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รายงานวิจัยฉบับสมบูรณ์

โครงการ

“การศึกษาวิธีการสังเคราะห์ และสมบัติของสไปโรซิลิเคท/เบนซอกซาซีนเรซิน”

โดย นางสุจิตรา วงศ์เกษมจิตต์

พฤศจิกายน 2545

Scan 52

สัญญาเลขที่ RSA/02/2543

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วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

Scan SL

กิตติกรรมประกาศ

ผู้วิจัยขอขอบพระคุณสำนักงานกองทุนสนับสนุนการวิจัย ที่ได้ให้การสนับสนุนโครงการวิจัยนี้ตลอดทั้งโครงการ

บทคัดย่อ

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ชื่อโครงการ : “การศึกษาวิธีการสังเคราะห์ และสมบัติของสไปโรซิลิเคท/เบนซอกซาซีนเรซิน”

ชื่อนักวิจัย : นางสุจิตรา วงศ์เกษมจิตต์
วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย

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ระยะเวลาโครงการ : 3 ปี

วัตถุประสงค์ของงานวิจัยนี้ คือ การศึกษาวิธีการสังเคราะห์ และสมบัติของสไปโรซิลิเคท/เบนซอกซาซีนเรซิน เพื่อหวังว่าจะนำไปใช้แทนฟีนอลิกเรซินที่กำลังจะขาดตลาด ซึ่งฟีนอลิกเรซินมีข้อเสียทางด้านการหดตัวของเรซินหลังจากผ่านกระบวนการให้ความร้อนสูง ดังนั้น งานวิจัยนี้จึงเริ่มจากการสังเคราะห์สารประกอบสไปโรซิลิเคท และอนุพันธ์ของสารประกอบสไปโรซิลิเคท หลังจากตรวจสอบโครงสร้างของสารประกอบสไปโรซิลิเคทที่สังเคราะห์ได้ ขั้นตอนต่อไป คือ การสังเคราะห์พอลิสไปโรซิลิเคทจากสารประกอบสไปโรซิลิเคท เพื่อศึกษาสมบัติการหดตัวของสารประกอบสไปโรซิลิเคท ซึ่งพบว่า สารประกอบสไปโรซิลิเคทเหล่านี้ มีสมบัติการหดตัวน้อยมาก ขณะที่สมบัติการหดตัวของสารประกอบเบนซอกซาซีนก็น้อยมากเช่นกัน โดยกลุ่มของ Ishida ได้ทำการศึกษาไว้แล้ว เพราะฉะนั้น เมื่อนำโคโมโนเมอร์ไปทำให้เป็นเรซิน สมบัติการหดตัวของเรซินน่าจะให้ผลออกมาดี ขั้นตอนที่สำคัญ คือ การสังเคราะห์โคโมโนเมอร์สไปโรซิลิเคท/เบนซอกซาซีน โดยใช้อนุพันธ์ของสารประกอบสไปโรซิลิเคทที่มีหมู่ฟังก์ชั่นอะมิโน ประโยชน์ของหมู่ฟังก์ชั่นอะมิโน เป็นการสังเคราะห์ส่วนของเบนซอกซาซีน โดยทำปฏิกิริยากับฟอร์มาล์ดีไฮด์ และฟีนอลผ่านกระบวนการทางเคมีที่เรียกว่า Mannich Reaction แต่ผลการทดลองในขั้นตอนนี้ ไม่สำเร็จดังที่หวังไว้ เนื่องจากการแตกของวงแหวนในส่วนของสไปโรซิลิเคท หรือส่วนของเบนซอกซาซีนก่อนที่จะได้โคโมโนเมอร์ออกมา

งานวิจัยอีกส่วนหนึ่งที่ได้กระทำ คือ การนำสารประกอบสไปโรซิลิเคทไปใช้ในการสังเคราะห์ซิลิกาให้มีพื้นที่ผิวสูง และจากผลการศึกษา พบว่า สารประกอบสไปโรซิลิเคทเหมาะที่จะนำไปเป็นสารตั้งต้นในการสังเคราะห์ซิลิกาให้มีพื้นที่ผิวสูงได้ โดยผ่านกระบวนการโซล-เจล

คำหลัก : การสังเคราะห์ สไปโรซิลิเคท การหดตัวใกล้ศูนย์ กระบวนการโซล-เจล เบนซอกซาซีน

Abstract

Project Code : RSA/02/2543

Project Title : "Study of Synthetic Method and Properties of Spirosilicate/Benzoxazine Resin"

Investigator : Ms. Sujitra Wongkasemjit
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Project Period : 3 Years

The objective of this research work is to study the synthetic method and properties of spirosilicate/benzoxazine resin to hopefully be able to replace the shortcoming phenolic resin having a disadvantage of shrinkage after curing. Therefore, this work was started with the synthesis of spirosilicate compounds followed by their structural identification. Next step is to synthesize polyspirosilicate to study its volumetric property. It was found that those synthesized spirosilicate compounds gave near-zero shrinkage values. With near-zero shrinkage benzoxazine studied by Ishida and coworker, spirosilicate/benzoxazine comonomer is expected to result in near-zero shrinkage after curing, as well. The important step of this research work is to synthesize the spirosilicate/benzoxazine comonomer using the corresponding spirosilicate derivative containing the amino group. The use of this amino group is for benzoxazine synthesis with formaldehyde and phenol via the Mannich Reaction. However, the result did not show the expected comonomer product. Instead, either spirosilicate or benzoxazine ring was broken before reaching the final comonomer product.

Another research work was done under this fund was to apply synthesized spirosilicates in the synthesis of high surface area silica, and the result was found to be very satisfying. High surface area silica was obtained via sol-gel process.

Key words : Synthesis, Spirosilicate, Near-Zero Shrinkage, Sol-gel process, Benzoxazine

Table Content

CHAPTER I

INTRODUCTION

Background

For most applications, thermosetting resins are used to construct plastic tooling. Processing of thermosetting resins has received strong attention from the automotive, aerospace and construction industries due to the great potential of these products. These materials offer the advantages of strength, rigidity, dimensional stability, and higher operating temperatures than thermoplastics. They are generally supplied as liquid two-component systems except for modeling blocks and prepregs. Plastic tools can be constructed from various chemical classes of plastics. The most common types for rigid tool constructions are epoxy and unsaturated polyester resins. Flexible tooling applications may utilize modified versions of epoxy, unsaturated polyester resins or use silicone or polyurethane elastomers. For higher temperature systems, bismaleimides and cyanate esters are currently being investigated for possible tooling applications. Although in many cases the plastic is used in conjunction with wood, plaster, or metal, the finished product is usually classed as a plastic tool.

Phenolic resins were among the first commercial materials used in plastic tooling. Introduced in the late 1930s, they have been largely replaced by other classes of thermosetting resins. Their disadvantages include brittleness, long cure cycles, and corrosive nature of the acidic curing agent. The dimensional stability of the tool is limited by the migration of by-product water produced by the cure. Phenolic resins are used today mainly as impregnating matrices for laminated paper and wood modeling blocks. After unsaturated polyester resins became available in the early 1940s, they were used in a variety of plastics tooling applications, such as, the construction of trimming, drilling, and checking fixtures. They are still use today in tool fabrication where broad tolerances are acceptable and low cost is important. The largest application for polyester tool is probably in the construction of molds for boats and similarly polyester shells. The high shrinkage of material during cure is not critical for these applications.

For the epoxy resins, they are the most versatile thermosetting tooling plastics. Since their introduction into plastic tooling in the late 1940s, these materials have become the mainstays of the industry. Advantages include low shrinkage, high flexural and compressive strength, good dimensional stability, and good chemical resistance. These properties make possible the accurate and stable reproduction of a model. Through the use of suitable fiber reinforcement, lightweight laminate tools with high mechanical characteristics can be readily produced. Most epoxy tooling materials also contain fillers. They control flow in the application, reduce shrinkage, improve wear resistance, modify strength properties, modify heat of reaction, control thermal conductivity and coefficient of thermal expansion, impart color, and reduce cost.

In the process, thermosetting resins undergo a volumetric shrinkage 3-15% during polymerization under even the best system. Upon curing, the most epoxy resins also undergo 2-7% volumetric shrinkage too. However, resins without shrinkage would be advantageous for such applications as precision castings, dental composites, rock cracking materials and high strength composites. The superior mechanical interlocking to a substrate that would be possible with zero shrinkage or expanding materials makes them ideally be suited for high performance adhesives, sealants, and coatings.

Spiroorthoesters and spiroorthocarbonates[1] were synthesized and polymerized via ring-opening reaction. The new materials have shown volumetric expansion property. It was hypothesized that the strained ring of the monomers opened would thus occupy a larger volume. Although some type of spiroortho compounds show 2.7% of volumetric expansion, these substances have been found few useful applications besides complicated synthesis routes and low glass transition temperature (T_g). As homopolymers, these expanding polymers seem to have quite limited utility for mechanically demanding structural materials. As an additive into epoxy resins, they reduce shrinkage and improve the mechanical properties, for example, curing a copolymer of bisnorbornenyl spiroorthocarbonate and an epoxy[2], the resulting composite had higher impact strength and higher shear strength than the epoxy-carbon fiber composites.

The recently interesting benzoxazine materials were synthesized from phenol derivatives, primary amines and paraformaldehyde. Polybenzoxazines, the novel phenolic resins, as compared to epoxy resins and conventional phenolics, have indicated the excellent glass transition temperature (T_g), and moduli, low water absorption values, in additional to zero shrinkage or a slightly expansion upon cure[3-6].

Similarly, new benzoxazines using aminospirosilicate derivatives as primary amines are expected to present zero shrinkage upon cure although aminospirosilicates have not yet investigated their shrinkage or expanding property. Then the aim of this research is therefore to investigate whether the aminospirosilicates and benzoxazines based on these aminospirosilicates show shrinkage or expanding property. The effects of curing conditions on the volumetric measurement of aminosilicates and benzoxazines are studied by varying curing time and temperature.

Spirosilicates

Even though silicon and carbon are in group IV, still the silicon chemistry falls far apart from the carbon chemistry. Silicon has an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^2$ similar to carbon in the form of tetrahedral compounds[7]. However, the availability of 3d orbital of silicon brings about some striking differences from carbon in terms of forming compounds through sp^3 hybridization. Furthermore silicon forms very few coordination complexes with organic molecules.

Organosilicon compounds are nowadays of great importance in such diverse fields as organic synthesis (chemistry reagents), ceramics, polymers, and glasses. Many more simple starting inorganics and organometallics, which are missing, must be developed by chemists in order to realize the potential of inorganic and organometallic polymer chemistry. Moreover, the Si-O bond in silica is one of the strongest bond in nature [128 kcal (535kJ)/mol]. The advantage of this bond is good thermal, oxidative stability, and chemical resistance, thus curing of Si-O bonds is interesting and important. Unfortunately, the primary problem with developing any large-scale industrial process is based on silica. Raw material of silica is plentiful and extremely low cost, accounts for about 25% of the earth's crust which is an ideal starting material for new route to silicon feedstock chemistry.

Friedel and Crafts (1863) were the first group who discovered the synthesis of tetraethylsilane from diethylzinc and silicon tetrachloride[8], as showed in equation (1.1).

$$SiCl_4 + CH_3CH_2ZnCH_2CH_3 + H_2O \longrightarrow Si(OCH_2CH_3)_4 \qquad (1.1)$$

Kitahara and Asano (1973)[9] showed that SiO_2 could be dissolved to a higher extent in anhydrous methanol than in water, with the solubility being at a minimum at around 80% CH_3OH to 20% H_2O. as showed in equation (1.2).

$$SiO_2 + 4CH_3OH \xrightarrow[\text{Under Pressure}]{200\ ^{\circ}C} Si(OCH_3)_4 + 2H_2O \qquad (1.2)$$

Holmquist and Iler[10] showed that the dissolution of silica in strong base could provide access to a wide variety of inorganic silicates, as illustrated in equations (1.3) and (1.4), respectively.

$$SiO_2 + 3Na_2SiO_3 \xrightarrow[\text{Closed System}]{700\text{-}900\ ^{\circ}C} 2Na_2SiO_4 + Na_2SiO_3 + S \qquad (1.3)$$

$$SiO_2 + x'MOH \xrightarrow{\text{Under Pressure}} M_2SiO_3 + M_4SiO_4 + H_2O + \text{Other} \qquad (1.4)$$

where M is alkali metal

Stark *et al.*, 1982, and Hardman and Torklson, 1987, showed the carbothermal reduction of SiO_2 to metallurgilic grade silicon[11-12], see equation (1.5), which was then converted into tetrachlorosilane ($SiCl_4$) by reacting with Cl_2, as illustrated in equation (1.6).

$$SiO_2 + 2C \xrightarrow{1200^{\circ} C} Si + 2CO \quad (1.5)$$

$$Si + 2Cl_2 \longrightarrow SiCl_4 \quad (1.6)$$

The other way is the reaction with alkyl (most typically CH_3Cl) or aryl chlorides in the presence of Cu/Sn as catalyst at 200°-350°C, as illustrated in equation (1.7).

$$Si + CH_3Cl \xrightarrow[Cu/Sn]{200\text{-}350\ ^{\circ}C} MeSMeSiCl_3 + Me_2SiCl_4O \quad (1.7)$$

Moreover, Si metal can react with a variety of acids, for example, HCl, to obtain related compounds, as illustrated in equation (1.8).

$$Si + HCl \longrightarrow H_2 + HSiCl_3 + SiCl_4 \quad (1.8)$$

Tetrachlorosilane is used as feedstock in the preparation of $Si(OEt)_4$. Whereas trichlorosilane is disproportionated according to reaction (1.9) to form silane, the primary soursce of electronic grade Si metal.

$$4HSiCl_3 \xrightarrow{amine} SiH_4 + 3SiCl_4 \quad (1.9)$$

The tetrachlorosilane was also employed by Grignard reaction to form organosilanes, as illustrated in equation (1.10).

$$SiCl_4 + 2RMgX \longrightarrow R_2SiCl_2 + 2MgClX \quad (1.10)$$

The reaction of tetrachlorosilane and a Grignard reagent is complicated and expensive. In 1949, Rochow and Muller independently discovered the "direct or Rochow process" of organic halides with silicon metal in the presence of Cu as catalyst[13]. The most common reaction product is dimethyldichlorosilane, which is an important precursor to produce polydimethylsilanes-silicon rubbers, as illustrated in equation (1.11).

$$RX + Si \xrightarrow{Cu} RSiX_3 + R_2SiX_2\ (Most) + R_3SiX + R_4Si + \ldots \quad (1.11)$$

Kenney and Goodwin[14-15] demonstrated the formation of tetraethoxysilane, Si $(OCH_2CH_3)_4$, from ordinary Portland cement and other mineral silicates followed by careful azeotropic distillation to remove water from the system, as illustrated in equation (1.12). Unfortunately, some re-hydrolysis occurs invariably and yields are relatively poor.

