รายงานวิจัยฉบับสมบูรณ์

โครงการ

“การศึกษาวิธีการสังเคราะห์ และสมบัติของสไปโรซิลิเคท/เบนซอกซาซีนเรซิน”

โดย นางสุจิตรา วงศ์เกษมจิตต์

พฤศจิกายน 2545

Scan

สัญญาเลขที่ RSA/02/2543

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วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

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กิตติกรรมประกาศ

ผู้วิจัยขอขอบพระคุณสำนักงานกองทุนสนับสนุนการวิจัย ที่ได้ให้การสนับสนุนโครงการวิจัยนี้ตลอดทั้งโครงการ

บทคัดย่อ

รหัสโครงการ : RSA/02/2543

ชื่อโครงการ : "การศึกษาวิธีการสังเคราะห์ และสมบัติของสไปโรซิลิเคท/เบนซอกซาซีนเรซิน"

ชื่อนักวิจัย : นางสุจิตรา วงศ์เกษมจิตต์
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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).

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

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.

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

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

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).

$$SiO_2 + 2C \xrightarrow{1200^{\circ} C} Si + 2CO \tag{1.5}$$

$$Si + 2Cl_2 \longrightarrow SiCl_4 \tag{1.6}$$

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).

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

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

$$Si + HCl \longrightarrow H_2 + HSiCl_3 + SiCl_4 \tag{1.8}$$

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.

$$4HSiCl_3 \xrightarrow{amine} SiH_4 + 3SiCl_4 \tag{1.9}$$

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

$$SiCl_4 + 2RMgX \longrightarrow R_2SiCl_2 + 2MgClX \tag{1.10}$$

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).

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

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.

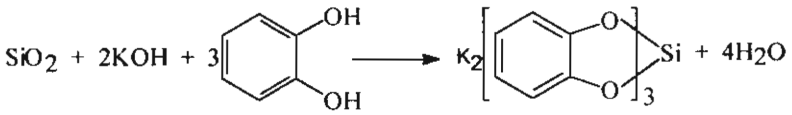
$$CaSiO_3 + 2HCl \xrightarrow[Axeotropic]{Toluene/EtOH} Si(OEt)_4 + CaCl_2 + 3H_2O \tag{1.12}$$

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).

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

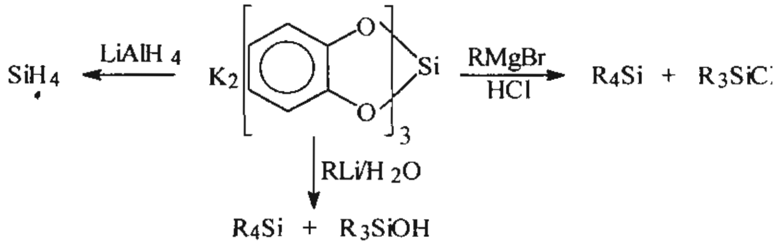
where R : Me, Et, Bu^n, Pr^i, and Ph.

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).



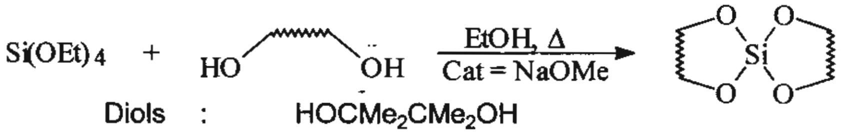
(1.14)

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

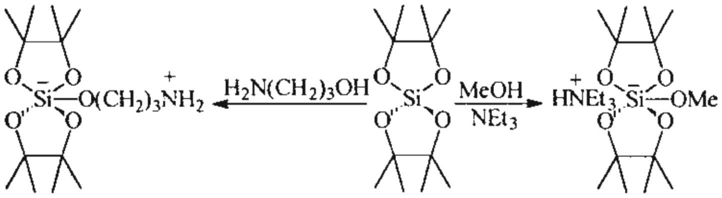
Frye[19-21] reported that the preparation of spirosiloxane from tetraethoxysilane, Si $(OEt)_4$, and 1,2-diols, was quite facile, if the reactions were run in ethanol with small amount of sodium methoxide, NaOMe, as catalyst. However, Frye found that with ethylene glycol, the product obtained was polymeric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



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

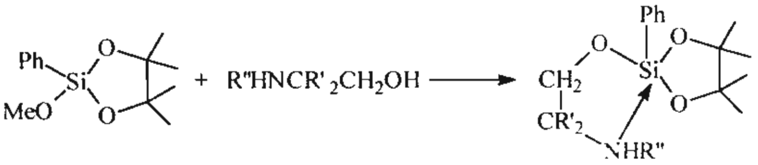
Scheme 1.2

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

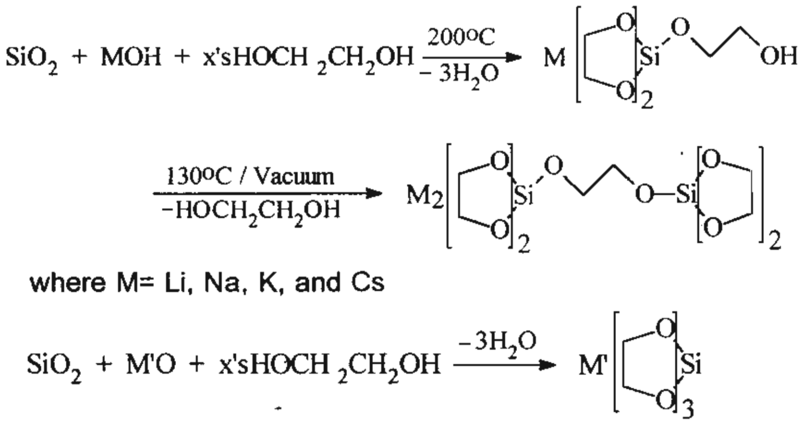
He also synthesized bispinacoloxy salts (pentacoordinated silicon derivatives) from heterocyclic pinacol derivative and alkanolamines. The result showed the partial bond between silicon and nitrogen atom, as illustrated in equation (1.15).



(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= Li, Na, K, and Cs

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.

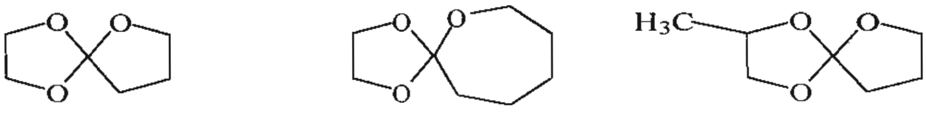
Like polyesters, epoxies are used for similar applications but are more expensive and manufacture is more complicated. Therefore, epoxies are used only if polyesters do not provide the desired properties.

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

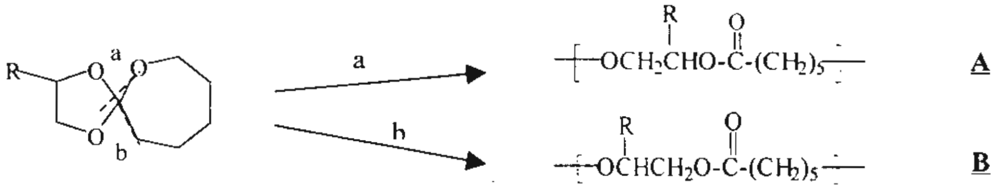
However, shrinkage in most thermosetting resins is quite high, 3-15 % and widely used epoxies undergo volumetric shrinkage of 2-7% upon curing. It causes residual stress, warping, premature debonding of the fiber from the matrix, fiber bulking, and delamination in fiber-reinforced composites. In dental 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' = $PhO\text{-}CH_2$

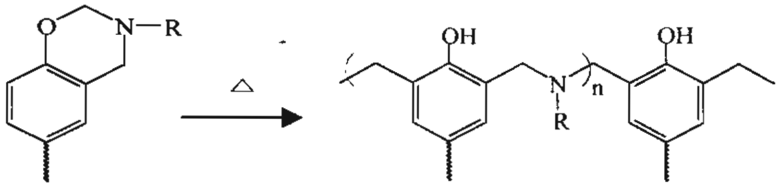
Scheme 1.6

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.

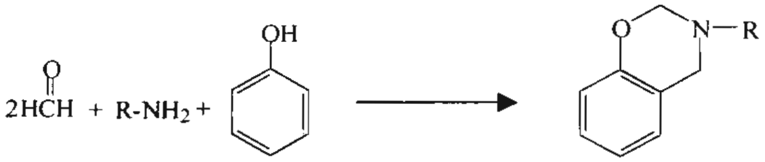
Benzoxazines, the novel phenolic resins which are the new materials that solve the problems related to traditional phenolic resins, were first synthesized by Holly and Cope[2] from aldehyde, phenol derivatives and primary amine that shown in scheme 1.7.



