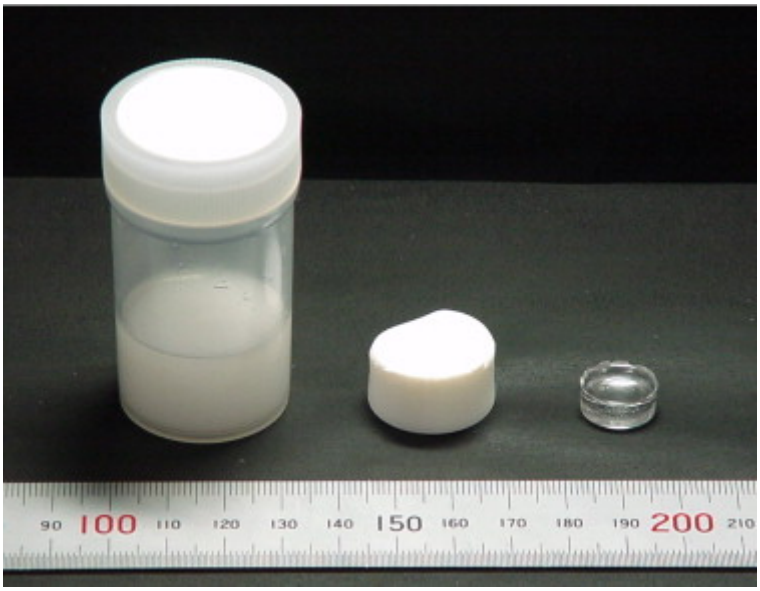


**Figure 2.** Comparison of the sizes of a wet gel, dried gel, and glass prepared from 25 mmol (Kajihara, 2013).

Due to such shrinkage the capillary pressure exerted may cause the fracture of the gel. Another problem of the Sol-gel process is the cost.

Sol gels are also used for coating. By coating it is possible to give active properties to a material. And in the case of sol-gel as it is done in low temperatures one advantage of it is also to coat materials that are not resistant to heat. There are a number of methods that can be used to coat materials with sol-gel. Namely, Dip coating, Spin coating laminar flow coating printing and spray coating (Sakka, 2013). Spin coating is a technique where the coating is done on an material that is spinning. The spinning speed effects the thickness of the coating. The dip coating the substrate is dipped into the solution and drawing it up in a desired speed after you put it to the oven to heat as to let the substrate stick with the film (Sakka, 2013).

# EXPERIMENTAL

Materials that were used;

- TEOS (Tetra ethylorthosilicate)
- Polycarbonate substrates
- Ethanol
- DI-water
- HCl and NaOH

Equipment that were used in the experiment;

- Laboratory Hood with adequate bench space
- Spin Coater
- Hot-plate (2x)
- pH-meter and thermometer
- Volumetric (Micropipettors) or weight-based measuring (Balance) units
- Conventional drying oven
- Borosilicate glass beakers (50 mL)
- Magnetic bars
- Polystyrene test tubes and tube holders
- Parafilm
- Volumetric measuring cylinders

## Procedure

First of all, to our beaker 12ml of TEOS was put. Then 24ml of ethanol was put to the same beaker. Afterwards 15 ml of distilled water was put on top of them. The solution inside of the beaker at this moment looked cloudy and white. To determine the solutions Ph litmus paper was used at this step. Carrying on, HCl as an acid catalyst was dripped into the beaker very slowly. The solution at this time looked clear and again litmus paper was used to determine the solutions Ph. The first sample was taken here. NaOH as base was added to the solution. The solution became much more viscous but the color remained the same. The Ph was once again determined with the use of litmus paper and a sample was taken. Then we carried on dripping NaOH until we observed the formation of the gel where we took our third sample. During all the addition to the beaker, magnetic stirrer was used.

## RESULT


**Figure 3.** Image of Sample 1

In figure 2 the image of sample 1 can be seen. This sample was taken when HCl as an acid catalyst was dropped into the solution containing TEOS, ethanol and distilled water. It has a clear color and the viscosity is relatively low.