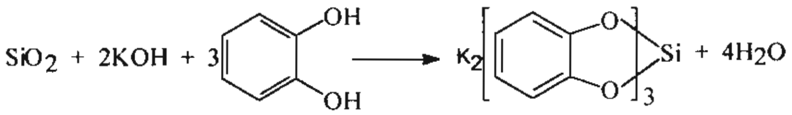
$$CaSiO_3 + 2HCl \xrightarrow[Axeotropic]{Toluene/EtOH} Si(OEt)_4 + CaCl_2 + 3H_2O \quad (1.12)$$

The direct reaction of alkoxy or aryloxy silanes[16-17] with the corresponding potassium alkoxides or aryl oxides afforded the anionic pentacoordinate hydridosilicate, which was used to react with alcohols with rapid evolution of hydrogen gas to form tetraalkoxysilane, as illustrated in equation (1.13).

$$HSi(OR)_3 + ROK \xrightarrow[DME]{THF} HSi(OEt)_4K \xrightarrow[-H_2]{ROH} Si(OR)_4 + EtOH \qquad (1.13)$$

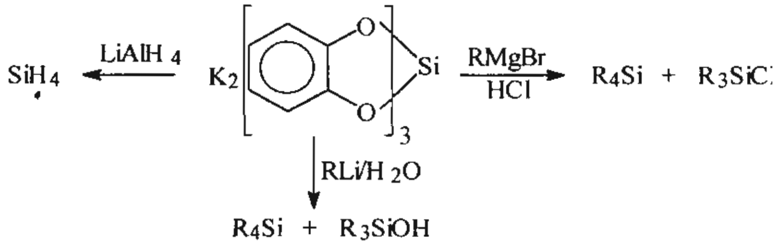
where R : Me, Et, Bu^n, Pr^i, and Ph.

Rosenheim and coworkers[18] were the first group to find that catechol could be used to transform a wide variety of metal oxide and silica into catecholato complexes, as illustrated in equation (1.14).



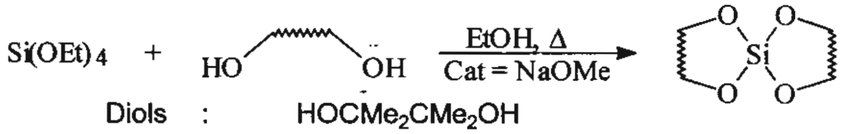
(1.14)

Corriu *et al.*[16-17] found new synthesis routes to silicon containing compounds from tricatecholato silicates by reacting with strong nucleophiles, such as aryl or alkyl Grignard or lithium reagents, as indicated in Scheme 1.1. Unfortunately, triscatecholato silicate is quite robust and reacts only under forcing condition with strong nucleophiles.



Scheme 1.1

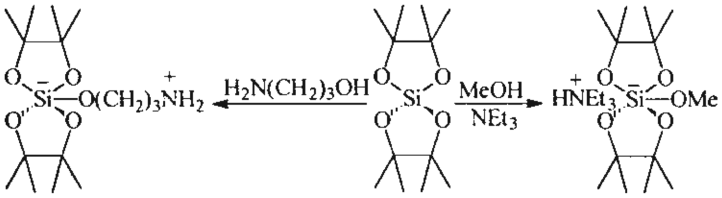
Frye[19-21] reported that the preparation of spirosiloxane from tetraethoxysilane, Si $(OEt)_4$, and 1,2-diols, was quite facile, if the reactions were run in ethanol with small amount of sodium methoxide, NaOMe, as catalyst. However, Frye found that with ethylene glycol, the product obtained was polymeric species, as showed in Scheme 1.2.



Diols : $HOCMe_2CMe_2OH$
$HOCH_2CEt_2CH_2OH$
$HOCMe_2CH_2CMe_2OH$
$HOCH_2CH_2OH$ (Polymerization)

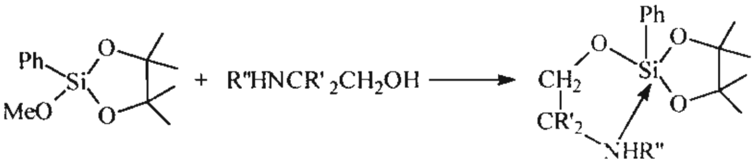
Scheme 1.2

He also discovered that in the presence of amine bases at ambient temperature, novel pentacoordinate species would be formed, Scheme 1.3. However, these species reverted to the tetra-coordinated spirosilicate, when the temperature was higher than 100°C. In this instance, even ethylene glycol gave a momomeric, penta-alkoxy silicate containing one monodentate and two bidentate glycol.



Scheme 1.3

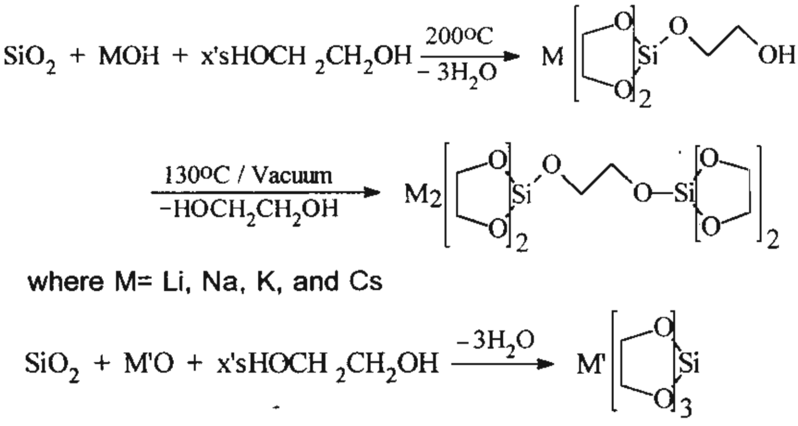
He also synthesized bispinacoloxy salts (pentacoordinated silicon derivatives) from heterocyclic pinacol derivative and alkanolamines. The result showed the partial bond between silicon and nitrogen atom, as illustrated in equation (1.15).



(1.15)

where: R' = H and CH_3, and R" = H and CH_3

Laine, *et al.*[22-25] synthesized penta-coordinated spirosilicates, at 200°C directly from silica and ethylene glycol using group I metal hydroxide or group II metal hydroxide as base, followed by drying under vacuum at 130°C, 0.1mmHg (Scheme 1.4).



where M'= Mg, Ca, and Ba

Scheme 1.4

The glycol groups were easily exchanged, unlike the triscatecho silicate. It permitted readily replacement of the glycol ligands with other diols. Thus, refluxing the potassium silicate in excess 1,2-prropanediol, pinacol (2,3-methylbutane-2,3-diol) or catechol (within equivalent of base) gave quantitative yields of new diol complexes. An interesting point was the fact that if 1,3 or larger "bite" diols (e.g. polyethylene glycol) were used in place of 1,2-dilos, then it was possible to prepare ionic polymers containing penta-alkoxy silicate centers. In this instance, it was necessary to distill out displaced glycol in order to force the reaction forward. Unfortunately, the procedures to synthesize these materials need strong bases, which are also expensive and low environmental stability.

Kingston and Sudheendra Rao[26] found that both tris(catecholato) silicate, $M_2[Si\ (o\text{-}C_6H_4O_2)_3]$ {M = Na, Et_3NH} and glycolato silicate, $K_2[Si(O_2C_2H_4)_5]$, react with PCl_3, $POCl_3$, $SOCl_2$, and SO_2Cl_2 at room temperature to give a variety of all purpose materials, such as polymers precursors and additives, surfactants, antiviral reagents, hydroxy alkylating agents, biological model compounds as well as reagents in organic synthesis.

Thus, the purposes of the first part, as described in Chapter II, were to synthesize and characterize glycolato spiro-silicate or bis(ethane-1,2-diyldioxy) silane, bis(3-aminopropane-1,2-diyldioxy)silane and bis(2-amino-2-methylpropane-1,3-diyldioxy)silane directly from silica (SiO_2) and ethylene glycol, silica and 3-amino-1,2-propanediol and 2-amino-2-methyl-1,3-propanediol, respectively, using triethylene- tetramine (TETA) as catalyst and solvent with/without alkali base as co-catalyst.

Shrinkage in Thermosetting resins

Generally, thermosets pass one through a soft plastic state and harden irreversibly, and the first observed irreverible reactions requried heat. Such plastics were called thersetting. Polyesters are classified as thermosettings for general purpose and specialty resins. They account for the bulk of applications. Specialty resins are groups into flame-resistant, light-stable, and weather- and chemical-resistant resins.

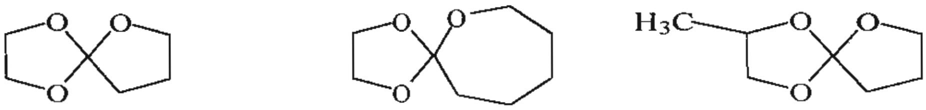
Like polyesters, epoxies are used for similar applications but are more expensive and manufacture is more complicated. Therefore, epoxies are used only if polyesters do not provide the desired properties.

The phenolic resins, which are developed in 1909, are the oldest thermosets plastics and have the wide range of uses. They are produced mainly from phenols and aldehydes. In the case of phenolic resins, volatiles, such as, water or small molecules, are released due to the condensation reaction. These volatiles sometimes reduce the properties of cured phenolic resins because of the formation of a microvoid leading to the shrinkage in the materials. Another problems are listed as followed

- brittleness of the materials
- use of strong acids as catalyst
- poor shelf life
- toxicity of raw materials (especially phenol)
- high viscosity of the precursors
- a narrow processibility window

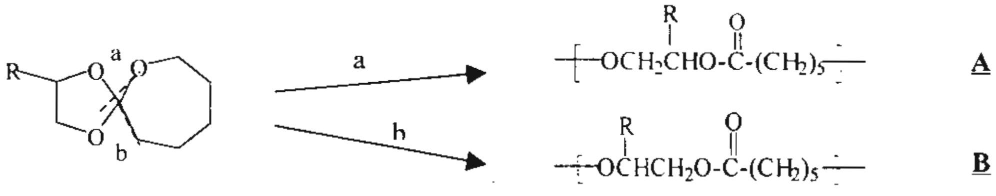
However, shrinkage in most thermosetting resins is quite high, 3-15 % and widely used epoxies undergo volumetric shrinkage of 2-7% upon curing. It causes residual stress, warping, premature debonding of the fiber from the matrix, fiber bulking, and delamination in fiber-reinforced composites. In dental industry, methyl methacrylate end-capped diglycidyl ether of bisphenol-A has been used as the matrix for dental filling, the shrinkage upon curing has been a major problem of this resin in this field. In molding industry, shrinkage is the most important problem because of nonunitormity in the dimension of the molded parts. For phenolic resins, they requires fillers, such as, cellulose flour, wood flour, and more commonly mineral fillers to reduce shrinkage[27], but these fillers can be abrasive to the mold surface. Various fillers are incorporated into the matrix and molding conditions are modified to reduce resins shrinkage but can not delete this problem, only reduce it.

Bailey and co-worker[1] (1977) introduced a series of spiroortho compounds which are spiroorthoesters and spiroorthocarbonates that expand upon curing. Spiroorthoesters as well as bicyclic orthoesters often undergo cationic polymerization involving double ring-opening.



Scheme 1.5

Because of the chemical transformation of compact bicyclic monomer to linear polymer, most of these monomers show little or no volume shrinkage on polymerization. Spiroorthoester containing a perfluoroalkyl group underwent double ring-opening polymerization to give a poly(ether-ester) consisting of two kinds of structural units, which are formed by ring-opening at the O(4)-C(5) bond (part a) and the O(1)-C(5) bond (part b), respectively[28], in Scheme 1.6. The former unit **A** dominated regardless of the polymerization temperature. Probably, the steric hindrance between the side chain of material and the propagating cation attacking the O(1) atom makes path b unfavourable.