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

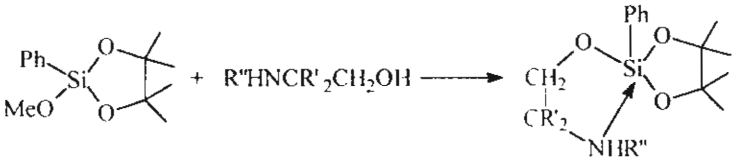
Abstract

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.

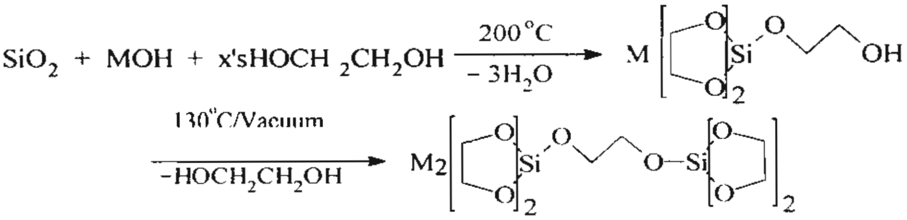
Introduction

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]

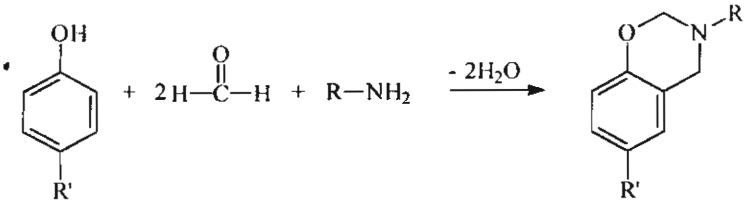
Frye reported the preparation of spirosiloxane from $Si(OEt)_4$ and ethylene glycol in ethanol with a small amount of NaOMe. The product obtained was polymeric species and in the presence of amine bases, novel pentacoordinated species would be formed.[14-16]



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.

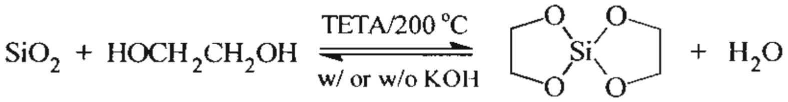
Preparation of bis(3-aminopropane-1,2-diyldioxy)silane and bis(2-amino-2-methyl propane-1,3-diyldioxy)silane

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 °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.

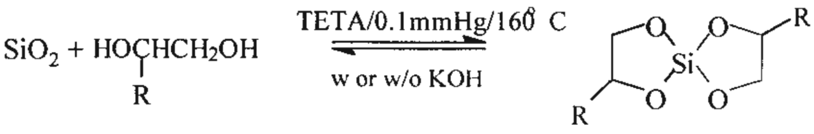
Results and Discussion

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;

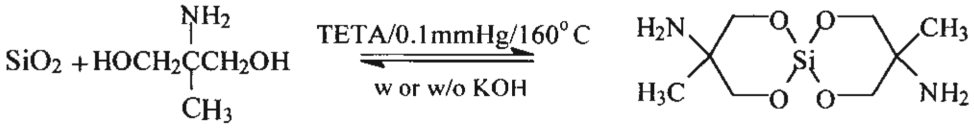


Bis(ethane-1,2-diyldioxy)silane



where R = -CH2NH2

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 pcint 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).

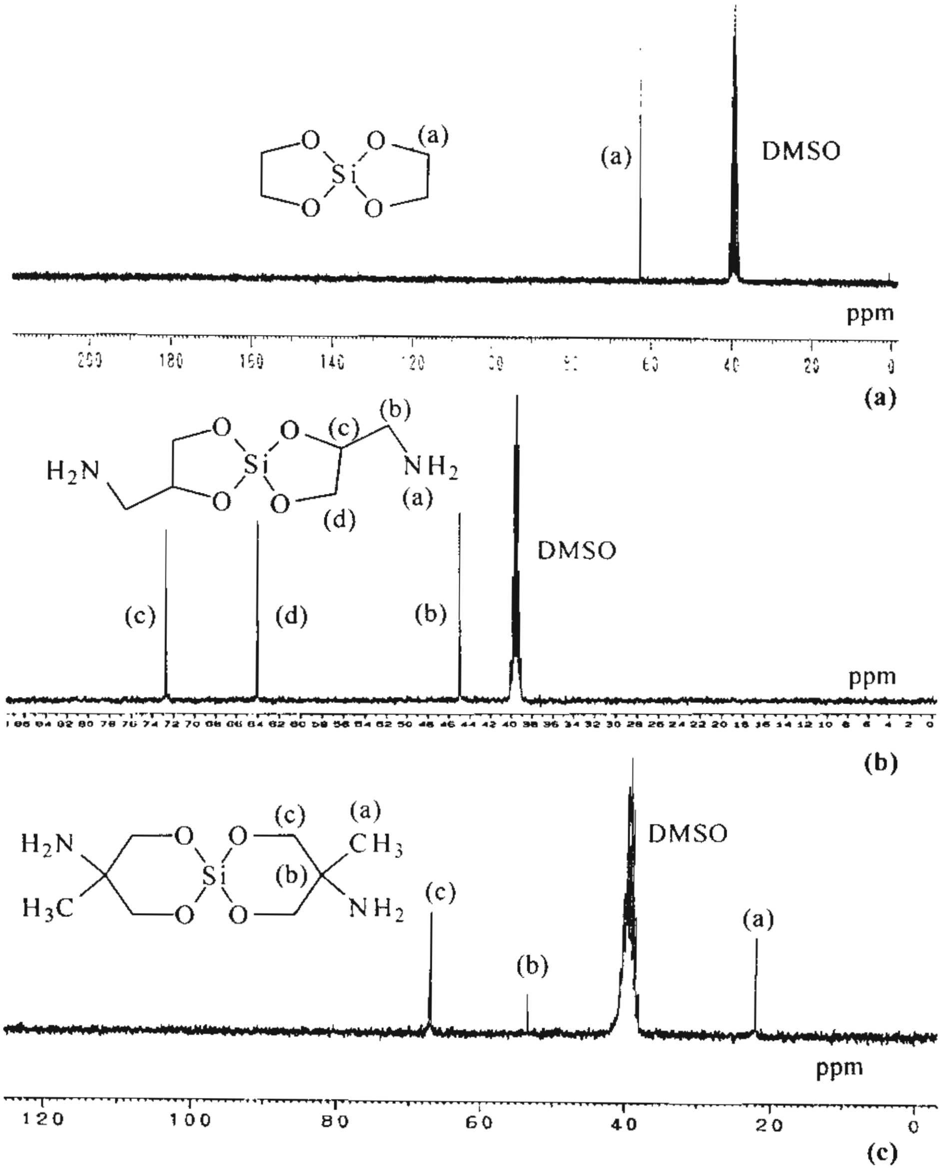


Figure 2.1 ^{1}H-NMR Spectra of a) bis(ethane-1,2-diyldioxy)silane, b). bis(3-aminopropane-1,2-diyldioxy)silane, and c) bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

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.