**Figure 4.** Image of Sample 2

In figure 3 the image of the second sample can be seen. This sample was taken when NaOH as base was added to the solution for some time. It has the same color as sample 1 which is a clear color. The viscosity is more than that of sample 1.

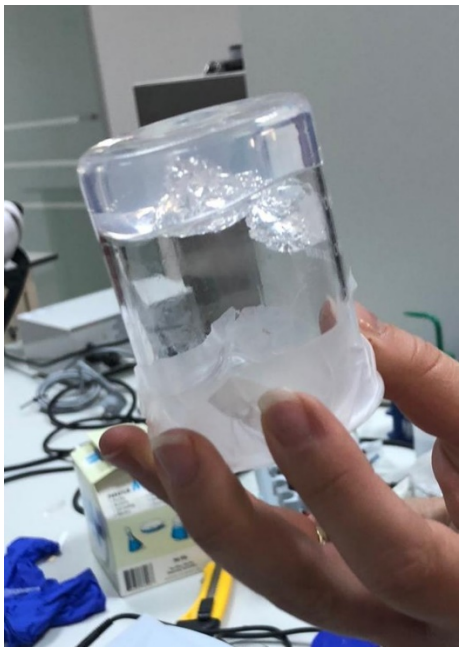

**Figure 5.** Image of Sample 3

In figure 4 the third and final sample can be seen. The sample was taken when more NaOH was added to the beaker at the time when sample 2 was taken. The solution became gel like and was the most viscous of the three samples. The color is also the same as sample 2 and sample 3.

**Figure 6.** Image of Sample 1 after a period of 4 days

In figure 5 the image shows of the state of sample 1 after 4 days. It can be seen that the color did not change and it is still in liquid state meaning that it did not gelify.

**Figure 7.** Image of Sample 2 after a period of 4 days

Figure 6 shows the state of sample 2 after a period of 4 days. It can be seen that it has still the same color and it did not gelify.

| *Properties* | **Color** | **Ph** | **Viscosity** |
|---|---|---|---|
| **Sample 1** | Clear | 0-1 | Low Viscosity (Liquid) |
| **Sample 2** | Clear | 4-5 | Moderate Viscosity (Liquid) |
| **Sample 3** | Clear | ? | High Viscosity (Gel) |

**Table 1.** Properties of the three samples

| *Properties* | **Color** | **State** |
|---|---|---|
| **Sample 1 after 4 days** | Clear | Liquid |
| **Sample 2 after 4 days** | Clear | Liquid |

**Table 2.** Properties of Sample 1 and Sample 2 after 4 Days

## Discussion

These are the points that should be addressed in this discussion part;

1. Why was 15ml of water was used instead of the theoretical value of 12ml?
2. Why was the color of the solution white and cloudy when the solution consisted of ethanol, TEOS and distilled water?
3. How does the change of Ph effect viscosity and the Hydrolysis and condensation reactions?
4. The estimation of the Ph of the third sample and the explanation of why litmus paper could not be used to measure the Ph of third sample.
5. Was the state of sample 1 and sample 2 after the period of 4 days expected?
6. In the process of making the glass by the sol-gel method what are the parameters that effect it.
7. The amount of time that would have taken to gelify for sample 1 and sample 2 where acid was not added.

To answer these points:

1) To answer this question, we must first mention of the reactions taken place in the sol-gel process;

Hydrolysis:

$$Si\text{-}OR + H_2O \rightarrow SiOH + ROH$$

Condensation:

$$Si(OH) + ROSi \rightarrow Si\text{-}O\text{-}Si + ROH$$

$$Si(OH) + (HO)Si \rightarrow Si\text{-}O\text{-}Si + H_2O$$

(Sakka, 2013)

From these equation and Figure 1 we conclude that the excess water after the hydrolysis will evaporate and would not affect the other reactions therefore to be on the safe side more water than necessary was added.