R = $CF_3(CF_2)_7CH_2CH_2OCH_2$
R' = $PhO-CH_2$

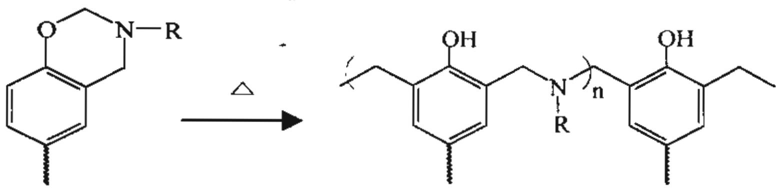
Scheme 1.6

Polymerization of spiroorthoesters which R is R′, perfluoroalkyl group accompanied a 2.7% volume expansion. This behavior is similar to that observed in the polymerization of nonfluorinated spiroorthoester (R = R′), 0.9% expansion. Thus, it appears that the perfluoroalkyl group does not give significant effect on the feature of zero shrinkage during the polymerization of spiroorthoesters.

Cationic polymerization of spiroorthocarbonates leading to a poly(ether-carbonate) alternating copolymer proceeds via the trialkoxycarbenium ion as a possible propagating species. Since this type of carbenium in was found to be quite possible, the growing chain end was expected to remain living after the completion of the polymerization[28].

Many reseacher groups have tried to introduce the spiroortho compound as an additive into epoxy resins to reduce shrinkage in the volume and improve the mechanical propertied. A copolymer of bisnorbornenyl spiroorthocarbonate and an epoxy were used by Lim and co-workers[2]. They found that the resulting composite had higher impact strength and higher shear strength than that of epoxy-carbon fiber composite. He and co-workers reported that 25% bisnorbornenyl spiroorthocarbonate content was found to be the suitable value for the mixture to expand upon cure. Unfortunately, spiroortho compounds by themselves found a few useful applications. Other disadvantages include complicated synthesis procedures and low glass transition temperatures (T_g); they have not thus been used as engineeing polymers.

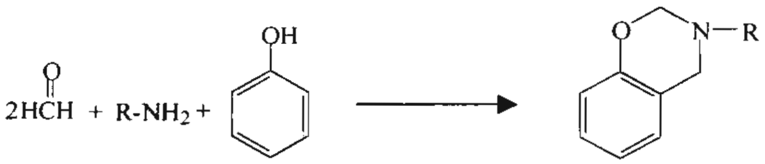
Benzoxazines, the novel phenolic resins which are the new materials that solve the problems related to traditional phenolic resins, were first synthesized by Holly and Cope[2] from aldehyde, phenol derivatives and primary amine that shown in scheme 1.7.



Scheme 1.7

Monofunctional heterocyclic compounds of benzoxazine resins were studied by Riess[29]. They found that only oligomeric phenolic structures could be obtained because the thermodissociation of the monomer was always competing with the chain propagation. Ning and Ishida[30-31] synthesized bifunctional benzoxazine precursors to overcome the low degree of cure of the compounds prepared by Riess (1986).

It is well known that the benzoxazine ring is heterocyclic structure consisting of a benzene ring fused with an oxazine ring, a six-membered ring that includes one oxygen and one nitrogen atom. This ring is stable at low temperature, but the ring-opening reaction occurs at high temperature, and novolac type oligomer having both the phenolic hydroxyl group and the tertiary amine group are produced, as shown in scheme 1.8.



Scheme 1.8

The properties of benzoxazines are typical for phenolic resins. They exhibit good heat resistance, flame retardance and have good dielectric properties in additional to excellent glass transition temperatures (T_g), moduli, low water absorption values and near zero shrinkage property[2] due to the consequence of molecular packing influenced by inter- and intramolecular hydrogen bonding. Some benzoxazines have been found to display interesting pharmaceutical properties including anti-inflammatory and central nervous system, depressing agents, an antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*[32].

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CHAPTER II

SYNTHESIS OF SPIROSILICATE AND SPIROSILICATE DERIVATIVES DIRECTLY FROM SILICA AND ETHYLENE GLYCOL/ ETHYLENE GLYCOL DERIVATIVES

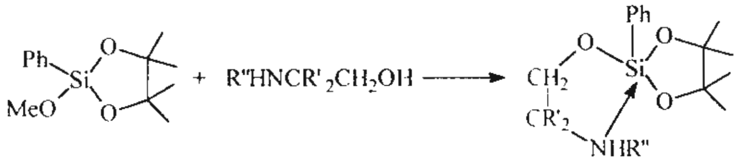
Abstract

Tetracoordinated spirosilicates have been synthesized directly from the reaction of a very inexpensive and plentiful material, SiO_2, and ethylene glycol in the presence of triethylenetetramine (TETA), as catalyst with and without potassium hydroxide as co-catalyst. The reactions are run under nitrogen gas with constant stirring at 200°C, and complete in a reaction time of 10-18 hr depending on the catalysts. The reactions using only TETA are complet in 18 hr, while with potassium hydroxide the reactions occur much more quickly. When 3-amino-1,2-propanediol, or 2-amino-2-methyl-1,3-propanediol is employed, the reaction must run under vacuum at 0.1mmHg, 160°C, and is complete in 14 and 24 hr, respectively. The structures of spirosilicates are fully characterized using FTIR, (^{1}H-, ^{13}C-, ^{29}Si-)NMR, FAB^{+}-MS, and TGA.

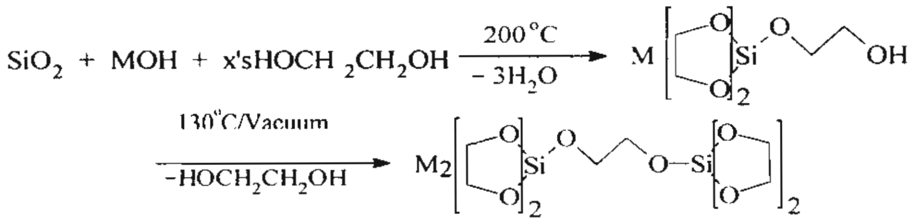
Introduction

Generally, thermosetting resins undergo a volumetric shrinkage (3-15%) during polymerization even using the best system.[1-3] However, resins without shrinkage would be advantageous for such applications as precision castings, dental composites, rock cracking materials, and high strength composites. The superior mechanical interlocking to a substrate that would be possible with zero shrinkage or expanding materials makes them ideally suited for higher performance adhesives, sealants and coatings.[4-7] Most of the spiroorthocarbonate and spiroorthoester monomers show little or no volume shrinkage or expansion in volume upon polymerization. However, they do provide a few useful applications with low glass transition temperature. Moreover, spiroorthocarbonates and spiroorthoesters can only be synthesized from complicated routes.[8-13]

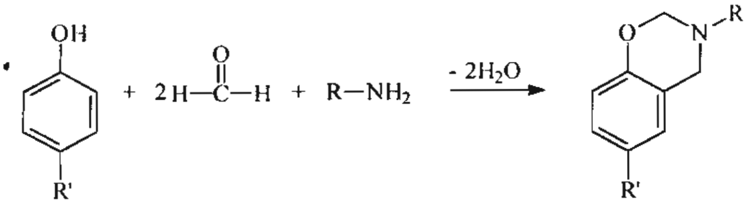
Frye reported the preparation of spirosiloxane from $Si(OEt)_4$ and ethylene glycol in ethanol with a small amount of NaOMe. The product obtained was polymeric species and in the presence of amine bases, novel pentacoordinated species would be formed.[14-16]



Laine *et al.* synthesized pentacoordinated and hexacoordinated spiro-silicates directly from silica and ethylene glycol in the presence of group I metal hydroxides and II metal oxides.[17-18] These strong bases are expensive and have low environmental stability.



Ishida, H. *et al.* synthesized benzoxazine monomers from phenol derivatives, paraformaldehyde, and primary amine derivatives.[19] Benzoxazines have good heat resistant, flame-retardant, and dielectric properties and reduce environmental and health risks. Polybenzoxazines, the ring-opening polymerization phenolic resins, as compared to epoxy resins and conventional phenolics, have indicated excellent glass transition temperatures (T_g), and moduli, low water absorption values, in addition to near-zero shrinkage or slight expansion upon curing.[20-21]



Despite the position of silicon directly below carbon in-group IV, the properties of the two elements are entirely different, for example, Si-O bonds are 22 kCal/mol more stable than C-O bonds. As a result, polymers having recurring Si-O linkages are of interest and importance, because they offer good thermal, oxidative stability, and chemical resistance.[22] We report herein an extension of silicon chemistry by the synthesis of neutral alkoxysilanes, tetracoordinated spirosilicates. In particular, we focus on synthesis starting from an inexpensive and abundant material, silica, and ethylene glycol or 3-amino-1,2-propanediol or 2-amino-2-methyl-1,3-propanediol. Ethylene glycol is of particular interest because it is the prototypical 1,2-diol and the expected product has the same structure as spiroorthocarbonate and spiroorthoester, which give little shrinkage in volume on polymerization. We thus investigated how to synthesize these spirosilicates. 3-Amino-1,2-

propanediol or 2-amino-2-methyl-1,3-propane diol are principally interesting as raw materials for the development of benzoxazine resins containing silicon species.

Experimental

Materials

All reactions were equilibrium reactions and products were sensitive to either moisture or air. Thus, all glassware used for these experiments was dried in an oven at 100 °C overnight. All reactions were carried out in an inert atmosphere (Nitrogen gas).

Fused silicon dioxide (HI-SIL 927 silica, SiO_2 with surface area of 182 m^2/g) was donated by PPG Siam Silica Co., Ltd. Fumed silica, 3-amino-1,2-propanediol and 2-amino-2-methyl-1,3-propanediol were purchased from Aldrich Chemical Co., Inc. (USA), used without purification and kept under nitrogen atmosphere. Triethylenetetramine (TETA) was also purchased from Facai Polytech. Co., Ltd. and was used as received. Sodium hydroxide and potassium hydroxide were purchased from Merck Company Co., Ltd., and used as received. Ethylene glycol, acetonitrile and isooctane were purchased from Lab-Scan Company Co., Ltd., purified by standard methods under nitrogen atmosphere and kept in sealed flasks. Methanol was purchased from J.T. Baker Company Co., Ltd., and purified by distillation over magnesium activated with iodine.

Instruments

Mass spectra (MS) were obtained using a VG Autospec model 7070E from Fison Instruments with VG data system. Samples were run in the positive fast atomic bombardment ($FAB-MS^+$) mode using glycerol as the matrix, cesium gun as initiator and cesium iodine (CsI) as a reference. Thermograms were obtained using thermogravimetric analysis (TGA) mode on a Du Pont model TGA 2950 with a ramp rate of 10 °C/min from 25° to 750 °C in N_2 atmosphere. FTIR spectra were recorded using a FRA 106/s Bruker instrument with a spectral resolution of 4 cm^{-1}. The samples were mixed with KBr at an approximate ratio of sample:KBr of 1:20. ^1H- and ^{13}C-NMR spectra were recorded on a Bruker 200 MHz spectrometer at room temperature using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and reference for chemical shift measurements. ^{29}Si-NMR spectra were obtained using a Bruker 500 MHz spectrometer, DMSO-d_6 as solvent and tetramethylsilane (TMS) as reference for chemical shift measurements.

Syntheses

Preparation of bis(ethane-1,2-diyldioxy)silane

A mixture of 12.5 mmol silica (SiO_2), (0.75 g, surface area of 320 cm^2/g or 182 cm^2/g), 15 mL of ethylene glycol (EG), and 15.63 mmol TETA (2.29 g) with/without potassium hydroxide (KOH) at 10 mole percent equivalent to silica, was placed in a 50 mL two-neck round bottomed flask. The mixture was heated to the boiling point of ethylene glycol under nitrogen with constant magnetic stirring, to distill ethylene glycol and water formed as by-product. The reaction was complete, when it turned clear. The mixture was allowed to cool overnight. The product was filtered, washed with a 5% of dried methanol in acetonitrile, and dried overnight at room temperature under vacuum, 0.1 mmHg.

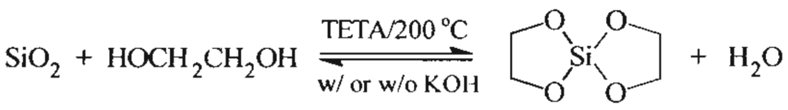
Preparation of bis(3-aminopropane-1,2-diyldioxy)silane and bis(2-amino-2-methyl propane-1,3-diyldioxy)silane

A mixture of 5 mmol fumed silica, (0.3 g, surface area of 320 cm^2/g), 7 mL TETA, and 30 mmol 3-animo-1,2-propanediol (2.73 g) or 30 mmol 2-amino-2-methyl-1,3-propanediol (3.1 g) with/without potassium hydroxide (10 mol% equivalent to silica), was placed in a 50 mL two-neck round bottomed flask. The mixture was heated under vacuum at 0.1mm/Hg, 160 ^{o}C with constant stirring, to distill TETA, 3-amino-1,2-propanediol or 2-amino-2-methyl-1,3-propanediol, and water formed as by product. The product was precipitated and purified, as described above.