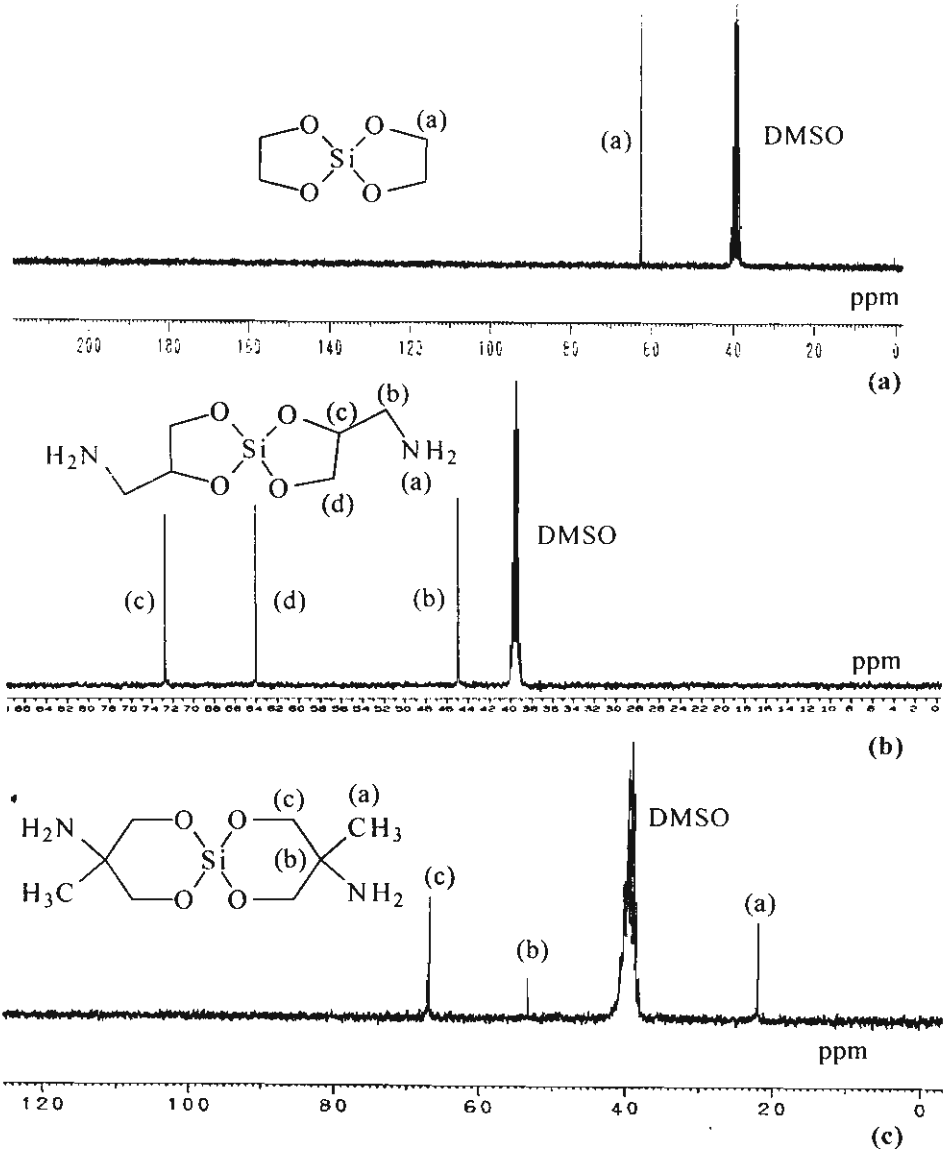


Figure 2.2 ^{13}C-NMR Spectra of a) bis(ethane-1,2-diyldioxy)silane, b) bis(3-amino propane-1,2-diyldioxy)silane, and c) bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

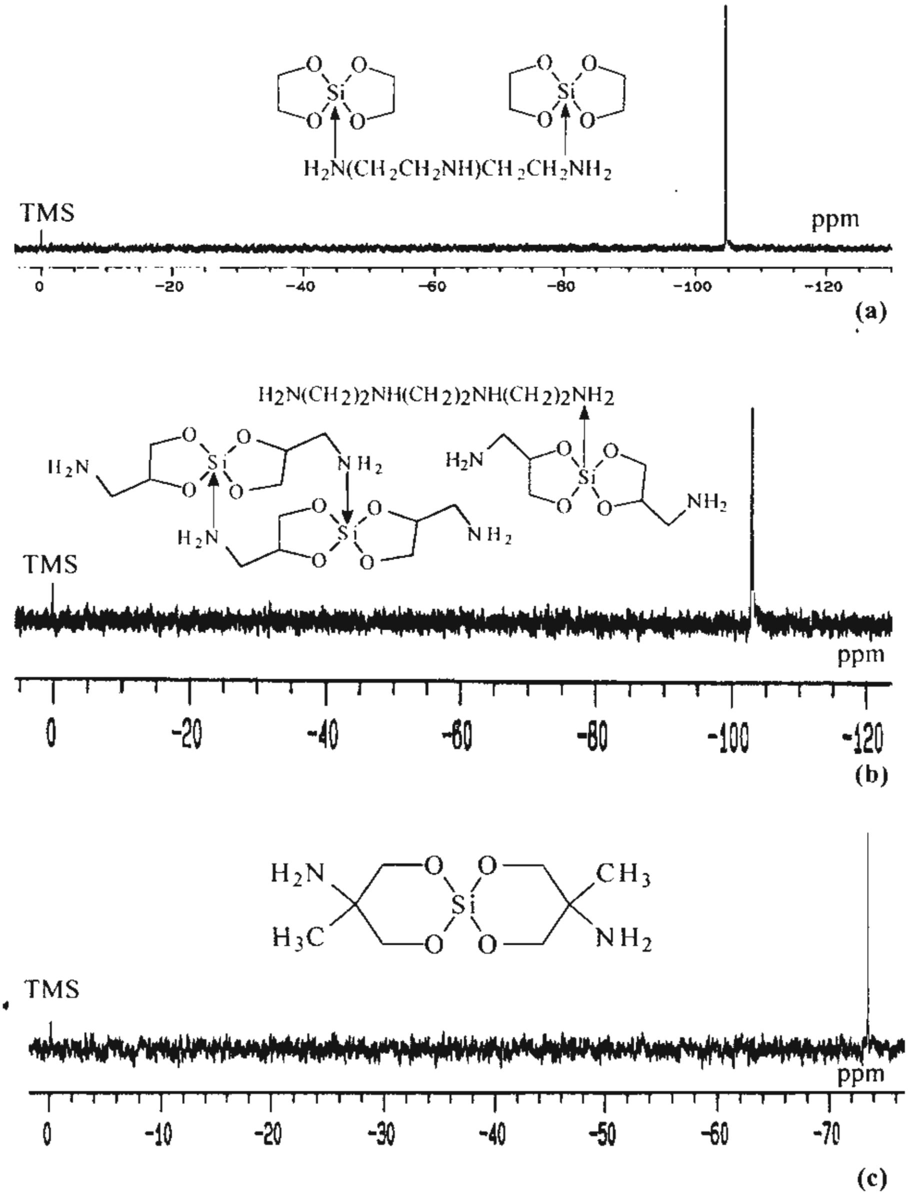


Figure 2.3 ^{29}Si-NMR Spectra of a) bis(ethane-1,2-diyldioxy)silane, b) bis(3-aminopropane-1,2-diyldioxy)silane, and c) bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

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

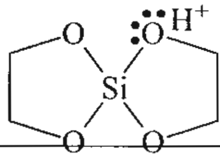
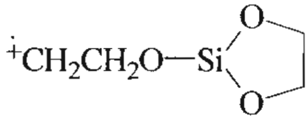
m/e	Intensities	Proposed Structure
149	7.00	
132	31.57	
72	9.11	$^{\dot{+}}CH_2CH_2O{-}Si$
58	100	$^{\dot{+}}CH_2O{-}Si$
44	80.94	$^{\dot{+}}O{-}Si$

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

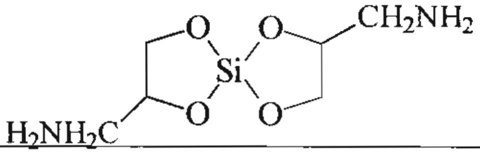
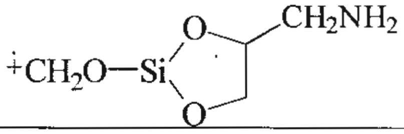
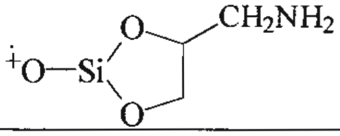
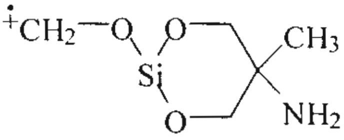
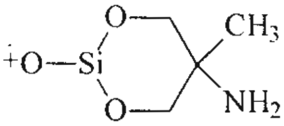
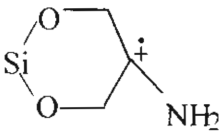
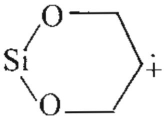
m/e	Intensities	Proposed Structure
206	0.77	
147	17.62	
133	100	
58	4.94	$^{\dot{+}}CH_2O{-}Si$
44	42.28	$^{\dot{+}}O{-}Si$

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.

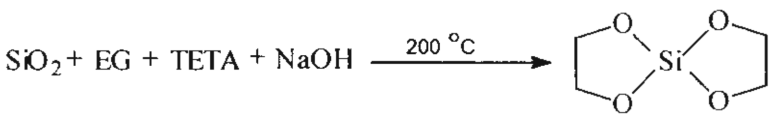
Instrumental

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.

