A FACILE APPROACH FOR THE EFFECT OF SOLUTION, CATALYST AND TEMPERATURE ON THE SYNTHESIS OF GLASS POWDER BY THE SOL-GEL METHOD

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In this study, the aim is to synthesize borosilicate glass powder with a particle size of approximately 50nm by the sol-gel method to be used as a hierarchical surface agent in hydrophobic coatings. Precursors used in the sol-gel reaction are Tetraethoxysilane (TEOS) as a source of silicon, boric acid as a source of boron and potassium hydroxide as a source of alkali. For this purpose, process optimization was simply investigated in three stages; solution, catalysis and reaction temperature parameters, respectively. In the first stage of the study, gelling behavior and amorphous structure formation were examined by using solutions prepared with different solvents at different pH values. The solution, which had an ethyl alcohol-water mixture as a solvent with an acidic start and alkaline second step, was found to be suitable. In the second step, the effect of catalysis was investigated by changing the catalyst type and amount in the solution which was found to be most suitable in the previous stage. Ammonium hydroxide and urea solutions that contain ammonium groups were used as catalysts. It was observed that the urea solution did not function as a catalyst due to its neutral character versus the base character of the ammonium hydroxide. In the last step of the study, the effect of reaction temperature was investigated. Upper and lower temperatures are limited due to the solution-based process. A temperature close to room temperature was included in the experiment in order to increase the controllability of the temperature. The gelation behavior at all stages was recorded with photoshoots of tilted beakers, the amorphous structures were examined using x-ray diffractometer (XRD) and microstructures were visualized with scanning electron microscopy (SEM). As a result of all the steps, a solution mixture of ethyl alcohol with a water molar ratio of 44.6: 33.9 and a starting pH of 2.3, a catalyst solution of 0.102 mol of ammonium hydroxide and a reaction temperature 30°C, were determined as optimal parameters.

Keywords: *Sol-gel, glass powder, catalysis*

1. Introduction

Glass spheres can be used for many applications, such as composite reinforcement material, sinter addition, coating and paint addition [1,2].

It is known that glass powders produced by the sol-gel method using metal alkoxides are purer and require lower temperatures than those produced by conventional melting processes [3-7]. Homogeneous glassy inorganic materials with desired properties, such as hardness, optical permeability and porosity can be obtained at temperatures close to room temperature by the sol-gel method [8-10]. The sol-gel method has become increasingly popular since the 1800s and has become a center of attention. One important reason for this is that every solution or suspension system can be used [11].

Any material capable of forming a reactive monomer may be used as a starting material in the sol-gel process. The most commonly-used starting materials are metal salts in MmXn form and metal alkoxides in the form of $M(OR)_n$ (M: metal, m and n: valence, R: alkyl group) [12-16].

The starting material for use is hydrolyzed in water or a suitable organic solvent to obtain a clear and stable solution or colloidal suspension. Condensation reactions occur between metal alkoxides and–metal hydroxides, which are formed by a hydrolysis reaction. An acid or base catalysis is used to control dissolution, hydrolysis, gelation and particle formation reactions [11]. As a result of the hydrolysis and condensation reactions of the starting materials, a gradual detachment of alkoxide groups forms M-O-M- bonds and gelation takes place together with the growing of the network structures [17,18]. The most important feature of these reactions is a transformation to a solid phase as a result of the process starting in a liquid phase.

Parameters, such as the starting materials and ratios used in the sol-gel method, ambient pH value, the solvent or dispersants used and concentrations, the addition of acid or base catalysts, all control the rate of hydrolysis and condensation reactions and affect the formation and growth of particles [19].

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In this study, the aim is to produce borosilicate powders of 40-50 nm in size to be used as a hierarchical surface element in hydrophobic coatings to be applied to borosilicate glass surfaces. The effects of the solution used for the formation of particle size and amorphous inorganic material, catalysis and reaction temperature, respectively, are examined. In the sol-gel process, Tetraethoxysilane (TEOS) is used as the source of silicon, boric acid is used as a boron source and potassium hydroxide is used as the monovalent alkali metal source.