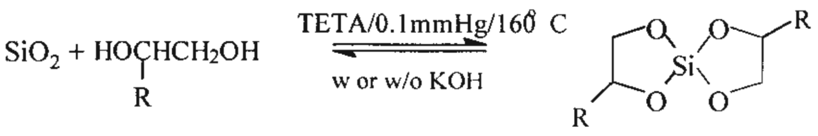
Results and Discussion

Synthesis

As discovered by Piboonchaisit's et. al [23] that triethylenetetramine (TETA) could be used as an accelerator to dissolve silica, all spirosilicates are thus prepared directly from silica and ethylene glycol, 3-amino-1,2-propanediol, or 2-amino-2-methyl-1,3-propanediol, using TETA as catalyst, in the absence or presence of KOH as co-catalyst according to the following reactions;

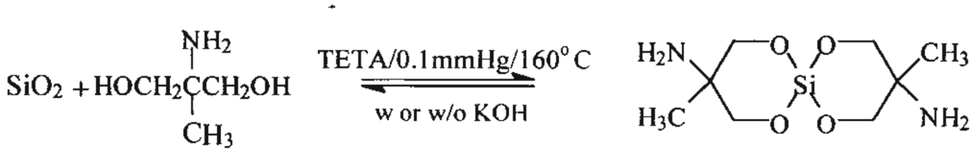


Bis(ethane-1,2-diyldioxy)silane



where R = -CH_2NH_2

Bis(3-aminopropane-1,2-diyldioxy)silane



Bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

Bis(ethane-1,2-diyldioxy)silane is prepared from either fused or fumed silica with > 80% overall yield at the boiling point of ethylene glycol in order to remove water and drive equilibrium to products. However, for fused silica, the reaction in the presence of TETA as catalyst and absence of KOH as co-catalyst takes 18 h, which is much longer than that for fumed silica, 6 h, to complete. In this case, fumed silica with a surface area of 280 m^2/g is more reactive than fused silica with a surface area of 182 m^2/g. It is likely that the higher the surface area of silica, the higher the reactivity. When the co-catalyst KOH is present, the reaction employing fumed silica is complete in 4 h while that using fused silica is finished in 10 h. The reason is that the strong base of KOH deprotonates ethylene glycol much faster than the catalyst TETA. If only KOH was used in place of TETA, according to Laine et al's work,[17-18] pentacoordinated spirosilicates were resulted.

As for the aminospirosilicate products of bis(3-aminopropane-1,2-diyldioxy)silane and bis(2-amino-2-methylpropane-1,3-diyl dioxy)silane, the reactions need to be carried out under vacuum at high temperature owing to the high boiling points of starting materials, 3-amino-1,2-propanediol (264 °C/739 mmHg) and 2-amino-2-methyl-1,3-propanediol (151 °C/10mm Hg). TETA, which has the boiling point 266 °C/760 mm Hg close to the boiling points of those aminodiols, is thus used as both solvent and catalyst. To obtain the highest yields of the products, the reactions must distill off the by-product H_2O along with the solvent TETA. As a result, the starting materials, aminodiols, were also distilled off while the reaction was running. This is why a high amount of both aminodiols must be employed to achieve the highest percentage yields of the products. Both products are synthesized directly from fumed silica with > 70% and > 80% overall yields, respectively. The first product was obtained in 10 and 14 h with and without KOH, respectively. On the other hand, the second product takes a longer time of 14 h with KOH and 24 h without the catalyst. This is due to the higher boiling point of the second aminodiol, 2-amino-2-methyl-1,3-propanediol, requiring longer reaction time to complete the reaction.

Characterization

The structures of spirosilicate products were identified by FTIR, ^{1}H-, ^{13}C-, and ^{29}Si-NMR, TGA, and FAB^+- MS.

The FTIR spectra of all spirosilicates show similar bands at 3386 cm^{-1} due to the combined hydrogen bonded N-H stretching modes and the intermolecularly hydrogen bonded O-H stretching modes,[24] 2949-2882 cm^{-1} corresponding to the C-H group, 1085, 966, and 883 cm^{-1} belonging to the Si-O-C stretching. The results are summarized in (Table 2.1).

Table 2.1. FTIR assignments of bis(ethane-1,2-diyldioxy)silane, 1, bis(3-aminopropane-1,2-diyldioxy)silane, 2, and bis(2-amino-2-methylpropane-1,3-diyldioxy)silane, 3

Products	Wave number (cm^{-1})	Assignment
1	3386, broad	-OH: water absorbed by the product
	2949-2882	C-H stretching
	1085, 966 and 883	Si-O-C stretching
2	3397, broad	-OH: water absorbed by the product; $-NH_2$
	2955-2889	C-H stretching
	1090, 966 and 872	Si-O-CH stretching
3	3406, broad	-OH: water absorbed by the product; $-NH_2$
	2953-2868	C-H stretching
	1082, 962 and 883	Si-O-CH stretching

The ^{1}H-NMR spectra, as illustrated in Fig. 2.1, show resonances that belong to the corresponding products. They all show the H_2O contained in deuterated DMSO and absorbed by the product at δ = 3.27 ppm, in agreement with the FTIR results. For bis (ethane-1,2-diyldioxy)silane, there appears to be a singlet at δ = 3.38 ppm, resulting from the four hydrogen atoms (4H) of CH_2-O-Si. For bis(3-aminopropane-1,2-diyldioxy)silane, the ^{1}H-NMR spectrum shows a singlet at δ = 2.05 ppm corresponding to the 4H of $-NH_2$, multiplet at δ = 2.45 ppm belonging to the 4H of CH_2-N, doublet at δ = 3.29 ppm referring to the 4H of CH_2-O-Si. The 2H of CH-O-Si is unfortunately overlapped with the H_2O peak. This, however, can be confirmed by ^{13}C-NMR data. The ^{1}H-NMR spectrum of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane shows clearer chemical shifts at δ = 0.83 ppm belonging to $-CH_3$ and δ = 3.13 ppm corresponding to CH_2-O-Si.

Besides the deuterated DMSO peak, the ^{13}C-NMR spectra, as shown in Fig. 2.2, show only one resonance at δ = 62.7 ppm (CH_2-O-Si) for bis(ethane-1,2-diyldioxy)silane; chemical shift for bis(3-aminopropane-1,2-diyldioxy)silane at δ = 44.9 ppm (CH_2-N), δ = 64.0 ppm (CH_2-O-Si) and δ = 72.7 ppm (CH-O-Si); and also 3 resonances for bis(2-amino-2-methylpropane-1,3-diyldioxy)silane at δ = 22.0 ppm ($-CH_3$), δ = 53.5 ppm (C) and δ = 67.1 ppm (CH_2-O-Si).

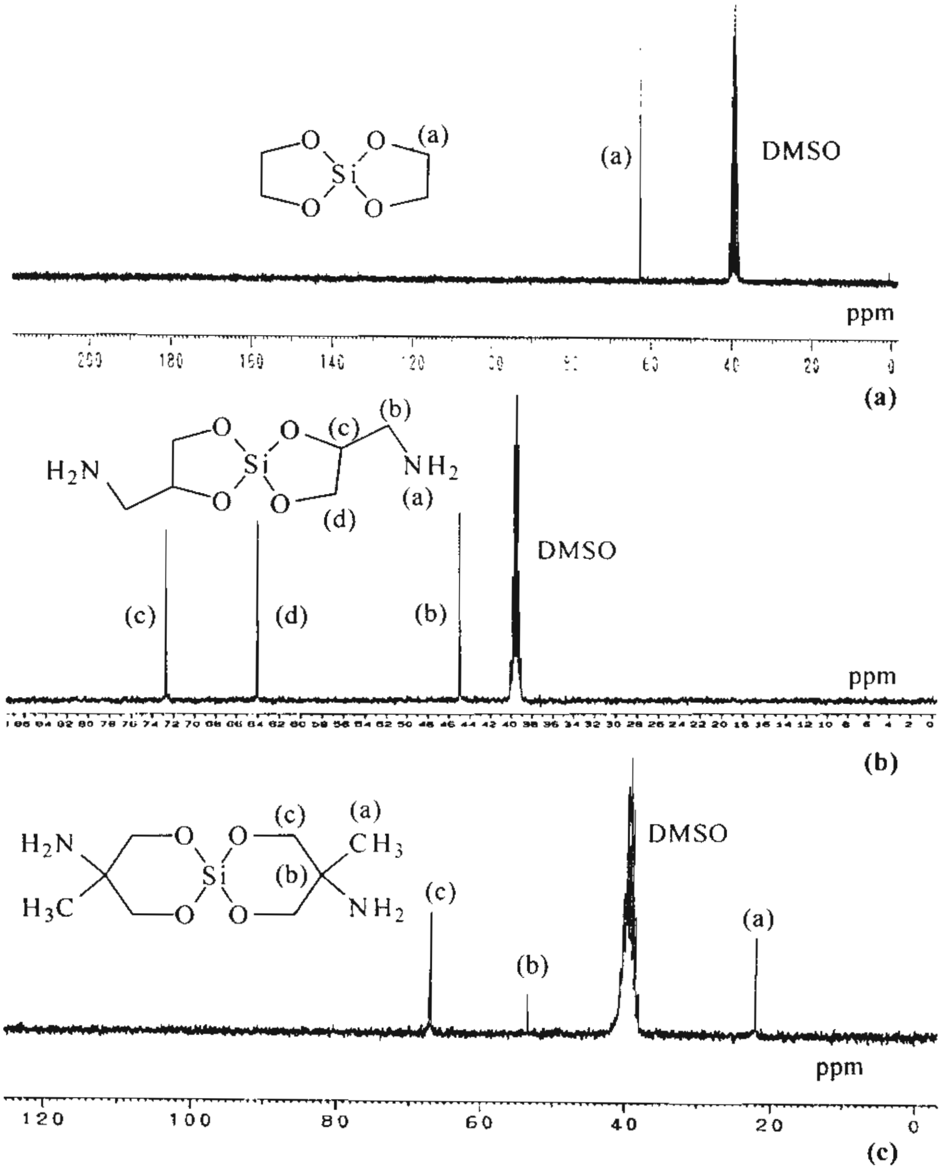


Figure 2.1 ^{1}H-NMR Spectra of a) bis(ethane-1,2-diyldioxy)silane, b). bis(3-aminopropane-1,2-diyldioxy)silane, and c) bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

The results of ^{29}Si-NMR spectra (Fig. 2.3) support that we have obtained tetracoordinated spirosilicate products, although the first two products showed the resonances at δ = -104 and -103 ppm, respectively, which are assigned to pentacoordinated species,[17, 25] The reason is simply that the ^{29}Si-NMR spectra were carried out using the reaction solution containing TETA. Therefore, there is a partial bonding between the product and TETA. Intermolecular bonding between the second product, which contains amino groups is also possible to form pentacoordinated species, as described previously by Frye.[15] The ^{29}Si-NMR spectrum of the last product indicates tetracoordinated species at δ = -77 ppm. In this case, there is no partial bonding between this product with TETA or the product with itself due to the steric hindrance of the structure.

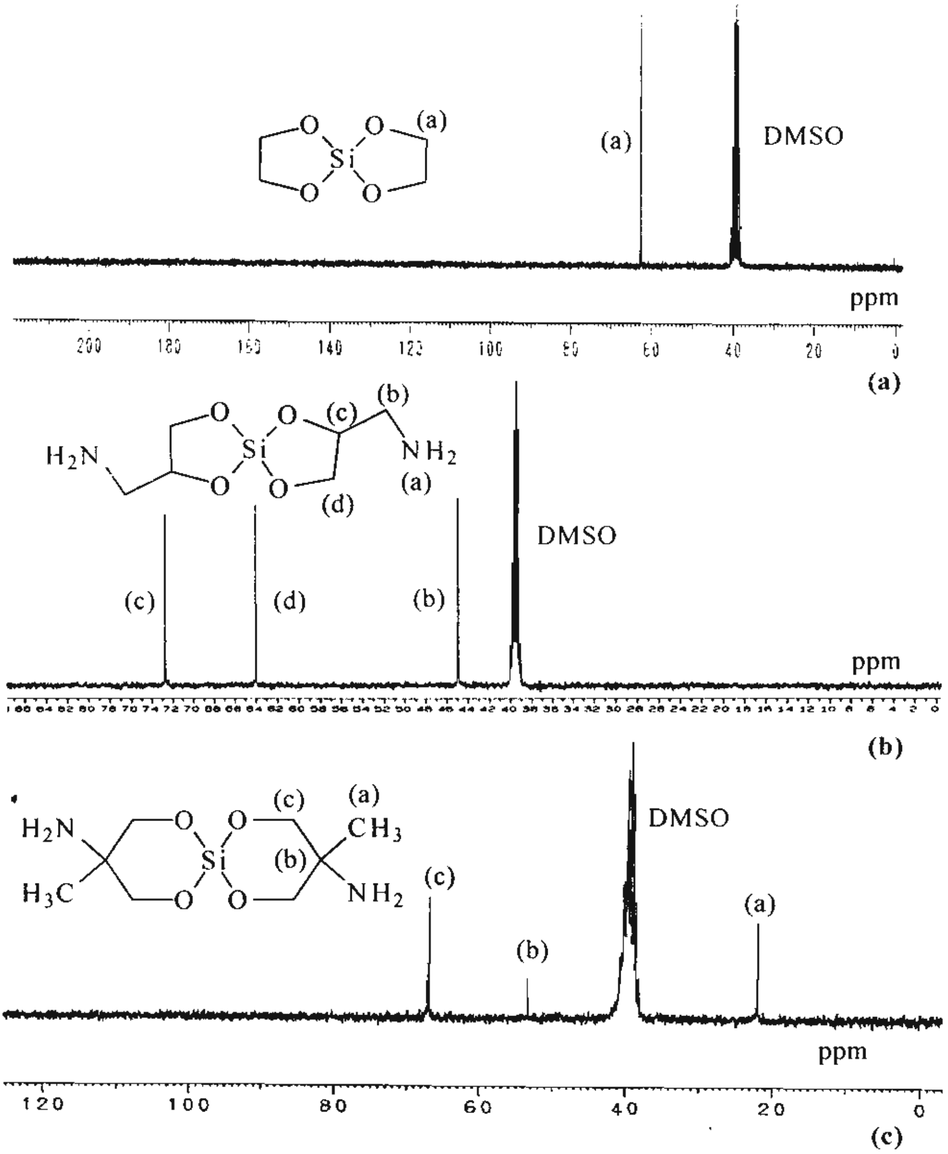


Figure 2.2 ^{13}C-NMR Spectra of a) bis(ethane-1,2-diyldioxy)silane, b) bis(3-amino propane-1,2-diyldioxy)silane, and c) bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