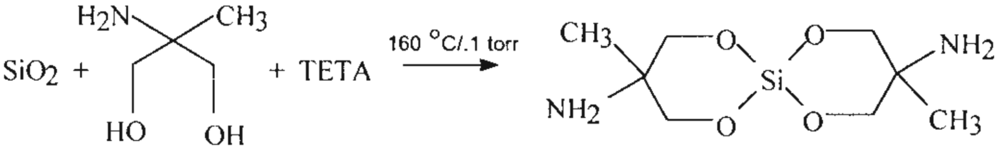
Methodology

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.

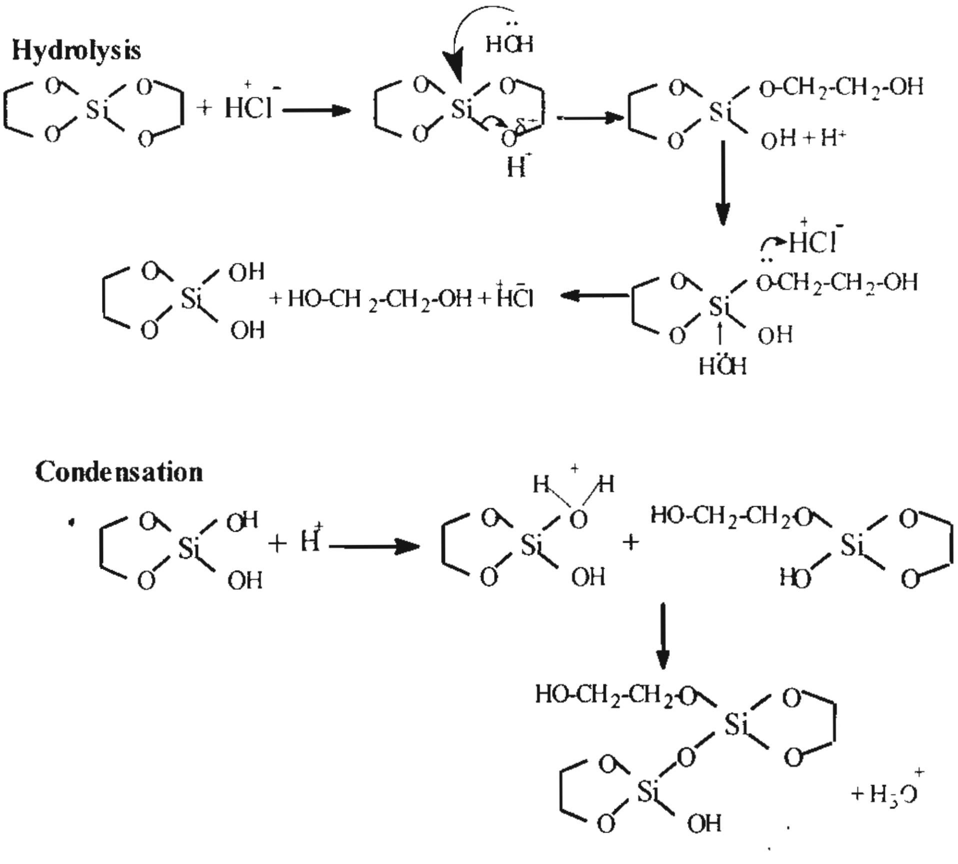


Figure 3.1 Schematic of hydrolysis and condensation under hydrochloric acid solution.

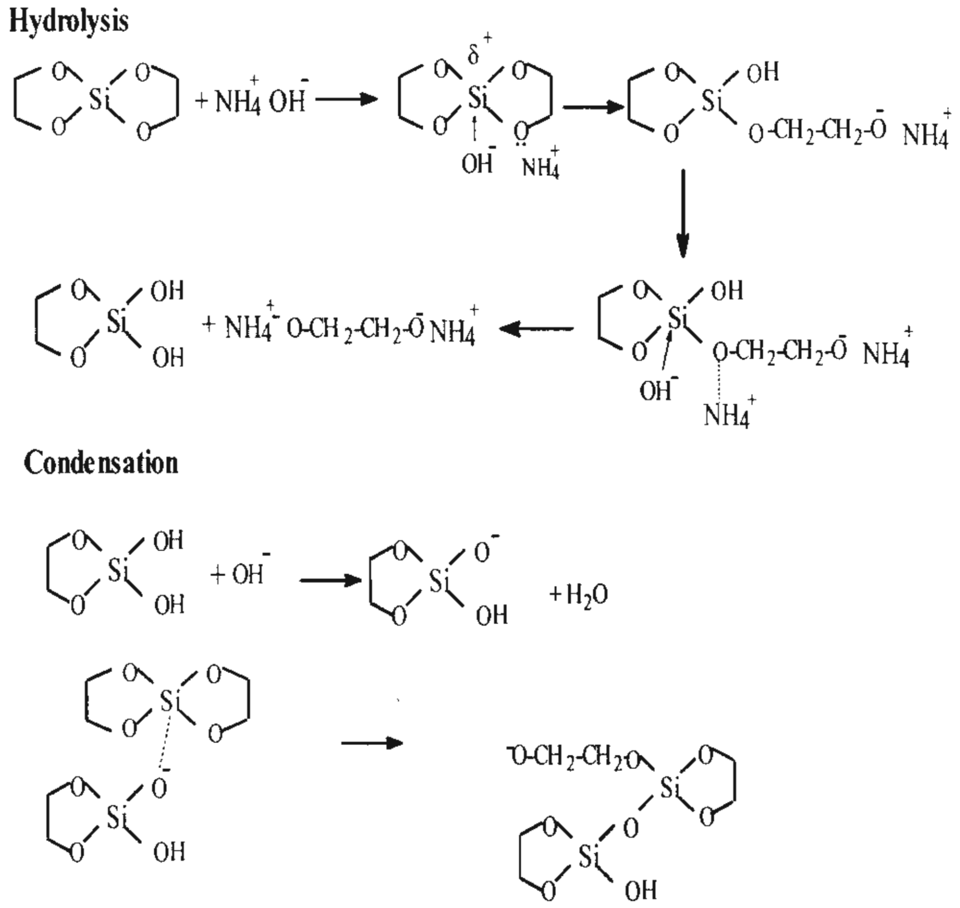


Figure 3.2 Schematic of hydrolysis and condensation under ammonium hydroxide solution.

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.

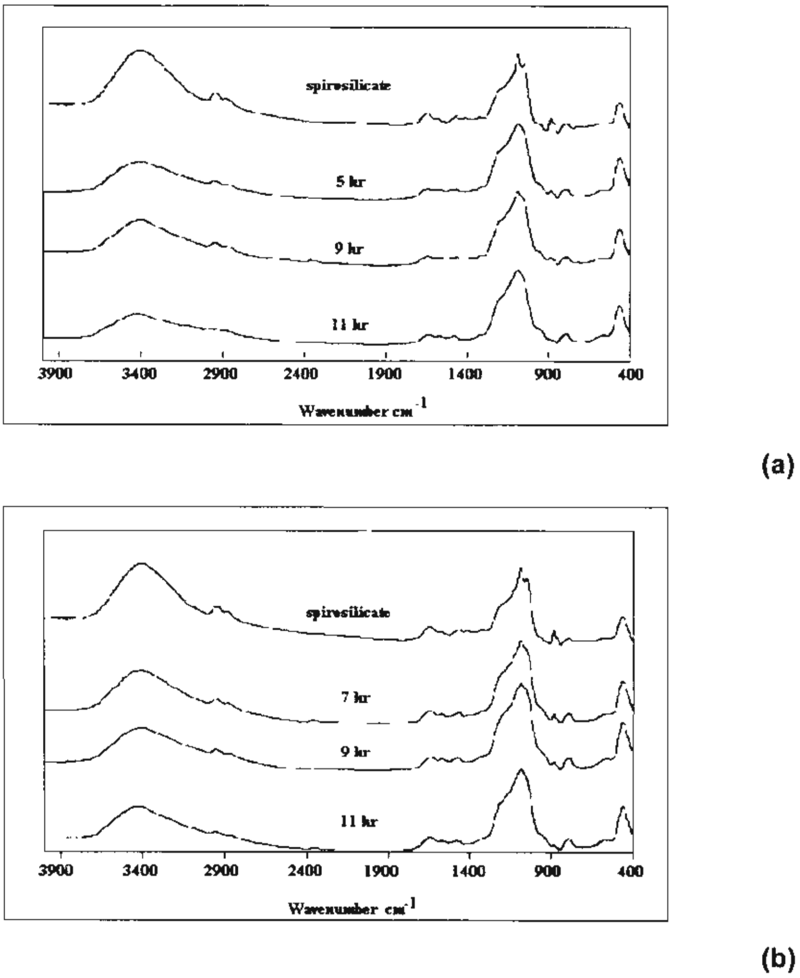


Figure 3.3 FTIR spectra of hydrolyzed spirosilicate with (a) 0.001 and (b) 0.002 M HCl at room temperature.