2.Experimental

2.1.Materials

Tetraethoxysilane at %99 was purchased from Abcr chemicals, Germany. Boric acid and ammonium hydroxide solution at %25 were purchased from Merck, Germany. Potassium hydroxide and glacial acetic acid were purchased from VWR Chemicals, ABD. Urea was purchased from Carlo Erba Reagents, France and ethanol was purchased from JT Baker Chemicals, Acids and Solvents. Deionized water with 18.2 MΩ resistance was obtained using a Millipore milli-Q Direct 8 water purification system.

2.2.Glass powder synthesis by the sol-gel method

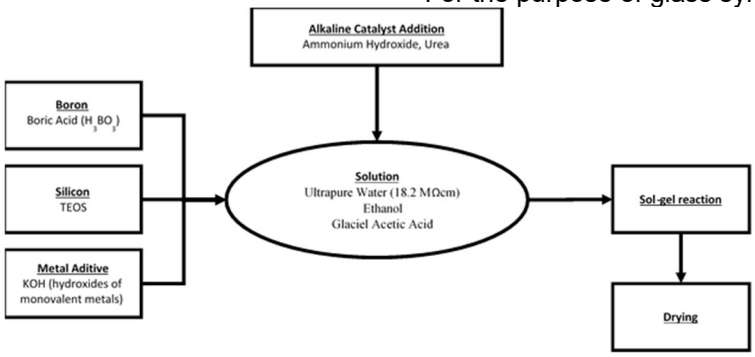

Fig 1 - Synthesis of glass powder by sol-gel method.

To obtain glass powders, a two-step sol-gel process was used (Fig. 1). For the first step of the process, boric acid used as a boron source, potassium hydroxide as an alkaline source monovalent metal hydroxide and tetraethoxysilane as a silicon source were mixed in a water-ethanol mixture in the presence of glacial acetic acid as a solubility promoter. For the second step of the process, a catalyst solution (ammonium hydroxide and urea) was added drop by drop in the mixture [20]. After the gelation occurred, a drying process was performed in a drying oven at 100°C to finalize synthesis and to obtain powders. Agglomerated particles were crushed gently in an agate mortar.

The initial pH of the solution was controlled to increase the soluble amount of precursors by adding acetic acid. Catalyst types, quantities and solution pH are the most critical variables of the process that affect the particle size of the final products. Additionally, the sol-gel temperature is a parameter that determines the possibility of occurrence, rate and effectiveness of reaction and properties of the resulting product. Therefore, the effects of the first-step initial solution, catalyst type/amount and sol-gel reaction temperature on the particle size of the fabricated glass powder were investigated.

Characterization

Gelation behavior was examined manually by tilting the beaker daily with gelation times being recorded. Structural characterization of the sol-gel synthesized powders was made using a Rigaku, MiniFlex600, (Rigaku™ Co., Ltd., Tokyo, Japan) X-ray diffractometer in the 2θ range, between 10° and 70°, at a scan speed of 1°/min with Cu Kα radiation. The amorphous structure was investigated by comparison with a control experiment using a glass specimen holder and conventional borosilicate glass powder.

Morphological characterization and particle size analysis of the obtained powders were carried out using ZEISS Supra 50 VP scanning electron microscopy with 20 kV accelerating voltage and secondary electron imaging after gold sputtering.

3.Results and Discussion

3.1.Effect of Solution

For the purpose of glass synthesis by the sol-gel method, firstly the effect of the solution was studied. Different sols were prepared and, after the gelation and drying steps, amorphous structure formation was investigated by XRD analysis. Twelve test samples prepared for optimizing the sol ution composition and are shown in Table 1. The aim was to view the effect of water content on gelation for the SD-01 and SD-02 samples and the effect of reaction time before catalyst addition for the SD-03 and SD-04 samples, including an equal amount of water.

For the SD-05 and SD-06 samples, basic solutions were prepared to consider the initial pH. In the following examples, water and ethyl alcohol were used together for a sequential evolution of the hydrolysis and condensation reactions. For all of the prepared sols, gelation times and amorphous structure formations were monitored.