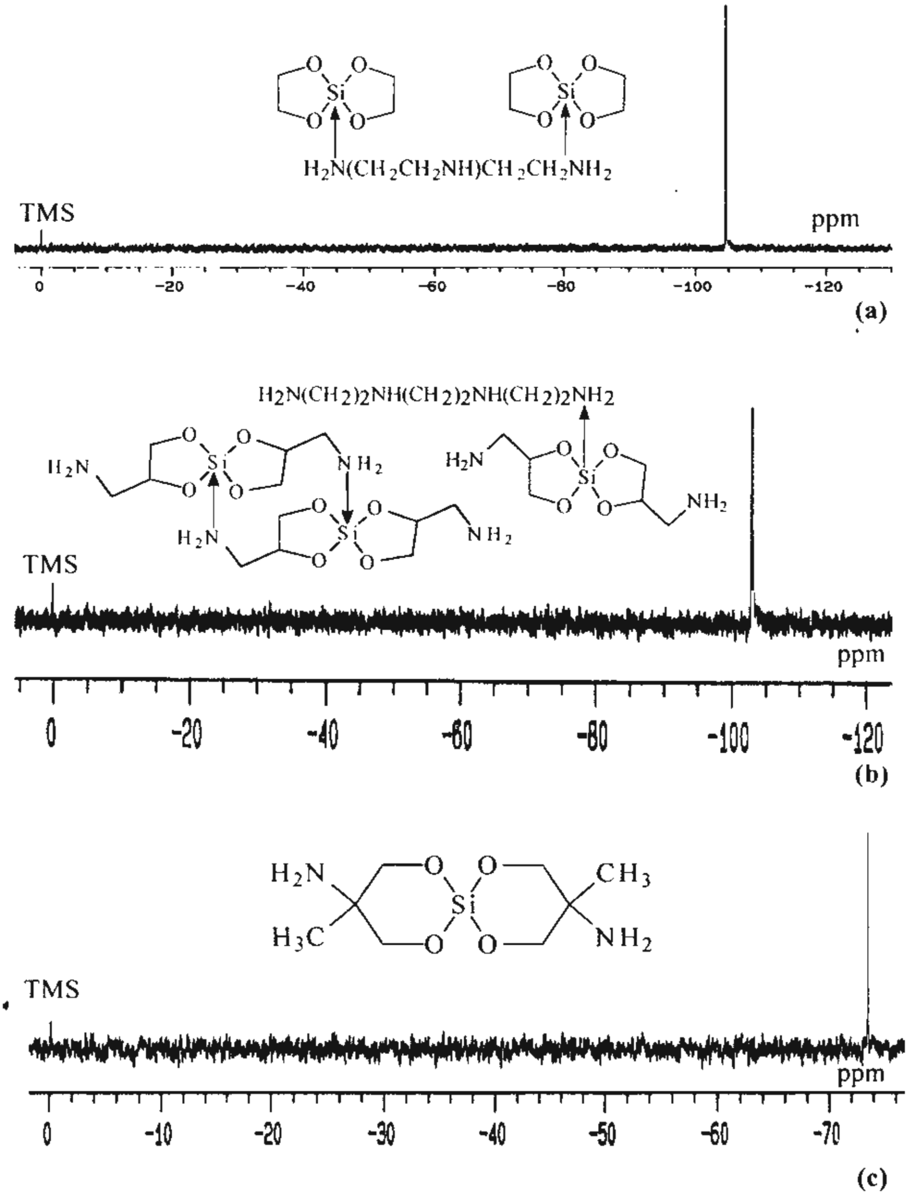


Figure 2.3 ^{29}Si-NMR Spectra of a) bis(ethane-1,2-diyldioxy)silane, b) bis(3-aminopropane-1,2-diyldioxy)silane, and c) bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

FAB^{+}-MS results are shown in Tables 2.2, 2.3 and 2.4 for bis(ethane-1,2-diyldioxy) silane, bis(3-aminopropane-1,2-diyldioxy)silane and bis(2-amino-2-methylpropane-1,3-diyldioxy)silane, respectively. The proposed structures according to their fragmentation also indicated the desired products.

Table 2.2 The proposed structure and fragmentation of bis(ethane-1,2-diyldioxy) Silane

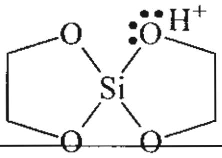
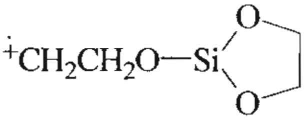
m/e	Intensities	Proposed Structure
149	7.00	
132	31.57	
72	9.11	$\dot{+}CH_2CH_2O{-}Si$
58	100	$\dot{+}CH_2O{-}Si$
44	80.94	$\dot{+}O{-}Si$

Table 2.3 The proposed structure and fragmentation of bis(3-aminopropane-1,2-diyldioxy)silane

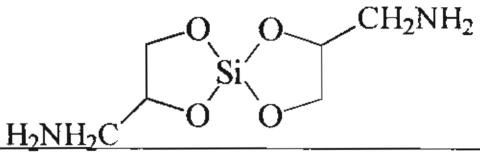
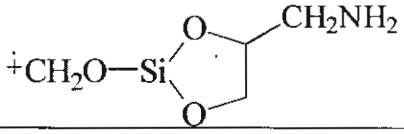
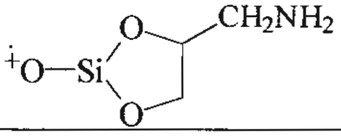
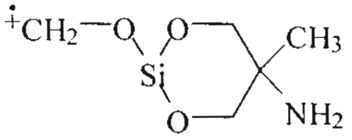
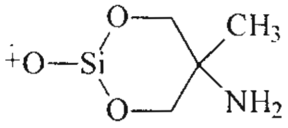
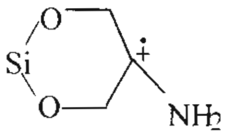
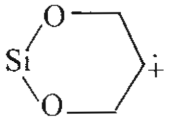
m/e	Intensities	Proposed Structure
206	0.77	
147	17.62	
133	100	
58	4.94	$\dot{+}CH_2O{-}Si$
44	42.28	$\dot{+}O{-}Si$

Table 2.4 The proposed structure and fragmentation of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

m/e	Intensities	Proposed Structure
161	0.8	
147	1.2	
116	13	
100	28	
74	46	$\dot{+}CH_2O-Si-O$
58	54	$\dot{+}CH_2O-Si$
44	100	$\dot{+}O-Si$

The other results, which support that the synthesized spirosilicates are truly the tetracoordinated not pentacoordinated species, were obtained by TGA (Table 2.5). They gave ceramic yields in close agreement with the calculated values based on the tetracoordinated species.

Table 2.5 % Ceramic yields of bis(ethane-1,2-diyldioxy)silane, **1**, bis(3-aminopropane-1,2-diyldioxy)silane, **2**, and bis(2-amino-2-methylpropane-1,3-diyldioxy)silane, **3**

Product	% Ceramic yield	
	Calculation	Experiment
1	40.5	40.8
2	29.1	30.4
3	25.4	26.9

Conclusions

Spirosilicates have been successfully synthesized directly via an one step process from very inexpensive materials, silica and ethylene glycol/its derivatives in the presence of triethylenetetramine, as catalyst/solvent with/without potassium hydroxide, as co-catalyst. The reactions are much faster when the co-catalyst and silica with a higher surface area are employed.

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CHAPTER III

SOL-GEL PROCESSING OF SPIROSILICATES

Abstract

The sol-gel transition of tetra-coordinated spirosilicate via hydrolysis and condensation under acidic and basic conditions is examined to elucidate the effect of catalyst, reaction time and temperature on the properties of obtained gel. The main advantage of this process is the low temperature employed, producing a solid network with a high specific surface area. FTIR spectroscopy and TGA analysis were used to characterize the formation of siloxane bonds (Si-O-Si). It is found that spirosilicate can be hydrolyzed under both acid and base catalyzed conditions. The condensation rate to silicates is shown to be at a minimum in 0.001M HCl, which is the iso-electric point of silica. The prepared xerogel has a low-density and is an amorphous material with a specific surface area of 596 m^2/g. Besides the catalyst media, the type of precursor also has a strong influence on the gel formation. An aminospirosilicate, six-membered ring, containing methyl and amino groups as substituents, was chosen for this study. The resulting xerogel is determined by the fact that to obtain the Si-O-Si bonds, a higher concentration of solvent and higher temperature are more favorable, due to the length and branching of alkyl portion.

Introduction

The limited number of simple silicon containing starting materials restricts the potential role of inorganic and organometallic silicon compounds in the development of new polymeric glasses and ceramics. The main reason is that silicon-containing chemicals are almost exclusively prepared from element silicon, obtained from the carbothermal reduction of silica around 1200 °C, which is energy-intensive[1]. Organosilicate compounds are of interest for their potential as precursors in sol-gel processing to form complex preceramic shapes and structures, not readily accessible by melt processing [2-3].

Sol-gel chemistry of silicon alkoxides is rather simple, compared to that of complexes of transition metal alkoxides in which metal atoms may exhibit several coordination states[4]. Molecular precursors of silicon alkoxides are always monomeric tetrahedral species $Si(OR)_4$. One of the usual starting materials for silica glasses is tetraethylorthosilicate (TEOS) [5-6]. The size and shape of the primary sol particles and the rate of its gelation can be controlled by varying pH[7-8]. Amount of water introduced into the reaction affects the hydrolysis rate and completeness as well as the porosity of the silica to be obtained[9-12].

Other alkoxide precursors can also be used to impart different properties to the gels[13-15]. Recently, Wongkasemjit et.al have synthesized many types of metal alkoxides using an inexpensive and simple method, referred to the "OOPS" process[16-18]. The advantages of these species are hydrolytically stable, low cost, easy processability and environmental friendliness[19]. Wongkasemjit et.al also studied the sol-gel processing of synthesized silatranes, and found that pyrolyzed ceramic products showed homogeneous microporous structure with high surface areas, 313-417 m^2/g[19].

The purpose of this work is to study the sol-gel processing of spirosilicates under conditions of varying solvent content, acid versus base conditions, aging time and temperature and to investigate whether the resultant xerogels of spirosilicate and aminospirosilicate[18] exhibit different product properties.

Experimental

Materials

Fused silicon dioxide or HI-SIL 927 silica (SiO_2), with a surface area of 168 m^2/g, by BET, was donated by PPG Siam Silica Co., Ltd., and dried in oven at 100°C for 10 h. 2-amino-2-methyl-1,3-propanediol ($HOCH_2C(CH_3)(NH_2)CH_2OH$) was purchased from Aldrich Chemical Company, used without purification and kept under nitrogen atmosphere. Ethylene glycol (EG, $HOCH_2CH_2OH$), purchased from Labscan, was used as reaction solvent. Triethylenetetramine [TETA, $H_2N(CH_2CH_2NH)_3$] was purchased from Facai Polytech Co., Ltd., and used as a catalytic base. Potassium hydroxide (KOH) was purchased from Baker Analyzed Reagent, and used as co-catalyst. Methanol (CH_3OH) and acetonitrile (CH_3CN) were purchased from Baker Analyzed Reagent and Lab-scan Analytical Science, respectively. Each was distilled using standard method to use as precipitating agents. UHP grade nitrogen gas with 99.99% purity was purchased from Thai Industrial Gases Public Company Limited (TIG). Hydrochloric acid (HCl) and ammonium hydroxide (NH_4OH) solutions were purchased from Aldrich Chemical Company. They were diluted with deionized water at various concentrations to use as electrolytes.