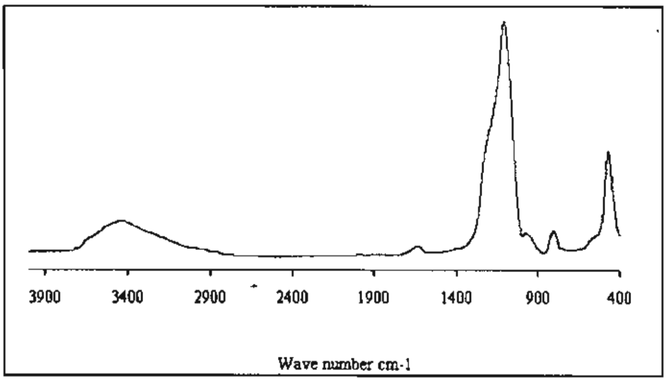


Figure 3.4 FTIR spectrum of fused silica starting material

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.

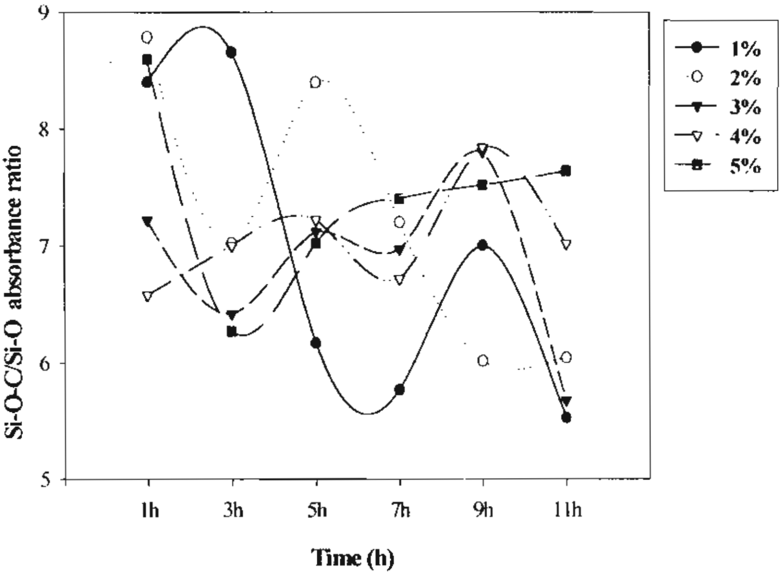


Figure 3.5 The time-dependence of hydrolyzed spirosilicate with 0.001-0.005 M HCl at room temperature.

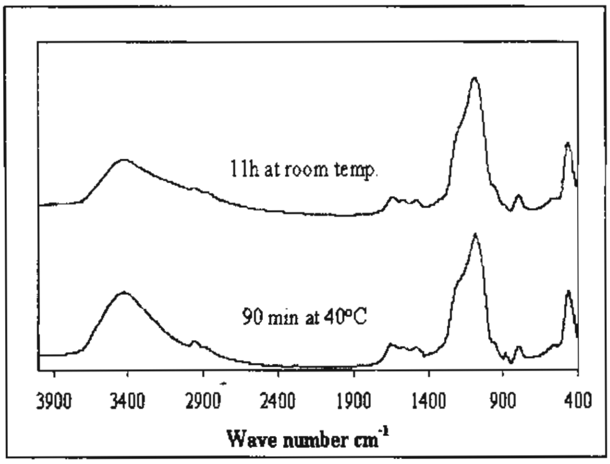


Figure 3.6 FTIR spectra showing the effect of temperature on the hydrolyzed product.

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.

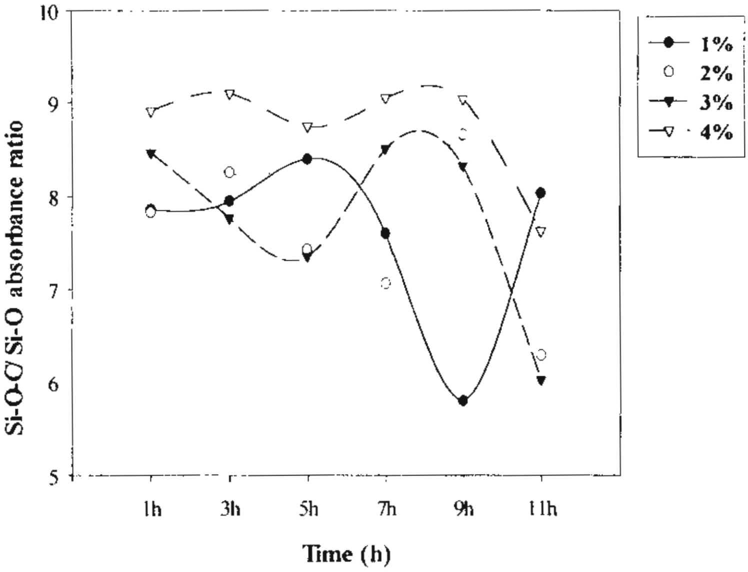


Figure 3.7 The time-dependence of hydrolyzed products of spirosilicate with 0.001-0.004 M NH_4OH at room temperature.

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.

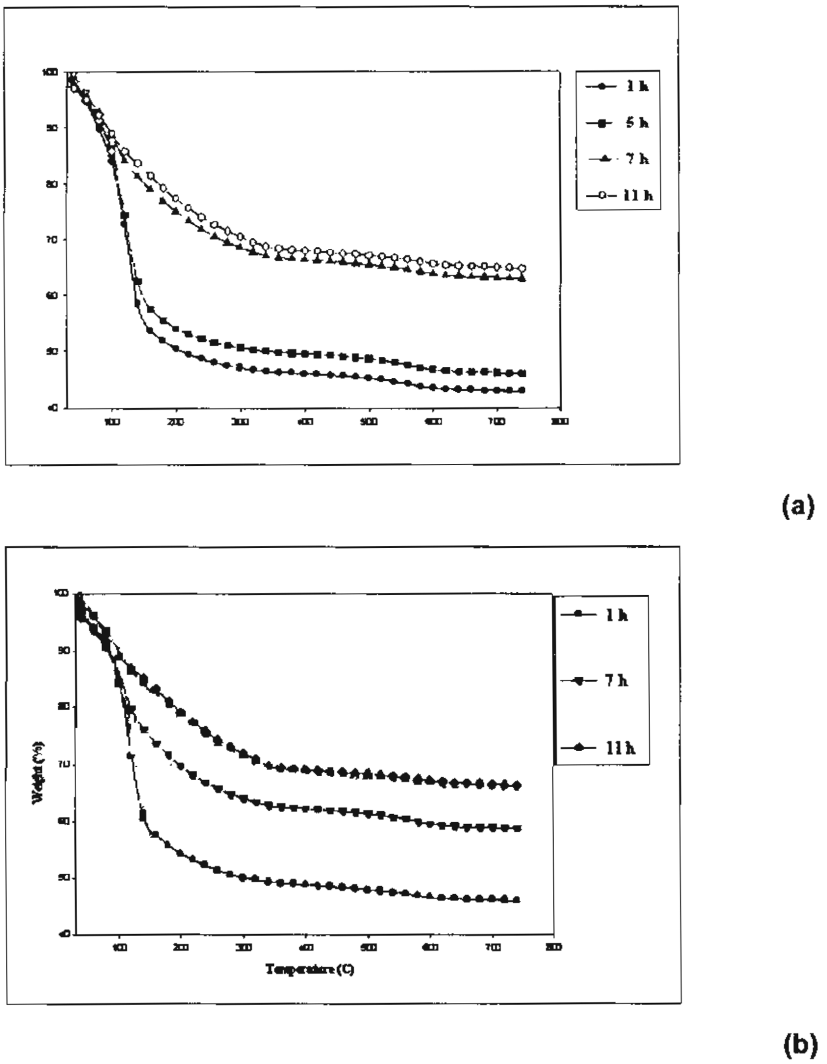


Figure 3.8 TGA thermograms showing percent ceramic yields at various time after hydrolysis with HCl at (a) 0.001M and (b) 0.002M.

