SOL-GEL PREPARATION OF DICALCIUM SILICATE GLASSES

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ABSTRACT

In the past few decades, sol-gel technology was widely used in industrial and their applications are numerous and diverse. Meanwhile, dicalcium silicate is one of the major components in the Portland cement clinker which recently found that have great potential in new biomaterials to regenerate damaged bone. This paper mainly study on sol-gel synthesis of dicalcium silicate at lower temperature, than normal used. Glass powders of dicalcium silicate were prepared from TEOS and calcium nitrate tetrahydrate in present of HCl as catalyst and ethyl alcohol to speed up the polycondensation process. Acidic condition will favor the hydrolysis reaction instead of alkaline condition. Gel was sintering at different temperature in which 400°C, 600°C, 800°C and 1000°C. The combination of techniques involving TGA, FT-IR, and SEM has been used to recognize all the transformation occurring in the processing which involved hydrolysis and condensation polymerization and the formation of the final product. From the above analyze, result shown there are about 70% weights lost occur in elastic gel due to the elimination of unwanted compounds like water and organic residual such as nitrate. This outcome was indicated by the TGA thermal treatment curve in the temperature range from 20-700°C. Then, the FTIR spectra suggested that formation of the ordered Si tetrahedral in dicalcium silicate was started at temperature below 600°C. The glass powders that sintering at temperature 1000°C for 4 hours give a fine spherical crystallites in range of 1.2-1.9µm. As a conclusion, the route of sol-gel method is successfully applied in the preparation of dicalcium silicate glass.

ABSTRAK

PENYEDIAAN DICALCIUM SILICATE DENGAN SOL-GEL KAEDAH

Sejak beberapa dekad dahulu, teknologi sol-gel telah luas dipergunakan dalam industri dan keguanaannya adalah kepelbagaian. Pada masa yang sama, dicalcium silicate adalah salah satu sebatian utama dalam simen Portland yang mana didapat tahu mempunyai keupayan dalam biomaterial sabagai pemulihan tulang-tulang yang telah patah dan rosak. Dalam penyelidikan ini, tumpuan dilakukan atas sintesis dicalcium silicate dengan kaedah sol-gel dalam suhu yang lebih rendah daripada keadah tradisional. Serbukan kaca dicalcium silicate telah disediakan dengan TEOS dan calcium nitrate tetrahydrate dengan kehadiran HCl sebagai mangkin dan ethanol berfungsi mempercepatkan prosess polycondensation. Dalam keadaan acidic, prosess hydrolysis adalah lebih cepat berbanding dengan keadaan alkali. Seterusnya, gel dibakarkan dalam beberapa suhu berbeza yang mana itu adalah 400℃, 600℃, 800℃ dan 1000℃. Satu siri penggabungan ujian teknik melibatkan TGA, FT-IR dan SEM telah dijalankan untuk mengenali segal perubahan yang berlaku dalam prosess hydrolysis dan polycondensation dengan pembentukan sampel akhir. Daripada panganalisis tersebut, keputusan menunjukan bahawa sabanyak 70% kehilangan berat dalam gel disebabkan daripada penyingkiran air dan sisa baki organic seperti nitrat. Kejadian ini dapat ditunjuk dengan lengkungan TGA terma dalam suhu julat 20-700℃. Seterusnya, spectra FTIR menjelaskan bahawa pembentukan susunan ciri Si tetrahedral dalam dicalcium silicate berlaku pada suhu bawah 600℃. Serbukan kaca yang mana bakar dengan suhu 1000℃ dalam masa 4 jam akan memberikan hablur berbola yang sangat halus dalam julat 1.2-1.9μm. Sebagai kesimpulan, kaedah sol-gel dapat digunakan untuk membentuk dicalcium silicate dengan berjaya.

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LIST OF SYMBOL NAD ABBREVIATIONS

nm	Nanometre
T_m	Melting point
T_g	Glass-transition temperature
°C	Degree Celsius
Pa	Pascal (pressure)
E	Young Modulus
J	Joules
g	Standard gravity
K	Kelvin (temperature)
α	Alpa
β	Beta
γ	Gamma
Å	10^{-10}
cm^{-1}	wavelength
V	voltage
k	kilo
D	Average grain size of the spherical particle
S	Surface area
ρ	Density

CHAPTER 1

INTRODUCTION

1.1 Introduction

In the past few decades, the method of sol-gel was introduced use to produce highly purified glasses which mainly for industrial used. The differences of sol-gel glass making and the traditional conventional melting method is which the sol-gel process able to produce better quality glasses at low sintering temperature.