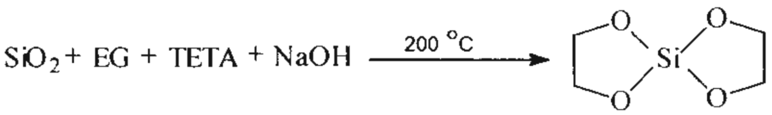
Instrumental

FTIR spectra were obtained on a Vector 3.0 Bruker Spectrometer with 32 scans at a resolution of 4 cm^{-1}. The powder samples were pressed to form pellets by mixing with pure and dry crystalline potassium bromide, KBr. TGA measurement data were obtained on a Du Pont instrument, Du Pont TGA 2950, using a platinum pan, using samples of 12-15 weight. The temperature program was started from room temperature to 750°C, with a heating rate of 10°C/min and a nitrogen flow rate of 25 mL/min. SEM digitized micrographs were obtained from a JEOL 5200-2AE (MP 15152001) scanning electron microscope with magnification range of 35-20,000X. Surface area of pyrolyzed product was determined by Autosorb-1 Gas sorption system (Quantachrome Corporation) with the Brunauer-Emmett-Teller method (BET). Each sample was degassed at 300°C for 3 h before measurement. The surface area of the samples was obtained from five-point adsorption.

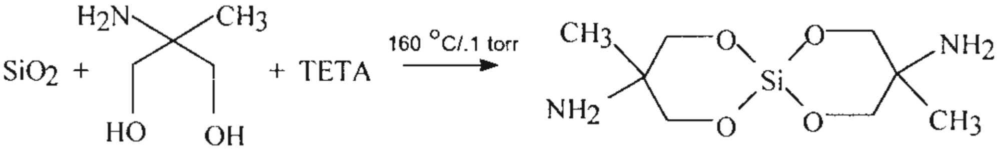
Methodology

Synthesis method

Following the synthetic methods described by Wongkasemjit, et. al[18], spirosilicates were synthesized, as shown in eqs.1-2.



(2.1)



(2.2)

Sol-gel transition study

Hydrolysis of the spirosilicate products was carried out by addition of either HCl or NH_4OH solution at various concentrations. The mixture was prepared directly in a crucible at room temperature, resulting in a formed-gel product. The gel was aged at room temperature. To study the sol-gel transition, at each hour the aliquots of mixture were deducted and dried using high vacuum (0.1 mmHg) to remove solvent. The hydrolysis reaction also carried out was at 40° and 60°C.

Pyrolysis of hydrolyzed products

The hydrolyzed gel was pyrolyzed in a furnace at a heating rate of 10°C/min to 750°C, and maintained at 750°C for 7 h. The pyrolyzed products were then characterized by TGA, FTIR, BET, SEM and WXRD.

Density Measurement

The volumetric property of spirosilicate, the stable hydrolyzed product, was determined using a 25 mL pycnometer (for powder form product) and distilled isooctane as media. The measurement was performed at 25°C. The purified product in the bottle was weighed in the range of 0.5-1.0 g. The media was added until covering the product. Then the bottle was sonicated and incubated at 25°C for 2 h before adding the media to the marked point. The same procedure was made with fused silica for comparison.

Results and Discussion

It is well known that the catalyst used in a gelation reaction can have large effects on the microstructure of the gels formed as well as on the rapidity of the gelation process[20]. During the sol to gel transition induced by applying solvent, the polymerization occurs via hydrolysis and polycondensation reaction. Figures 3.1 and 3.2 show two proposed mechanisms of hydrolysis and condensation for tetracoordinated spirosilicates under acidic and base conditions.

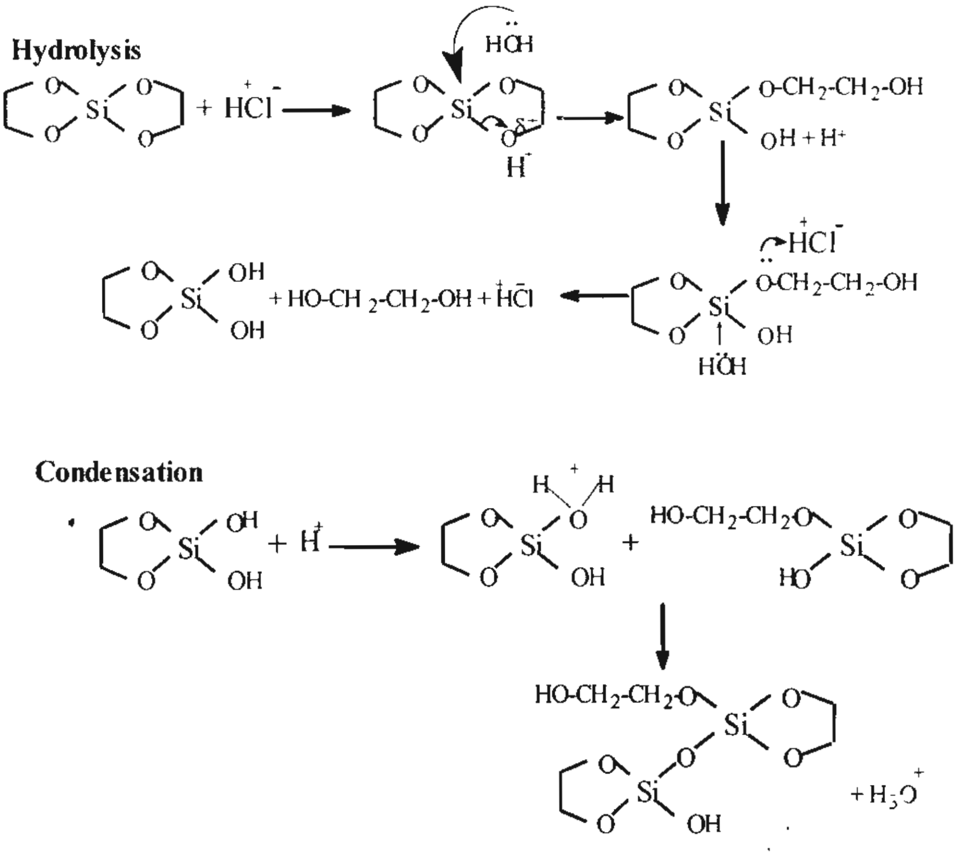


Figure 3.1 Schematic of hydrolysis and condensation under hydrochloric acid solution.

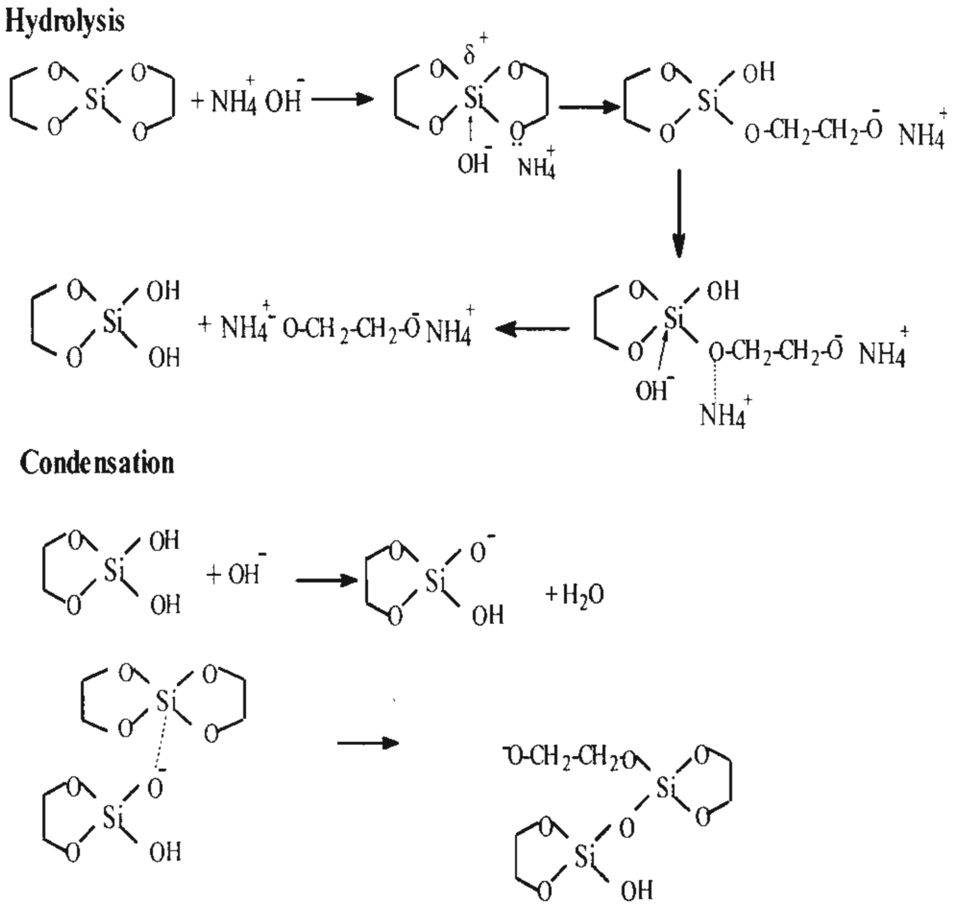


Figure 3.2 Schematic of hydrolysis and condensation under ammonium hydroxide solution.

Spirosilicate

FTIR spectra of products obtained using 0.001M HCl, see Figure 3.3 (a), showed that the characteristic peaks at 3405, 2951, 2883, 1086 cm^{-1} decreased as the time increased. The decrease in the absorption at 3405 cm^{-1} was attributed to the decrease in the amount of Si-OH due to the condensation of silanols[21]. At the same time, the peak around 1648 cm^{-1}, which was assigned to the OH bending[22], also decreased in the same manner. The increase in the absorption peak at 1086 cm^{-1} suggested that crosslinking of Si-O-Si bonds occurred via hydrolysis and condensation. This was confirmed by comparison with the disappearance of absorption peaks at 3405, 2951 and 2883 cm^{-1}, indicating a decrease of organic ligands. It should be noted that, at 9 h., the peaks at 3405, 2951, 2883 and 1086 cm^{-1} change in the reverse direction. This phenomenon was also detected by Brinker et al that when hydroxyl groups on the surface of the particles condense to form siloxane bonds, the particles coalesce in an irreversible sol-gel transition, and when coalescence occurs without forming siloxane bonds, the sol-gel transition may be reversible[23-24]. The structure obtained at 11 h. of hydrolysis was very close to that of silica (Figure 3.4). Using a higher concentration of catalyst, 0.002M HCl, the obtained results were essentially identical (Figure 3.3 (b)). However, the change of absorption peaks at 3405, 2951, 2883 and 1086 cm^{-1} decreased faster as compared to a lower concentration of HCl.

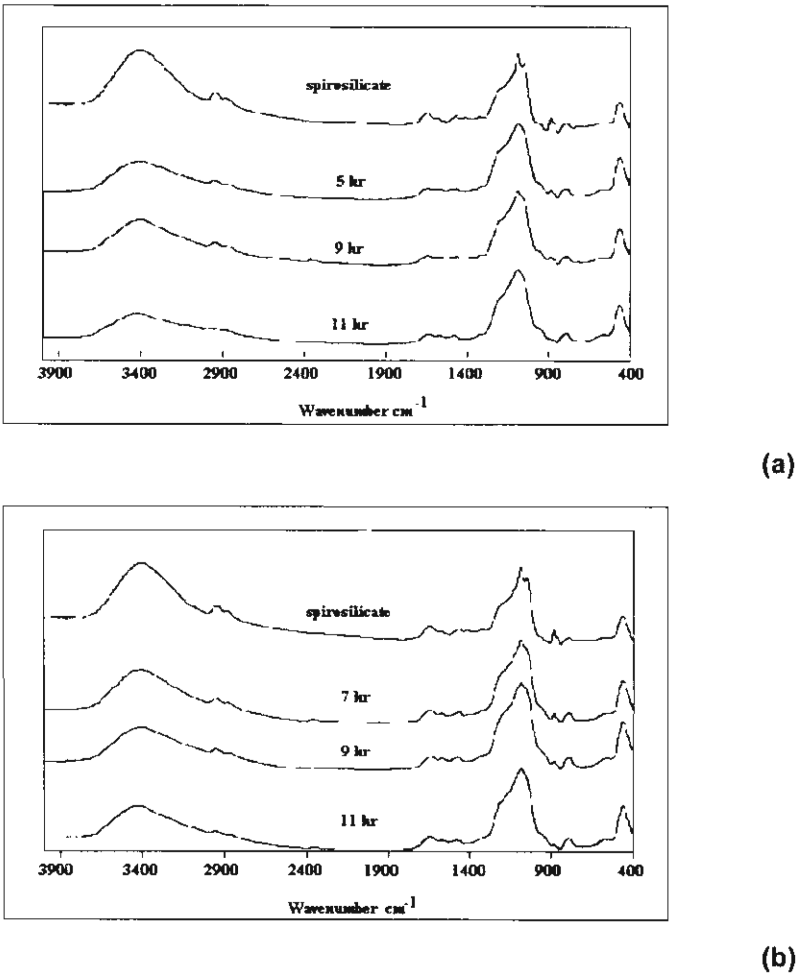


Figure 3.3 FTIR spectra of hydrolyzed spirosilicate with (a) 0.001 and (b) 0.002 M HCl at room temperature.