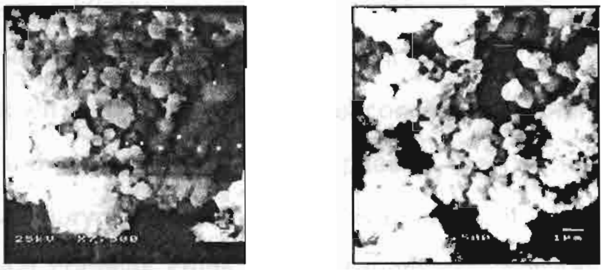
Thus these suggest surprisingly that the reaction can proceed in the reverse direction, so called "reesterification", in which an alcohol molecule displaces a hydroxyl group to produce an alkoxide ligand and water as a by product[24].

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.

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

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.

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

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.

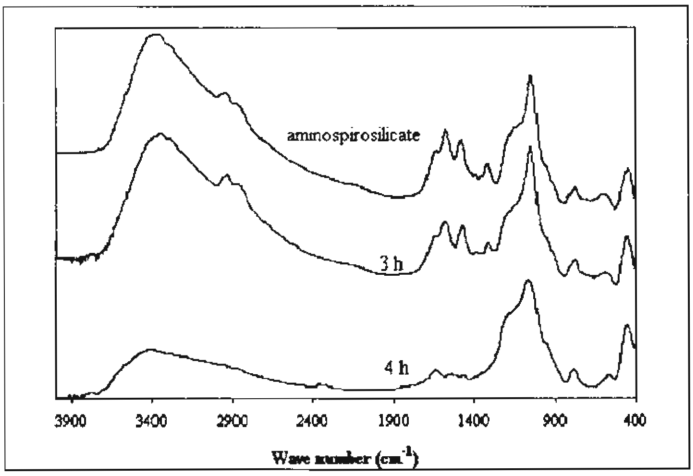


Figure 3.10 FTIR spectra showing the effect of time on the hydrolyzed aminospirosilicate product at 60°C.

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].

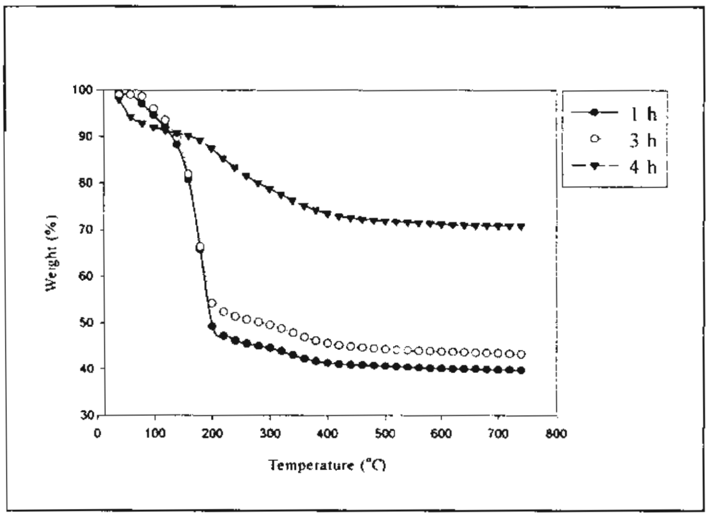


Figure 3.11 TGA thermograms showing percent ceramic yields of hydrolyzed aminospirosilicate at 60°C for 1, 3 and 4 h.

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].

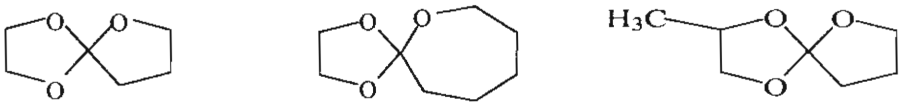


Figure 4.1 Examples of spiroorthoesters

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.

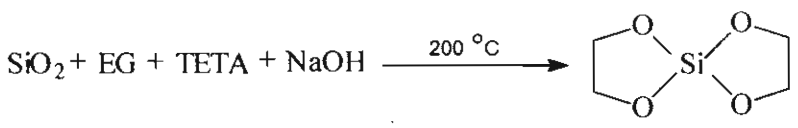
Characterization

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.

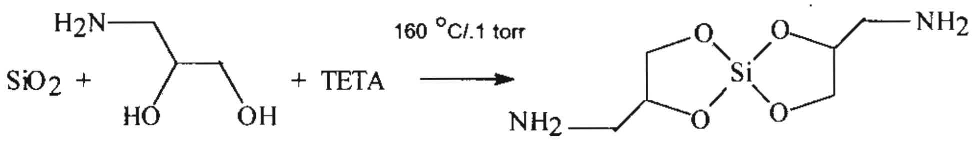
Procedure

Synthesis of spirosilicates from silica and ethylene glycol/aminopropanediols

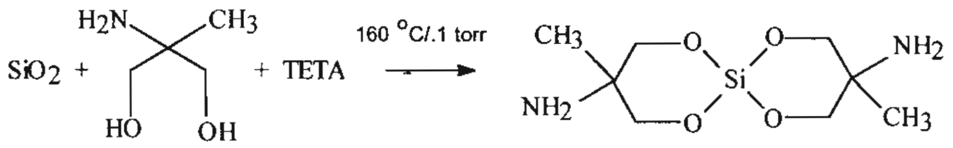
By following the synthetic methods published by Wongkasemjit, et. al[1], spirosilicates were synthesized, as shown in eqs.4.1-4.3.



(4.1)



(4.2)



(4.3)

Determination of Curing Conditions

To determine the density of monomers in order to compare with their corresponding polymers, the suitable time and temperature for curing monomers to obtain fully crosslinked polymers were first investigated. The optimum curing temperature was obtained by fixing curing time at 1 hr and varying temperature from 80° to 180°C in a vacuum oven. %Ceramic yield data from TGA was used to clarify the amount of crosslinking, meaning that the higher %ceramic yield, the higher crosslinking. The suitable curing temperature was the point that the % ceramic yield started to approach constant. Like-wise, the optimum curing time was obtained by fixing the selected temperature and varying the time in range of 1 to 5 h. in a vacuum oven. The suitable time was again the point that the %ceramic yield started to approach constant.

Density Measurement

The volumetric property of each product was obtained by comparing the densities of monomer and its corresponding polymer. The density measurements were performed according to ASTM D792 (Method A), using a 25 mL pycnometer (for powder form product) and distilled isooctane as media. In the process, the pycnometer bottle was first weighed and tarred. The purified product in the bottle was weighed in the range of 0.5-1.0 g. The media was added to the bottle until covering the product. The bottle-containing sample and media was then sonicated in an ultrasonic bath to eliminate bubbles. The sample was then incubated at 25°C for 2 h. The media was then added to the bottle until it reached the marked point. The bottle was wiped and covered with the cap having a thermometer. The weight was measured and the density of the sample was finally calculated. The steps of density measurement are followed;

the weight of sample = (A) g.
the weight of sample + isooctane = (B) g.
the density of isooctane at the set temperature obtaining from reference
= (C) g/cm^3
the weight of isooctane = (B) - (A) = D g.
the volume of isooctane = D / (C) = E cm^3
the volume of sample = the volume of the bottle - E
= G cm^3
then the density of sample = (A) / G g/cm^3

Results and Discussion

The synthesized products of spirosilicate, A, aminospirosilicates from 3-amino-1,2-propanediol and 2-amino-2-methyl-1,3-propanediol, B and C, respectively, were used further in the density measurement to compare with their corresponding polymers thermally obtained from ring-opening polymerization. Finding the optimum conditions for polymerizing each monomer was first conducted by studying the variation of curing temperature and time.

For spirosilicate A, the product was cured by first varying temperature and fixing the time at 1 h. and 1 torr. The %ceramic yield obtained from the TGA result was approaching constant when the temperature reached 120°C (Figure 4.2a). This temperature was thus selected to find the optimum time. The curing time studied was ranged from half an hour to 5 h. It was found that the 1 h. curing time gave the highest %ceramic yield (Figure 4.2b). As a result, the optimum curing condition for the spirosilicate A was 1 h. at 120°C, 1 torr.