2) When the solution consisted of only TEOS, Ethanol and water the interaction between ethanol and water is the cause of the solution looking white and cloudy. When the

3) To show the effects of Ph on the reaction the graph ph vs reaction as can be seen in figure 8 should be considered.

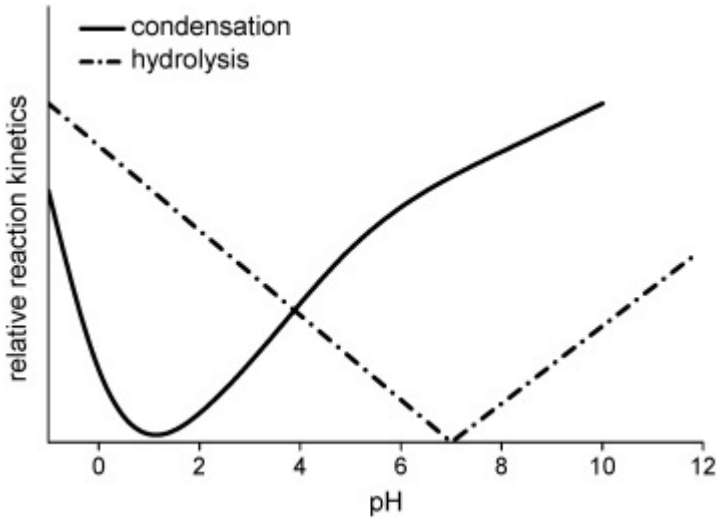


**Figure 8.** Ph vs reaction kinetics graph (Bartosz Babiarczuk, 2016)

From this graph it can be concluded that hydrolysis happens faster in low Ph values while the condensation reactions happens faster in high Ph values. Therefore, in the case of our first sample that was gotten when the acid was added and had a ph value between 0-1, it can be said that the hydrolysis happened very quickly but the condensation reactions were happening very slowly. Since that was the case the viscosity was very low as well.

In the case of the second sample the ph value was between 4 and 5 meaning that the rate of the condensation reaction increased. This resulted in viscosity increasing as well.

As for the third sample the Ph value could not be measured with the litmus paper. The reason of this and the estimation of the ph for sample 3 will be given in the fourth answer. But it is obvious that the ph has increased more resulting in a very viscous gel like state.

4) The Ph could not be determined for sample three because sample 3 was not in a liquid state and the litmus paper can be used only for liquid states. From the fast completion of the condensation reactions it can be determined that the rate of the reaction increased meaning that the ph should be around the value of 10-11 based on figure 8.

5) To give a comment to the states of sample 1 and sample 2 after a period of 4 days, sample 1 was expected to be still in liquid form meaning that the condensation reactions should not have finished as the rate of condensation reaction is very small in low Ph but it has been expected of the second sample to gelify after the passing of 4 days. In figure 7 it can be clearly seen that this has not been the case. The reason for this could be that the rate of the condensation reaction was not high enough meaning that the amount of NaOH added before taking sample 2 has not been enough.

6) The sol-gel process can be considered as a complex process therefore it can be said that there are certain factors affecting the end result. Namely, concentration, Ph, Temperature and the chemistry of the precursors. These parameters should be considered during the sol-gel process.

7) In question number 3 we mentioned that it was expected for sample 1 to be still in a liquid state after 4 days as it is expected for it to gelify in a time of a month while for sample 2 it was expected to gelify after a period of two days but it did not. The reason for such a case to occur is also mentioned in question 3.

## CONCLUSION

In this experiment the sol-gel process was observed. The importance of the environments Ph was seen as in a Ph scale where the condensation or the hydrolysation reactions happens slowly the reaction can take a lot of time. In the experiment this was observed and tested with the addition of HCl and NaOH to increase or decrease the ph values. This experiment also showed the potential of sol-gel as to make glass there were not any need to use high temperatures like the traditional way of making glass. Sol-gel in general is an important method to create ceramics or glass and it used in variety of places.

## REFERENCES


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## APPENDIX

No calculations or raw data to put here