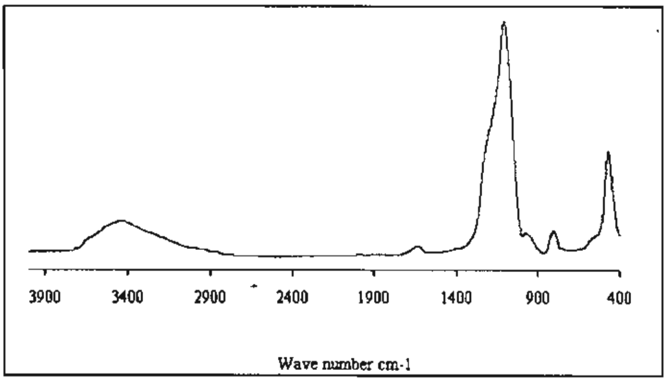


Figure 3.4 FTIR spectrum of fused silica starting material

The overall results are summarized in Figure 3.5, which displays the relationship between the ratio of Si-O-C/Si-O-Si (the peaks at 1086 and 463 cm^{-1}) plotted against time for hydrolysis of the spirosilicate at various acid concentrations at room temperature. Figure 3.5 indicates that the optimum condition, showing more effective hydrolysis occurs when 0.001M HCl is applied, as referred by Lippert for TEOS in 1988[25]. Thus, this condition was selected to further study the effect of temperature, as shown in Figure 3.6. It was found that at 40 °C the hydrolysis rate was much faster than that at room temperature. At 40 °C it took less than one hour for spirosilicate to become silica while more than 10 h. was needed to obtain silica at room temperature.

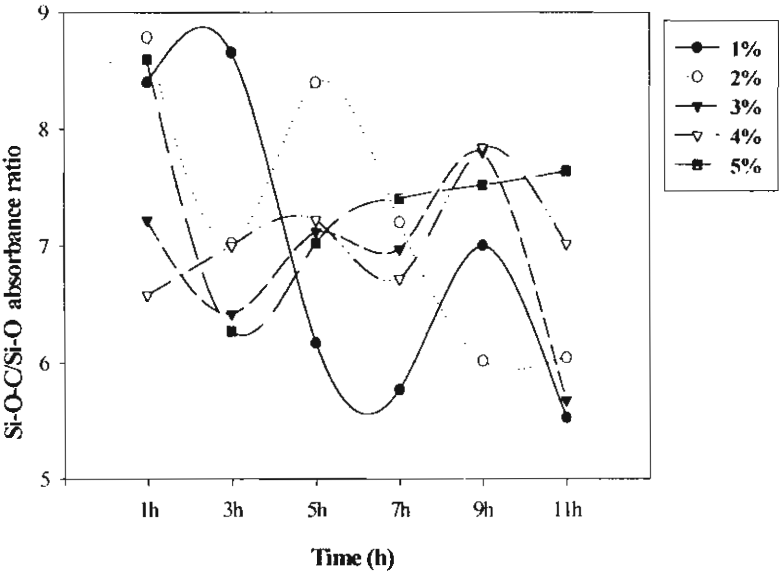


Figure 3.5 The time-dependence of hydrolyzed spirosilicate with 0.001-0.005 M HCl at room temperature.

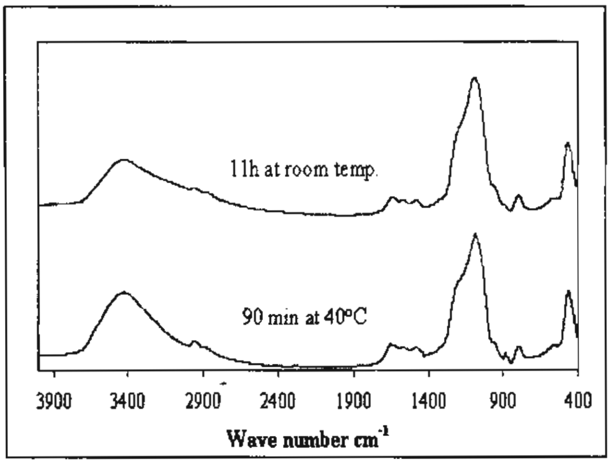


Figure 3.6 FTIR spectra showing the effect of temperature on the hydrolyzed product.

Changing the catalyst from acid to base using 1M ammonium hydroxide solution gave different results, as shown in Figure 3.7. 0.001M NH_4OH gave little change in the structure of Si-O-C and Si-O-Si during the time period of 1 to 8 h. After 9 h, a substantial decrease of the peak ratio was observed. Subsequently, however, after 11 h, the ratio increased again.

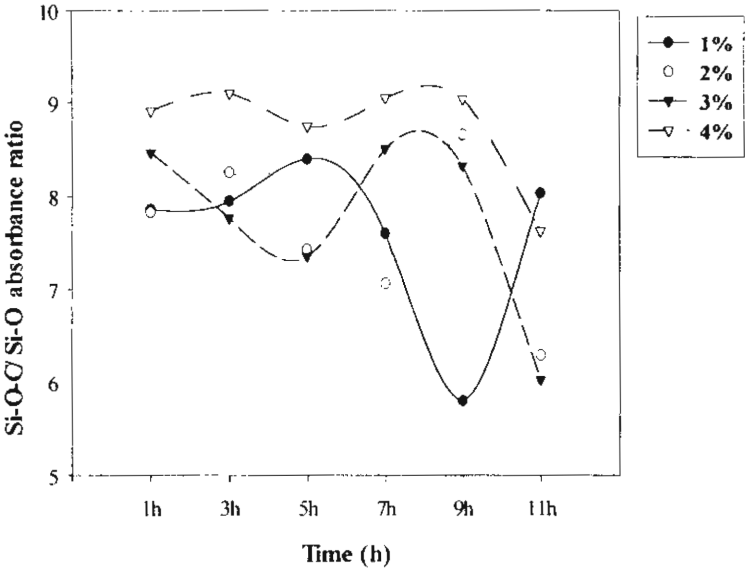


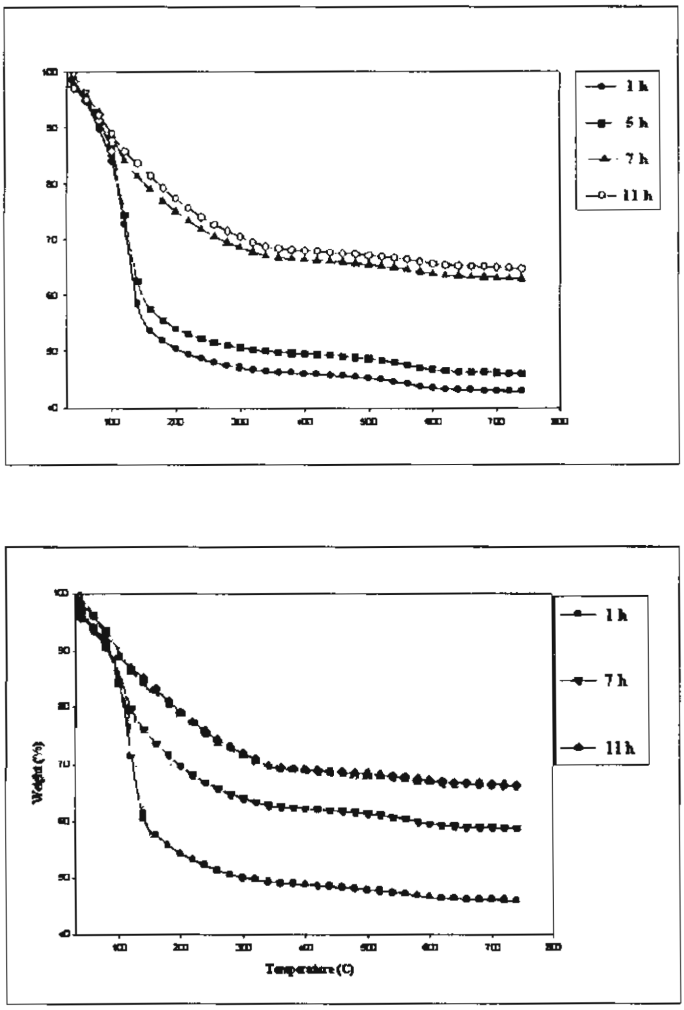
Figure 3.7 The time-dependence of hydrolyzed products of spirosilicate with 0.001-0.004 M NH_4OH at room temperature.

In summary, the kinetics of the sol-gel transition of spirosilicate are slowest at 0.001 and 0.002 M HCl, for which pH ≈ 2, due to the absence of ionized hydroxyl groups [$Si\text{-}O^-$ or $Si\text{-}(OH_2)^+$][26], see Table 3.1, as monitored by a decrease of the peaks at 3405, 2951, 2883 and 1086 cm^{-1}. This result is consistent with experimental studies of Brinker and coworkers[24], who determined the optimal gel time of TEOS to be at pH near 2.

Table 3.1 The pH results of different catalyst concentration.

Concentration of HCl (1M)	pH result	Concentration of NH_4OH (1M)	pH result
1%	2.14	1%	9.56
2%	2.03	2%	9.67
3%	1.97	3%	9.72
4%	1.81	4%	9.80
5%	1.73	5%	10.1
15%	0.65	15%	10.2

TGA analysis of spirosilicate (Figure 3.8) after hydrolysis with 0.001 and 0.002 M HCl were used to confirm the FTIR results shown in Figures 3.3 and 3.5. Evidently, the kinetic data obtained from FTIR spectra and the ceramic yields obtained from TGA are in agreement. A decrease in the Si-O-C peak long with an increase in Si-O-Si peak correlates to an increase in ceramic yield. Notably, the increase of Si-O-C peak at 9 h compared to 7 and 10 h using 0.001M HCl, correlates with a decrease of ceramic yield obtained from TGA.



(a)

(b)

Figure 3.8 TGA thermograms showing percent ceramic yields at various time after hydrolysis with HCl at (a) 0.001M and (b) 0.002M.

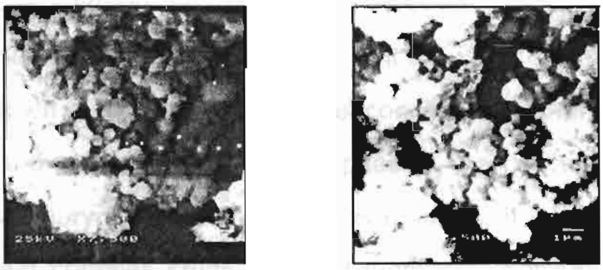
Thus these suggest surprisingly that the reaction can proceed in the reverse direction, so called "reesterification", in which an alcohol molecule displaces a hydroxyl group to produce an alkoxide ligand and water as a by product[24].

The BET surface area study of pyrolyzed product obtained from hydrolysis of spirosilicate at 750°C for 7 h is shown in Table 3.2. The results from FTIR spectra, TGA and BET surface area measurement show that a decrease of –OH and Si-O-C peaks correlates to an increment of ceramic yield and surface area.

Table 3.2 The BET surface area measurement of spirosilicate after hydrolysis with 0.001M HCl and NH_4OH at various time, followed by pyrolysis at 750°C for 7 h, as compared to fused-silica starting material.

Time (hr.)	Surface area (m^2/g)	
	1% of 1M HCl	1% of 1M NH_4OH
3	307	296
5	354	278
7	369	307
9	339	347
11	596	280
Fused silica	167	168

The morphology of the hydrolyzed aggregates was observed by scanning electron microscopy, as shown in Figure 3.9. Figures 3.9(a) and 3.9(b) show the characteristics of the dried gel, under acidic and basic conditions, respectively. Certain differences in morphology are evident, which can be traced to the effect of the different catalyst used.



(a) Hydrolyzed w/ 1% of 1M HCl (b) Hydrolyzed w/ 1% of 1M NH_4OH

(c) Pyrolysis of material (a) at 750°C, 7 h. (d) Pyrolysis of material (b) at 750°C, 7 h.

Figure 3.9 SEM of hydrolyzed (a and b) and pyrolyzed (c and d) spirosilicate

Under acid catalysis, the hydroxylated monomer is formed via electrophilic (H^+) reaction. The condensation reaction continues via these hydroxylated monomers.

$$\mathrm{HO}-\underset{\mathrm{OR}}{\overset{\mathrm{OR}}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\underset{\mathrm{OR}}{\overset{\mathrm{OR}}{\mathrm{Si}}}-\mathrm{OH} \longrightarrow \mathrm{HO}-\underset{\mathrm{OR}}{\overset{\mathrm{OR}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{OR}}{\overset{\mathrm{OR}}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{H_2O}$$

Using basic catalysis, (b) the sol particles formed tend to repel each other due to a high surface charge of SiO^- groups formed according to the following reaction.

$$\mathrm{Si\text{-}OH} + \mathrm{OH^-} \longrightarrow \mathrm{SiO^-} + \mathrm{H_2O}$$

Obviously, each condition has a distinct influence on the rate of condensation and porosity of the dried gel product. Thus, two variables were studied, namely, effect of catalysts on reaction time and gel properties.

As discussed previously, acid catalysis promotes the slowest reaction at 0.001M HCl corresponding to pH = 2-2.5. This is the pH near the iso-electric point, which gives no electrostatic particle repulsion[26]. By increasing the acid catalyst concentration, the reaction rate is increased whereas the gelling time is reduced. On the other hand, the base-catalyzed reaction takes place via nucleophilic attack[21], and the condensation reaction provides SiO^-, resulting in faster condensation before completely hydrolysis. Furthermore, with the base catalysis, repulsion of the sol structure gives more time for the particles to rearrange. Larger particles tend to form first. This is different from using the acid catalyst, occurring via addition reaction in which many small molecules tend to grow slowly[27]. This phenomenon is confirmed by the SEM micrograph in Figure 3.9(b), showing that the porosity of the sol structure is greater than that in Figure 3.9(a).