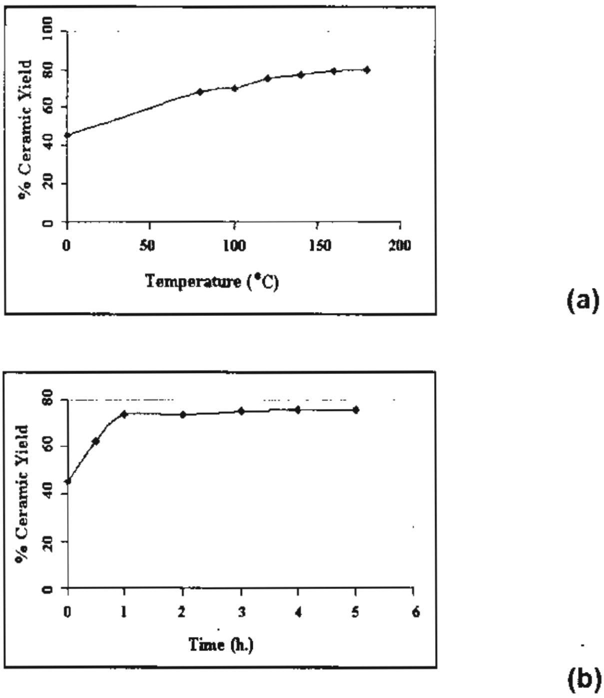


Figure 4.2 %Ceramic yields of cured spirosilicate A at a). various temperatures and b). various times

As for aminospirosilicates B and C, the optimum curing conditions were carried out in the same manner. The results are shown in Figures 4.3-4.4. The optimum conditions at 1 torr for curing B and C products were at 140°C for 1 h. and 160°C, 2 h., respectively. Clearly, spirosilicate C product needs higher temperature and longer time for curing as compared to spirosilicates A and B. This is due to the fact that stability of six- membered ring structure of spirosilicate C is higher than those of five-membered ring spirosilicates A and B.

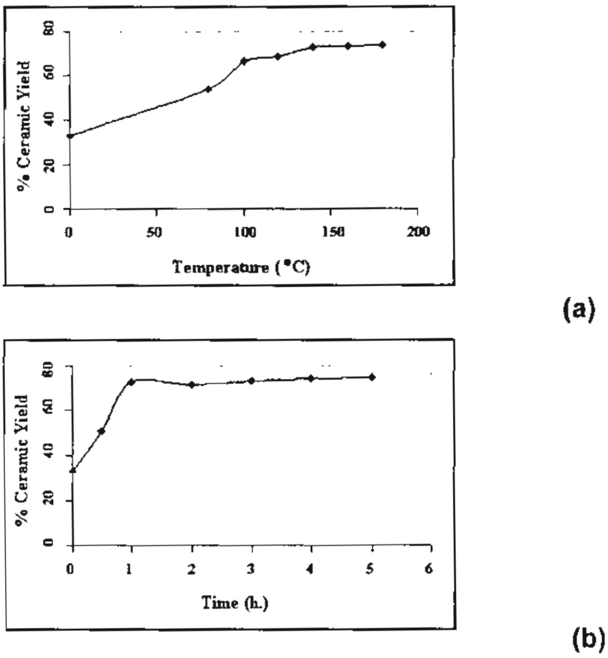


Figure 4.3 %Ceramic yields of cured spirosilicate B at a). various temperatures and b). various times

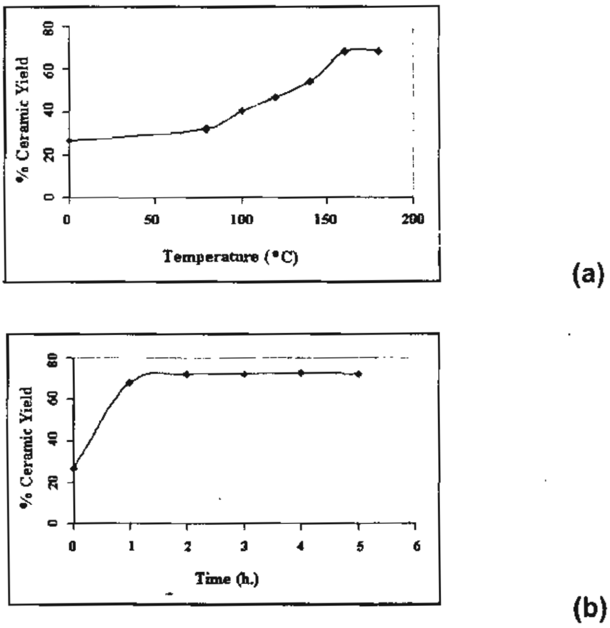


Figure 4.4 %Ceramic yields of cured spirosilicate C at a). various temperatures and b). various times

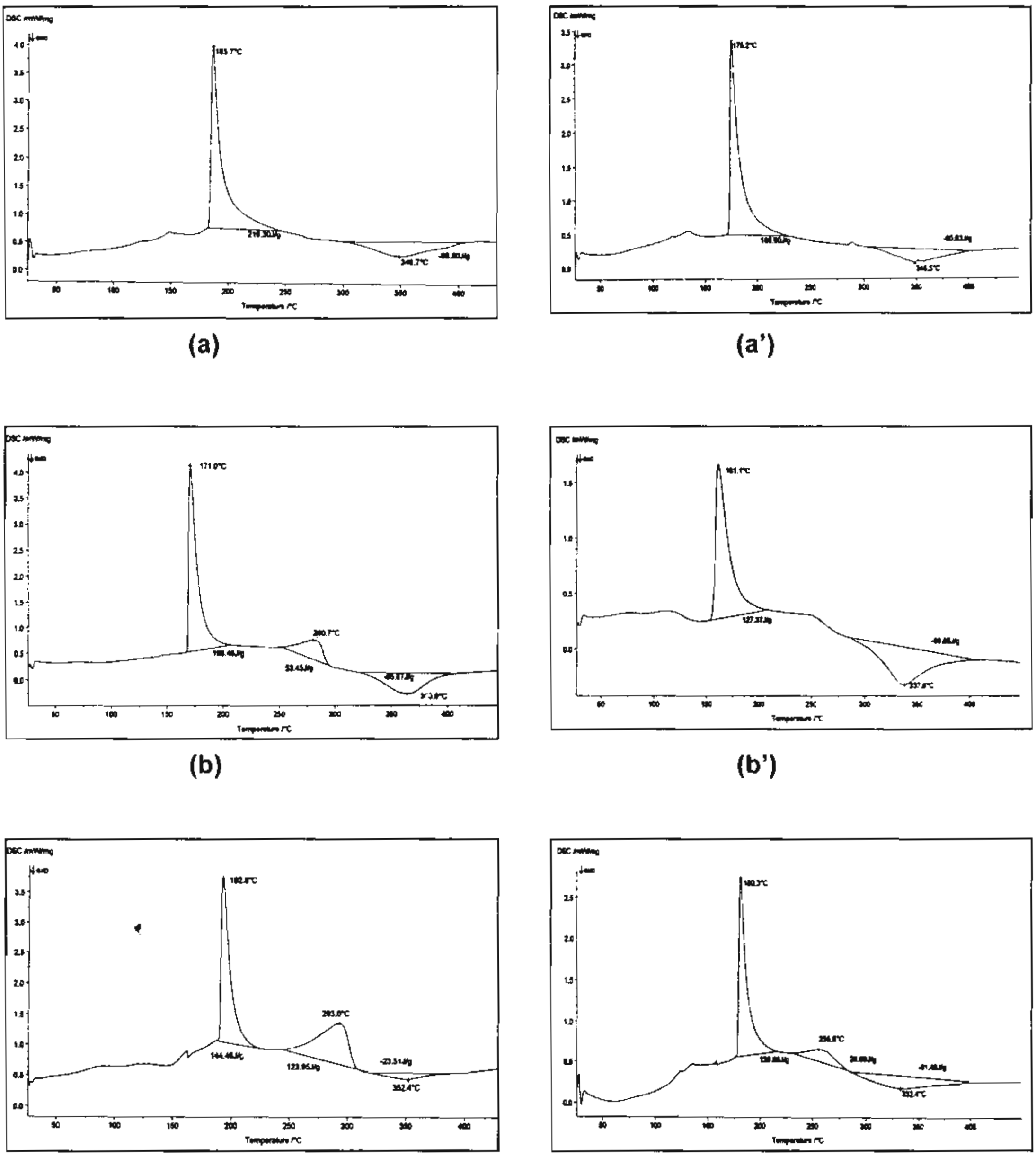
The cured spirosilicates were characterized using FTIR, DSC, TGA, FAB$^+$-MS, ^{1}H- and ^{13}C-NMR. Interestingly, the DSC results of all polymers, as shown in Figure 4.5, indicated that the first endothermic peak occurred approximately 10 °C lower as the monomer became to its corresponding polymer. Generally, the product showed one major endothermic peak on heating, and no exotherm appeared on cooling. It is due to the degradation of the product at elevated temperatures with slow heating rate. Thus a second heating cycle (after the first heat-cool cycle) revealed no endothermic transition as the material had undergone degradation. In case of aminospirosilicates, there was also one small endotherm occurring next to the major one. Probably, this peak was from the cleavage of the hydrogen bondings between amino groups and alkoxy groups since it became smaller when it was a polymer. It is owing to the steric effect of network structure in polymer, resulting in less hydrogen bondings. All DSC results of both monomers and polymers showed one small exotherm around 350 °C corresponding to the oxidative reaction.