The better quality of glasses will be more in purity and in homogeneity. At the same time, fewer components of precursors are required and wider spectrum of the positions in order that good quality glasses may be achieved. Further more, after sintering, only light polishing is typically required to render the glass into final shape. This is because the initial gel can be cast into complex shapes of exacting geometry (Pope, 1994).

The general principles of the sol-gel process is that transition system of liquid(sol) in which will be converted into solid (gel). A sol is a colloidal of solid particles in a liquid whereas a gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase (Brinker, 1990).

The applications of the sol-gel process are very wide, which includes thin coating and fibers, and gradient index glass. One thing that should be remembered is that the application of sol-gel process not only able to produce good quality glass, but sol-gel process also has the potential for fabrication of large-scale, bulk optical component.

According to Woolfrey and Bartlett (1998), there are few main adventages in the sol-gel process includes:

1. Good mixing for multi-component systems
2. Good control of particle size, shape and properties
3. Allows mixing of components at the colloidal (nm) level to promote product formation and crystallization at low temperature, hence minimizing energy consumption
4. Since the sol-gel transition is reversible, materials can recycled and waste minimized.

Commonly, dicalcium silicate, Ca_2SiO_4 is the second important most abundant compound in the Portland cement. Besides that, belite (common name for dicalcium silicate) also important in refractories, heat-resistant coating and biomaterials. Bioactive ceramic in medicine have become one of the major fields in biomaterials (Gao *et al.*, 2005). The dicalcium silicate glasses from sol-gel process are belief to be useful for the regeneration of damaged bone. From the point above, dicalcium silicate has been studies and also applied into bioactive glasses.

1.2 Objective of study

1. To learn the sol-gel process and the properties and usage of the dicalcium silicate.
2. To prepare the dicalcium silicate glass by using the sol-gel technology.
3. To characterize the nature and properties dicalcium silicate by using the combination of techniques such as thermogravimetric analysis (TGA), Fourier transforms IR (FTIR), and Scanning electron microscope (SEM).

1.3 Scope of study

In this study, the dicalcium silicate glass is prepared from the sol-gel techniques. This will follow by characteristic using a set of combination analysis techniques on the products. The set of combination analysis techniques that are used;

thermogravimetric analysis (TGA) to record the sintering reaction of the xerogel, fourier transform IR (FTIR) to identify the final product, scanning electron microscope (SEM) for characterizing the morphology of the sintered glass powders.

CHAPTER 2

LITERATURE REVIEW

2.1 Sol-gel Technology

The goal of sol-gel technology is use low temperature chemical processes to produce net-shape, net-surface objects, films, fibres, particulates or composites that can be used commercially after a minimum of additional processing steps. The sol-gel processing can provide control of microstructure in the nanometer size range which 1-100nm which approaches the molecular level whiles traditional ceramic processing only produces materials have microstructures typically range of 1-100 micrometer diameter (Hench *et al*,. 1997).

2.1.1 History of Sol-gel Technology

For the first time in 1846, Ebelman who had synthesized ethyl ortosilicate observed that on standing at room temperature, it was slowly converted into a glassy gel due to slow process of hydrolysis. It was regarded as the first 'precursor' for glassy materials (Mehrotra, 1989).

As mentioned above, tetraethyl orthosilicate, TEOS undergoes hydrolysis under acidic conditions that yields silica, SiO_2 this was the early common examples of sol-gel method to produce new materials or inform of glass-like materials at low temperature. Fibers could be drawn from the viscous gel and even from the monolithic optical lenses or composites formed (Hench *et al.*, 1997).

The periods between late 1800s through 1920s, the literature regarding the sol-gel was much descriptive on the growth of crystals from gels which leads by the periodic precipitation phenomenon. But the understanding of the physical chemistry principles was limited. For early 1900s, sol-gel method started used to produce highly silica gels and the silica-supported catalysts. Wide range of oxides were also developed, such as Fe, Cr, Mn, Cu, Bi, Pb, Th, Ni, V, and also the mixed gels of silica with Fe, Cu, Ni, Sn, W, or Al oxides (Hench *et al.*, 1997).

Move on to early 1930s through 1950s, the sol-gel methods were applied to the commercial use. The sol-gel technology was first to used partially hydrolyzed alkoxysilane in impregnations of porous stone, concrete, brick and coating silica on interior light bulb and vacuum tubes. Then, the sol-gel industrial grew with use of sol-gel-derived catalysts. Precursors such as metal alkoxides with the used of catalysts where in order to help control the homogeneity of multiphase systems. The processing antireflection of thin film coating on TiO_2 in the used of automobile rear-view mirrors and sunshielding window were started. By the mid-1980s, there are around 50 different sol-gel made optical glasses in the market (Hench *et al.*, 1997).