It is known that, generally, the gel consists of two phases, the network solid phase and the connected pores filled with liquid phase[4]. As the heat treatment is applied, the gel shrinks under capillary force as the liquid evaporates. It is evident in Figure 3.9(a), that the HCl catalyzed gel contains small pores. If there was originally a large amount of water in the pore generated, upon heating the gel from the higher concentration of hydroxyl groups, this will result in a higher shrinkage of the gel, as shown in Figure 3.9(c). On the other hand, the ammonia-catalyzed gel contains large pores and a small amount of water molecules, therefore smaller shrinkage occurs.

The density of product obtained from the gel hydrolyzed using 0.001M HCl was determined to be 0.54 g/cm^3, a value much smaller than that of fused silica, 2.42 g/cm^3. This results from the fact that the removal of alkoxy and hydroxyl groups by condensation reaction when the gel is heated, causes a large weight loss, producing new crosslinks and stiffening the structure[28].

Aminospirosilicate C4

In the case of the 6-membered cyclic aminospirosilicate, ring is more stable than the 5-membered spirosilicate ring. Moreover, the aminospirosilicate has bulkier substituents. As a result, hydrolysis of the aminospirosilicate with either 1M HCl or 1M NH_4OH shows no significant reaction at room temperature and 40°C. 1M HCl also shows no reaction on hydrolysis even at 60°C. Thus, under acidic condition, protonation of alkoxy group is retarded due to the more stable ring structure, more steric hindrance, and the presence of amino group in the structure. This thus resulted in no structural change during hydrolysis of the products under acid condition.

Figure 3.10 shows only the results of C4 hydrolyzed using 1M NH_4OH at 60°C. Inspection of the decrease in the absorption peaks at 3405, 2951, 2883, 1086 cm^{-1} indicates a slower hydrolysis rate. This is confirmed by the fact that the aminospirosilicate hydrolyzed at 60°C for 4 h. gives the highest ceramic yield, 70.89%, as shown in Figure 3.11. The increased ceramic yield is due to a high concentration of reactive groups under base-catalysis and high temperature, allowing less time for the molecules to rearrange to form a crosslinked Si-O-Si network.

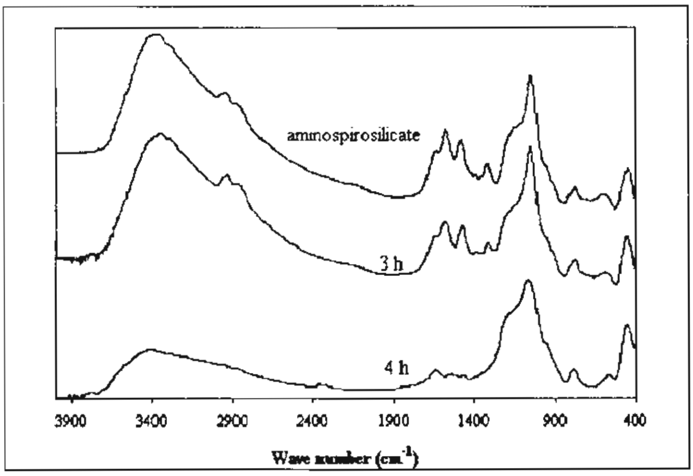


Figure 3.10 FTIR spectra showing the effect of time on the hydrolyzed aminospirosilicate product at 60°C.

The BET analysis of aminospirosilicate sol-gel product pyrolyzed at 750°C for 7 h indicated a surface area of 82.93 m^{2}/g, reflecting the increase of reaction rate because of the increase in concentration of catalyst and temperature[26].

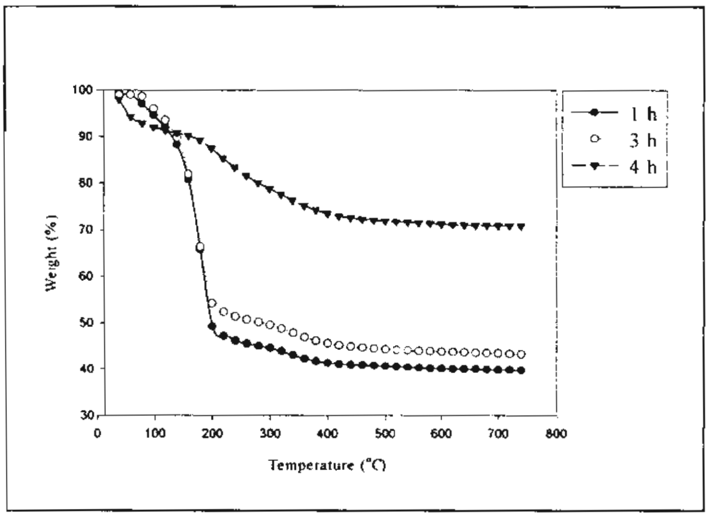


Figure 3.11 TGA thermograms showing percent ceramic yields of hydrolyzed aminospirosilicate at 60°C for 1, 3 and 4 h.

Conclusions

Spirosilicate can function as a reactive metal alkoxide group allowing sol-gel processing at room temperature or slightly elevated temperature. Near the IEP of silica particle (pH ~ 2.0), the product gives high ceramic yield and high surface area, which is required in ceramic precursor processing. A low-density of product is reported to be an important result of the sol-gel method. The other factors that influence the structure of ceramic product from spirosilicate are temperature and aging time.

In addition, aminospirosilicate can serve as a model material for investigation of the sol-gel transition. Because of its higher stability and increased steric hindrance due to the extent of substitution, one needs a higher catalyst concentration and higher temperature for reaction to occur. It is possible to produce products with high ceramic yield and less shrinkage, which can be suitable for engineering industry applications.

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CHAPTER IV

RING-OPENING POLYMERIZATION WITH NEAR-ZERO SHRINKAGE IN VOLUME OF SPIROSILICATES

Abstract

Idealistic materials used in many applications should have dimensional stability. However, almost all thermosets are cured with high shrinkage. The volumetric properties of the newly synthesized spirosilicate and new aminospirosilicate derivatives via ring-opening polymerization without catalyst were studied and measuring the change of density in the cured resins as compared to their corresponding monomers were measured. It was found that all spirosilicates showed little volumetric shrinkage due to the intermolecular hydrogen bonding in the system, resulting in close packing of polymer chains. The structures of cured spirosilicates were characterized using FTIR, DSC, TGA, FAB$^+$-MS, ^{1}H- and ^{13}C-NMR.

Introduction

Thermosetting resins are used in many applications, such as the automotive, aerospace and construction industries due to the advantages of strength, rigidity, dimensional stability, and higher operating temperatures than thermoplastics. However, as mentioned in previous paper [1], most thermosetting resins cure with volumetric shrinkage of 3-15% during polymerization[2]. An example can be seen in epoxy resin, which undergoes volumetric shrinkage of 2-7% upon curing[3]. The shrinkage, in general, causes residual stress, warping, premature debonding of the fiber from the matrix, fiber bulking, and delamination in fiber-reinforced composites. In dental industry, the shrinkage upon curing has been a major problem of this resin in this field[4]. In molding industry, shrinkage is the worst problem because of nonuniformity in the dimension of the molded parts. To reduce shrinkage in resins like phenolic resins, fillers, such as, cellulose flour, wood flour, and more commonly mineral fillers are required. However, these fillers can be abrasive to the mold surface. Various fillers are incorporated into the matrix and molding conditions are modified to reduce resins shrinkage[5].

Spiroorthoesters and spiroorthocarbonates[6-12] were synthesized and polymerized via ring-opening reaction (Figure 4.1). Because of the chemical transformation of compact bicyclic monomer to linear polymer, most of these monomers show zero or near zero shrinkage on polymerization. Sakai was the first to report the cationic ring-opening polymerization of three types of spiroorthocarbonates with boron trifluoride etherate as the initiator, concerning the three possible sites attacked by the monomer, irrespective solvent, initiator, and temperature[13].

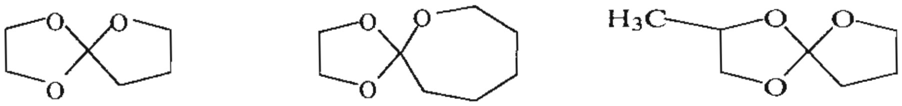


Figure 4.1 Examples of spiroorthoesters

Cationic polymerization of spiroorthocarbonates leading to a poly(ether-carbonate) alternating copolymer proceeds via the trialkoxycarbenium ion as a possible propagating species. Since this type of carbenium ion was found to be quite possible, the growing chain end was expected to remain living after the completion of the polymerization[7].

Many research groups have tried to introduce the spiroortho compound as an additive into epoxy resins to reduce volume shrinkage and improve the mechanical properties. A copolymer of bisnorbornenyl spiroorthocarbonate and an epoxy gave higher impact strength and higher shear strength than that of epoxy-carbon fiber composite[14]. 25% Bisnorbornenyl spiroorthocarbonate content was found to be the suitable value for the mixture to expand upon cure. Unfortunately, synthesis of spiroortho compounds was quite complicated and the compounds by themselves have low glass transition temperatures (T_g).

Spirosilicates synthesized directly from silica and ethylene glycol/ethylene glycol derivatives in one step[1], see eqs.4.1-4.2, on the other hand, have similar structure to those of spiroorthoesters and spiroorthocarbonates except that spirosilicates contain Si-O bonds, which are of importance. These bonds can provide thermal/oxidative stability and chemical resistance to the product[15]. Therefore, the aim of this research is to investigate whether the synthesized spirosilicates show shrinkage or expanding property.

Experimental

Materials

Fumed silica, 3-amino-1,2-propanediol and 2-amino-2-methyl-1,3-propanediol were purchased from Aldrich Chemical Co., Inc. (USA), and used without purification and kept under nitrogen atmosphere. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co., Ltd. and used as a catalytic base. It was distilled at 130 °C , 10^{-1} torr, prior to use. Potassium hydroxide was purchased from Merck Company Co., Ltd., and used as received and as a co-catalyst. Ethylene glycol was purchased from Lab-Scan Company Co., Ltd., and purified by fractional distillation. Acetonitrile and 2,2,4-trimethylpentane (isooctane) were also purchased from Lab-Scan Company Co., Ltd., and distilled over calcium hydride under nitrogen atmosphere. Methanol was purchased from J.T. Baker Company Co., Ltd. and purified by distilling over calcium chloride.

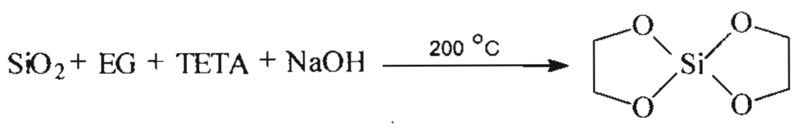
Characterization

Mass spectra (MS) were obtained using a VG Autospec model 7070E from Fison Instruments with VG data system. Samples were run in the positive fast atomic bombardment (FAB-MS$^+$) mode using glycerol as the matrix, cesium gun as the initiator and cesium iodine (CsI) as a reference. Thermal transition properties were determined using a Netzsch DSC 200 at a heating rate of 10 °C/min under nitrogen atmosphere. The thermal stability of the products was obtained using a Netzsch TGA 209 at a heating rate of 10 °C and flow rate of 10 mL per min, respectively, under nitrogen atmosphere. FTIR spectra were recorded using a FRA 106/s Bruker instrument with a spectral resolution of 4 cm^{-1}. The samples were mixed with KBr at an approximate ratio of 1:20 (sample:KBr). ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker 200 MHz spectrometer at room temperature using deuterated dimethyl sulfoxide (DMSO-d$_6$) as solvent and reference for chemical shift measurements.

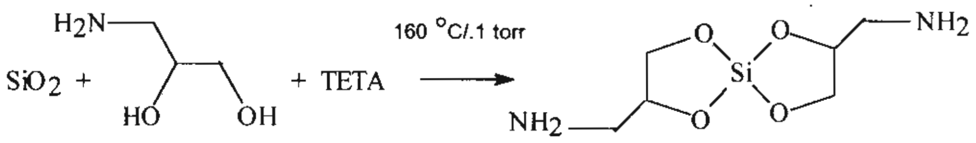
Procedure

Synthesis of spirosilicates from silica and ethylene glycol/aminopropanediols

By following the synthetic methods published by Wongkasemjit, et. al[1], spirosilicates were synthesized, as shown in eqs.4.1-4.3.



(4.1)



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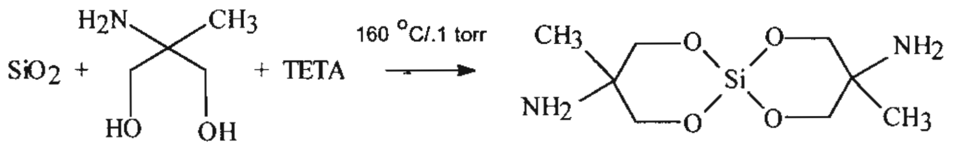

(4.3)