Through the analysis results of the twelve optimization samples, amorphous structure was formed for all the samples except for the SD-05,

Table 1

Solution optimization studies

	Glass Composition (Molar Ratios) 20:4:1			Solution Composition				
				pH values			Molar Ratios	
Sample	TEOS (g)	Boric Acid (g)	KOH (g)	Ammonium Hydroxide	Acedic Acid	HCl	Ethanol	Water
SD-01	2.603	0.1545	0.035	pH:6.0*	pH. 5.5	-	-	1.66
SD-02					pH: 5.0	-	-	2.77
SD-03					pH. 5.5	-	-	2.77
SD-04					pH: 5.0	-	-	1.66
SD-05				pH: 12.0*	-	-	0.4**	0.5**
SD-06					-	-	0.4	1.0
SD-07				-	pH: 2.3	-	0.4**	0.5**
SD-08				pH:12.8	pH: 4.2*	-		
SD-09				pH: 6.0*	pH: 2.3	-		
SD-10				pH: 4.0*	pH: 2.3	-		
SD-11				pH: 6.0*	-	pH: 1,5		
SD-12				pH: 6.0*	-	pH: 2,0		

* Catalyst was added at second step. ** water:ethanol mixture was used as 44,6:33,9 (molar ratio)

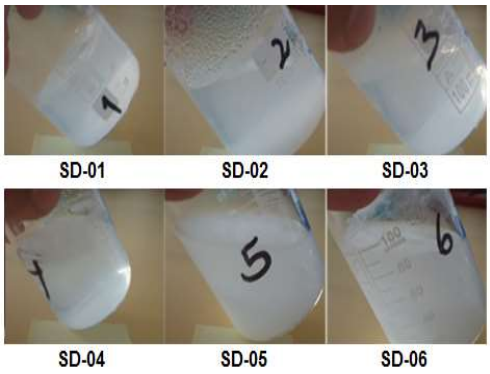

Fig 2. - Gelation of SD-01, SD-02, SD-03, SD-04, SD-05 and SD-06 after 5 days.

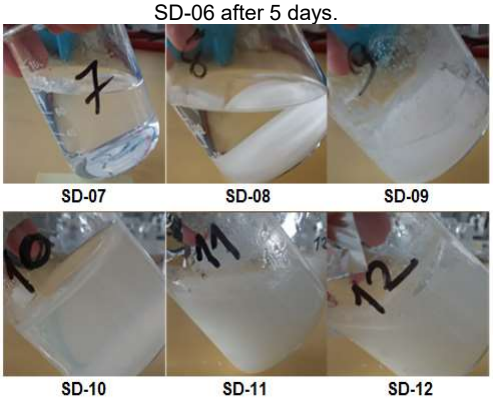

Fig 3 - Gelation of SD-07, SD-08, SD-09, SD-10, SD-11 and SD-12 after 5 days.

SD-06 and SD-11 samples. Samples SD-01 and SD-10 revealed complete gelation accompanied by amorphous structures. In the SD-07, SD-08 and SD-11 samples, no alterations were observed in the sol character (Fig. 2 and Fig. 3). Partial gelation occurred in the other samples. In consequence of the solution studies performed at ambient temperature, the SD-10 sample achieved the desired effect (Fig. 4).

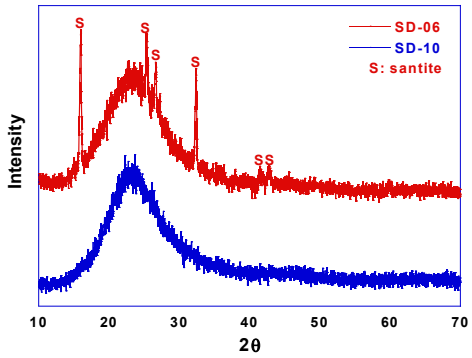

Fig 4 - XRD of SD-06 and SD-10.

3.2.Effect of Catalyst

A new six sampled-set was prepared based on the SD-10 samples, in order to examine the effect of the catalyst type and amount on particle shape and size. Detailed information regarding the test samples is shown in Table 2. Glass compositions and TEOS/ethanol/water/acetic acid molar ratio were the same for all samples, with different amounts of urea and ammonium hydroxide being used as catalyst. The SKD-1 sample was left for gelation after mixing the precursors in the absence of any catalyst. As a catalyst, ammonium hydroxide was used in the SKD-A1, SKAD-A2 and SKD-A3 samples and urea was used in the SKD-U1 and SKD-U2 samples.