From 1950s onward, the development of sol-gel method had achieved high level of chemical homogeneity and many type of ceramic oxide were synthesized (Hench *et al*,. 1997). These were a big different as compare with the traditional conventional melting method using high temperature needed but not able to produce high properties ceramic and limited to few type of ceramic oxide.

Early of 1980s was critical and a bright period for sol-gel technology in which development in many aspect to give better quality product and widen usage in sol-gel products. An important development in preparation of bulk sample where several millimeters monolithic pieces of optically transparent transition alumina by sol-gel methods.

2.1.2 Introduction and Basic Theory of Sol-gel

Until today, there are actually no standard definitions for "sol-gel". Usually, the term sol-gel is used for a solution process where initially formed a colloid then further that gel phase will be formed. According to Woolfrey and Bartlett (1998), the term had been used for any solution processes involving hydrolysis and formation of a gel, irrespective of whether an intermediate colloid is formed.

There are few term that regarding the sol-gel process and always emerge in most articles.

a. Sol

A sol is a colloidal of solid particles in a liquid and it have very small diameter to remain suspended in a liquid by Brownian motion.

b. Gel

A gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. Gels formed from the particulate sols when attractive dispersion forces cause them to stick and form a network (Brinker, 1990).

c. Colloid

A colloid is a suspension in which the dispersed phase is too small 1-1000nm in size. This will cause the gravitational forces are ignored and the interaction are take over by the Van der Waals attraction or surface charge (Brinker, 1990).

d. Aerogels

Aerogels is a colloid suspension of the particles which highly porous nanostructured materials might be transparent or translucent when in gas condition. It is produce under supercritical drying where the wet gel is has interface between liquid and vapor, therefore there is no capillary pressure and relatively little shrinkage.

e. Xerogels

Xerogels are produces while dried under normal condition give capillary pressures which bring result to the gel network. The volume will be smaller than the original wet gel by certain factors.

In the past few decades, the sol-gel process and its application has attracted much attention from many researchers try to develop more. There should be a reasonable foundation advantage of the sol-gel process compare with the traditional conventional melting method (Table 2.1). Beside that, the sol-gel method also consisted some disadvantages which delayed its application in the glass industry (Table 2.2).

Table 2.1 Advantages of sol-gel method compare with the conventional glass making (Friberg *et al*., 1993)

1.	Better homogeneity-from raw materials	
2.	Better quality-from raw materials	
3.	Lower temperature of preparation:	
	a)	Save energy
	b)	Minimize evaporative losses
	c)	Minimize air pollution
	d)	No reactions with container, thus purity
	e)	By-pass phase separation
	f)	By-pass crystallization
4.	New non-crystalline solid outside the range of normal glass formation	
5.	New crystalline phases from new non-crystalline solids	
6.	Better glass products from properties of gel	
7.	Special products such as films	

Table 2.2 Disadvantages of the sol-gel method (Friberg *et al*., 1993)

1.	High cost of raw materials
2.	Large shrinkage during processing
3.	Residual fine pores
4.	Residual hydroxyl
5.	Residual carbon
6.	Health hazards of organic solution
7.	Long processing

2.1.3 Basic Processing of Sol-gel

The general principle of the sol-gel process is that the transition system of a liquid (sol) will be converted into solid (gel). Heat is applied to the wet gel to strengthen the solid and become powder or the optical.

The sol-gel transition is not reversible. There are few common steps in processing of sol-gel silica glass making, based on mixing, casting, gelation, aging, drying, stabilization and densification.

In the first step, there is a mixing of precursors which involves $Si(OR)_4$ where the R can be CH_3, C_2H_5, water and alcohol in a range of ratio. The TEOS, $(OC_2H_5)_4$ would be often used by the researchers since the long chain will slower reaction rate. Sometime there is using of silica sol is replace the $Si(OR)_4$ as the Si source but without addition of the alcohol. In the mixing step, there are two chemical mechanism will occur to form the interconnection bond of the Si-O-Si. The two chemical mechanisms are hydrolysis and polycondensation.

a. Hydrolysis

In hydrolysis, water hydrolyzes the ethoxy group of TEOS, hence silanols is produced.

$$Si(OC_2H_5)_4 + 4H_2O \longrightarrow Si(OH)_4 + C_2H_5OH$$

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