The six different samples of this test set were compared in accordance with gelation and amorphous structure formation and electron microscopy images. Fig. 5 shows the gelation behavior of the sample set

Table 2.

Samples including different catalyst types and amounts

Sample	Glass Composition (Moar Ratios)			Solution Composition (Molar Ratios)					
	TEOS	H_3BO_3	KOH	TEOS	Ethanol	Water	Acedic Acid	Ammonium Hydroxide	Urea
SKD-1	20	4	1	0.83	33.9	44.6	0.25	-	-
SKD-A1	20	4	1	0.83	33.9	44.6	0.25	0.003	-
SKD-A2	20	4	1	0.83	33.9	44.6	0.25	0.102	-
SKD-A3	20	4	1	0.83	33.9	44.6	0.25	0.190	-
SKD-U1	20	4	1	0.83	33.9	44.6	0.25	-	0.102
SKD-U2	20	4	1	0.83	33.9	44.6	0.25	-	0.190

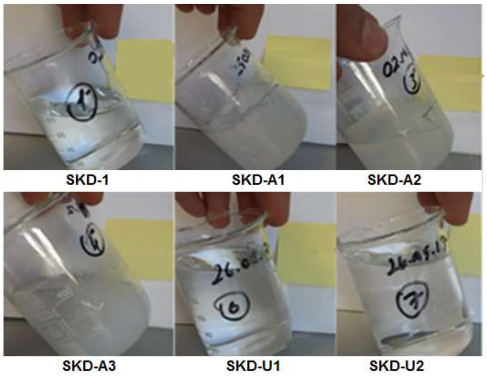

Fig 5 - Gelation behavior depending on catalyst type and amount after 5 days.

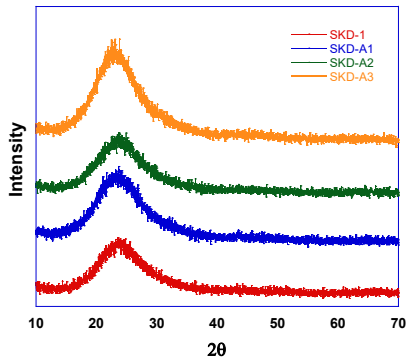

Fig 6 - XRD of SKD-1, SKD-A1, SKD-A2 samples.

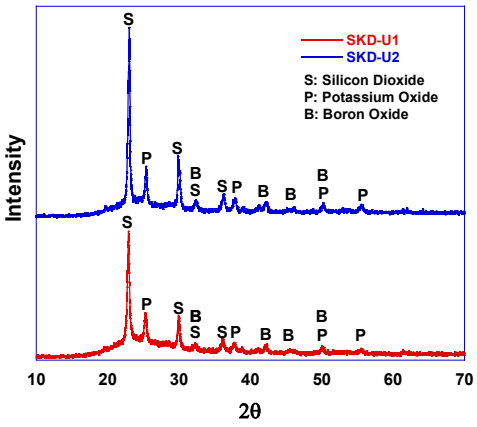

Fig 7 - XRD of SKD-U1 and SKD-U2 samples.

As can be seen in the XRD results, amorphous structure formation was identified in the uncatalyzed SKD-1 sample and ammonium hydroxide catalyzed in the SKD-A1, SKD-A2, SKD-A3 samples (Fig. 6). In the urea catalyzed SKD-U1 and SKD-U2 samples there were certain peaks, identified as silicon dioxide, potassium oxide and boron oxide peaks by qualitative analysis (Fig. 7). Although both samples contained the ammonium group, the obtained result was interpreted in relation to the neutrality of the urea versus the base character of the ammonium hydroxide. The pH value is of critical importance in the required gelation of the sol-gel reaction. Ammonium hydroxide plays an important role in the condensation and gelation stages due to its basic character.

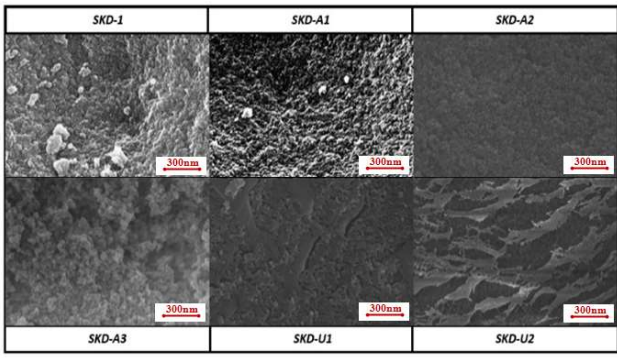

Fig 8 - SEM images of samples with carried catalyst types and amounts

In the SEM micrographs presented in Figure 8, it can be seen that while the SKD-1, SKD-A1, SKD-A2 and SKD-A3 samples have granular forms, the SKD-U1 and SKD-U2 samples do not have similar aspect. The SKD-U1 and SKD-U2 samples have inhomogeneous combined phases in contrast with the granular forms of the other samples, having ammonium hydroxide as a catalyst or no catalyst. When the amorphous-phased samples are evaluated, even though the SKD-1 sample has granular form in the absence of any catalyst, there is no uniform distribution of shapes or sizes. Spherical-like particles of the SKD-A1, SKD-A2 and SKD-A3 samples, which

Table 3

Sol compositions and reaction temperatures

Sample	Glass Composition (Molar ratios)			Solution Composition (Molar Ratios)						Reaction Temperature (°C)
	TEOS	H_3BO_3	KOH	TEOS	Ethanol	Water	Acetic Acid	Ammonium Hydroxide	Urea	
SSD-8	20	4	1	0.83	33.9	44.6	0.25	-	-	8
SSD-RT	20	4	1	0.83	33.9	44.6	0.25	0.003	-	RT
SSD-30	20	4	1	0.83	33.9	44.6	0.25	0.102	-	30
SSD-50	20	4	1	0.83	33.9	44.6	0.25	0.190	-	50

were catalyzed with ammonium hydroxide, have high dimensional homogeneity. There is an increase in average particle size with an increasing catalyst amount. When amorphous structure formation, gelling behavior and particle sizes are evaluated together, the SKD-A2 samples show the best results (Fig. 8).

3.3.Effect of Temperature

In light of the results presented in the earlier sections, a new 4-sample set, which can be seen in Table 3 in detail, was prepared based on favorable properties of the SKD-A2 sample, in order to examine the effect of reaction temperature. Glass composition, solution composition, catalyst type and amount were maintained and the reaction was performed at four different temperature values.

The SSD-RT sample was run to compare the repeatability of previous works. The SSD-30 sample was run to ignore seasonal changes on ambient temperature and to maintain the temperature constant at a close value to room temperature. Finally, the reaction was performed at relatively high and low temperatures, and the samples were named SSD-50 and SSD-8, respectively.

Fluctuations were observed in relation to gelation times depending on reaction temperatures. The SSD-50 sample, which reacted at 50°C, generated a gel form within only 24 hours. The SSD-RT and SSD-30 samples formed gel after about five days, similar to previous studies. The SSD-8 sample was left for gelation in a refrigerator set at 8°C, and the gelation occurrence time was reached after two weeks (Fig 9).

The SSD-50 sample does not have an amorphous structure. This result is interpreted in relation to a rapid vaporization of ethanol and a correspondingly incomplete condensation reaction. The other samples are amorphous (Fig.10).

Although the SSD-RT and SSD-30 samples are close to each other, the SSD-30 sample standing at a constant temperature without seasonal temperature fluctuations shows better results. The SSD-8 sample shows amorphous structure according to the XRD results with the gelation lasting longer. Based on scanning electron microscope images, the SSD-50 sample does not show a regular particulate structure, whereas the SSD-8 sample shows a structure containing particles of around 45 nm. Although the SSD-8 sample has a particle structure similar to the SSD-30 sample, the SSD-30 sample is determined as having the optimum process of preparation because of the long process time at low temperature, required by the SSD-8 preparation.

Fig 9 - Gelation times of SSD-8, SSD-RT, SSD-30 and SSD-50 samples.

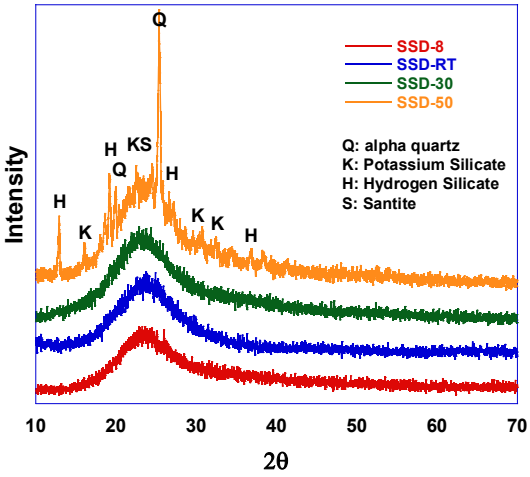

Fig 10- XRD of SSD-8, SSD-RT, SSD-30 and SSD-50 samples.

A comparative evaluation of the results presented above has established that according to the SEM images of the samples having different catalyst quantity and type, granular structure formation is achieved in the SKD-A1, SKD-A2 and SKD-A3 samples containing ammonium hydroxide hydroxide was added drop by drop to the solution at an amount of 0.102 moles for the TEOS/Boric

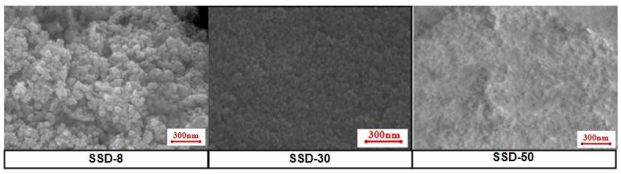

Fig 11 - SEM images of SSD-8, SSD-30 and SSD-50 samples.

as catalysts and the SKD-1 sample without any catalyst. There is no granular structure formation in the SKD-U1 and SKD-U2 samples. In the images of the SKD-U1 and SKD-U2 samples, a mixed structure with different phases is observed unlike the homogeneous grain structure of the other samples.

The samples which form the amorphous structure are especially evaluated in this study. The formation of granular structure is observed in the SKD-1 sample, which has no catalyst addition, but there is no uniform size distribution. In the SKD-A1, SKD-A2 and SKD-A3 samples, which were prepared in ammonium hydroxide catalysis, the dimensional homogeneity of the sphere-like particles is higher (Fig. 11). When amorphous structure formation, gelation, particle shape, particle size and distribution are evaluated together, the SKD-A1 and SKD-A2 samples yield the best results.

A number of changes in gelation times is observed depending on the reaction temperature. The SSD-50 sample gelled in 24 hours with a reaction at 50°C. The SSD-RT and SSD-30 samples showed gelation after five days. For the SSD-8 sample, which was left to gel in a refrigerator set at 8°C, gelling was observed after two weeks.

When the gelation times and XRD analyzes of these four samples prepared for the temperature experiments are examined, a rapid gelation is observed with the SSD-50 sample. The condensation reaction for the SSD-50 sample was not completed due to a rapid evaporation of the ethyl alcohol in the solution, and no amorphous structure was formed. Although the SSD-RT and SSD-30 samples have similar SEM and XRD results, the SSD-30 sample, which was maintained at a constant temperature without seasonal temperature fluctuations, is determined as the optimum sample due to its particle size and amorphous structure.

4.Conclusion

The aim of the study is to synthesize borosilicate glass powder having a particle size of approximately 50 nm by the sol-gel method to be used as a hierarchical surface agent in hydrophobic coatings. For this purpose, the sol-gel process is optimized by examining the effect of the solution, catalyst type/quantity and temperature parameters on the particle size of the resulting powder, respectively. The best results with a particle size of 40 nm were obtained in a water-ethanol mixture (molar ratio is 44.6: 33.9) with an initial pH of 4 (adjusted by the addition of acetic acid). Ammonium acid/Potassium hydroxide composition of 2,603 g/0,1545 g/0,035 g with the sol-gel reaction being carried out at 30°C.

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