The TGA profiles of both monomers polymers gave two regions of mass loss during heating process from room temperature to 950 °C, as shown in Table 4.1. The decomposition temperatures of monomers were higher than those of polymers. The first mass loss resulted from oxidative decomposition of organic ligands. The other mass loss corresponded to the oxidative decomposition of remaining organic residue in the product. The final ashes obtained from pyrolysis of polymers were dark-gray while for monomers they were almost white. This is also another indication of being network structure in polymer products.

Table 4.1 TGA profiles of both monomers and polymers

Sample	**Monomer (°C)**		**Polymer (°C)**	
	1st transition	**2nd transition**	**1st transition**	**2nd transition**
A	160-250	250-550	100-220	220-600
B	120-250	250-500	90-220	220-500
C	120-230	230-320	120-220	220-400

As for the results of FAB$^+$-MS (Tables 4.2-4.4), it is certain that the products had become polymers having network structure since there was no evidence of having monomer molecule or spirosilicate ring part in the spectra, as found in the spectra of monomers[1].



(a) (a')

(b) (b')

(c) (c')

Figure 4.5 DSC thermograms of spirosilicate monomers and their corresponding polymers of (a) A, (b) B and (c) C

Table 4.2 The proposed structure and fragmentation of polymer A

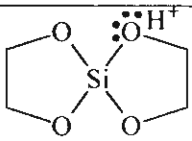
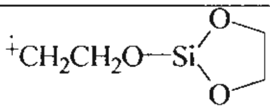
M/e	Intensities		Proposed Structure
	Polymer	Monomer	
149	-	7.0	
132	-	31.6	
72	41.7	9.1	$\dot{+}CH_2CH_2O{-}Si$
58	71.9	100	$\dot{+}CH_2O{-}Si$
44	100	80.9	$\dot{+}O{-}Si$ and $\overset{+}{\cdot}\,CH_2CH_2O$

Table 4.3 The proposed structure and fragmentation of polymer <u>*B*</u>

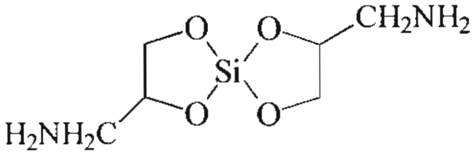
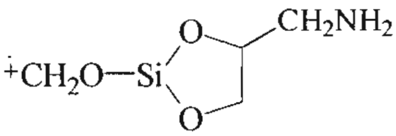
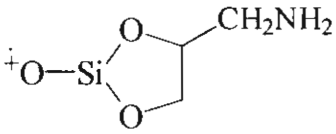
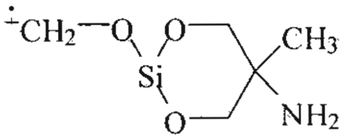
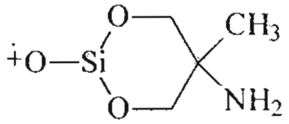
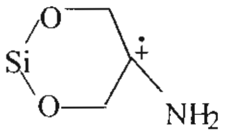
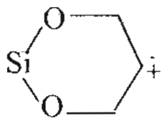
m/e	Intensities		Proposed Structure
	Polymer	Monomer	
206	-	0.8	
147	-	17.6	
133	-	100	
71	100	-	$\dot{+}$ $CHCH_2O$ - Si
58	17.9	4.9	$\dot{+}CH_2O$—Si
44	43.5	42.3	$\dot{+}$O—Si
43	31.5	-	$\dot{+}$ $CHCH_2O$

Table 4.4 The proposed structure and fragmentation of polymer C

m/e	Intensities		Proposed Structure
	Polymer	Monomer	
161	-	0.8	
147	-	1.2	
116	-	13	
100	-	28	
74	-	46	$\overset{\cdot}{+}CH_2O—Si—O$
70	42.9	-	$\overset{+}{\cdot}\,CCH_2O - Si$
58	12.8	54	$\overset{\cdot}{+}CH_2O—Si$
56	100		$\overset{+}{\cdot}\,CH_2CCH_2O$
44	62.9	100	$\overset{\cdot}{+}O—Si$
42	32	-	$\overset{+}{\cdot}\,CCH_2O$

Both ^{1}H- and ^{13}C-NMR spectra (Figures 4.6 and 4.7) gave similar results to those of monomer although the peaks were weaker due to the less solubility of polymers in deuterated dimethylsulfoxide. This is not unsurprising since it is often found in thermosetting polymers. All spectra showed the H_2O contained in deuterated DMSO and absorbed by the product at δ = 3.3 ppm, in agreement with the FTIR results (Figure 4.9). Polymer A showed one singlet at δ = 3.4 ppm, corresponding to the four hydrogen atoms (2H) of CH_2-O-Si. Polymer B gave three peaks at δ = 2.45 and 2.55 ppm (doublets) belonging to the 2H of CH_2-N being influenced from the adjacent chiral carbon atom, δ = 3.3 ppm (doublet) referring to the 2H of CH_2-O-Si. Again, the 1H of CH-O-Si was unfortunately overlapped with the H_2O peak. However, this missing peak can be confirmed by ^{13}C-NMR data. The ^{1}H-NMR spectrum of polymer C showed clearer chemical shifts at δ = 0.8 ppm belonging to -CH_3 and δ = 3.2 ppm corresponding to CH_2-O-Si.

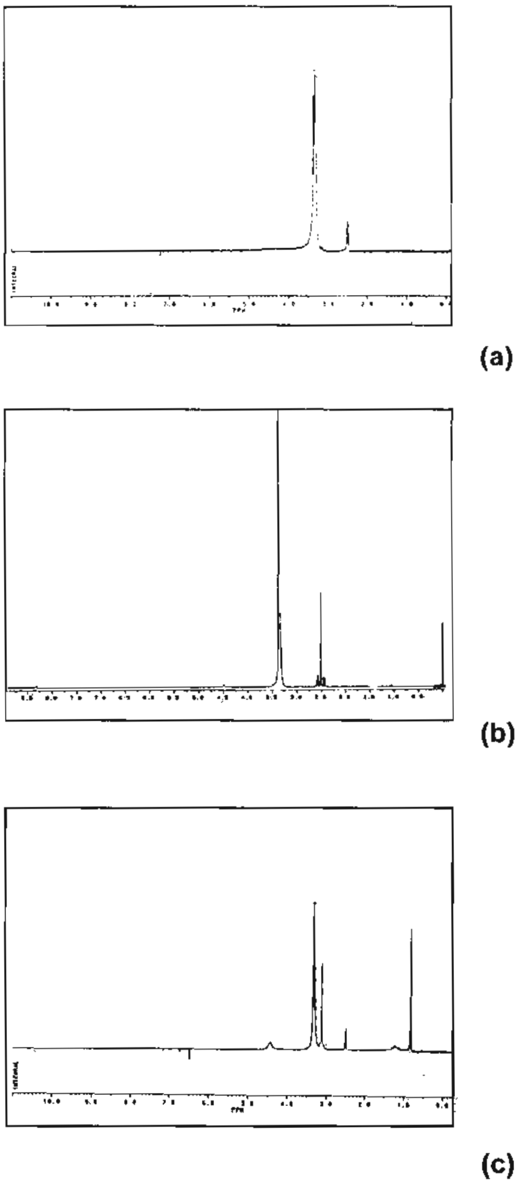


Figure 4.6 ^{1}H-NMR spectra of cured spirosilicate (a) A, (b) B and (c) C

The ^{13}C-NMR spectra, as shown in Figure 4.7, can confirm the structures of polymer products. Polymer *A* showed only one peak at δ = 63 ppm (CH_2-O-Si) while polymer *B* gave three peaks at δ = 45 ppm (CH_2-N), δ = 64 ppm (CH_2-O-Si) and δ = 73 ppm (CH-O-Si). Polymer *C* showed 3 corresponding peaks at δ = 23 ppm (-CH_3), δ = 54 ppm (C) and δ = 67 ppm (CH_2-O-Si).

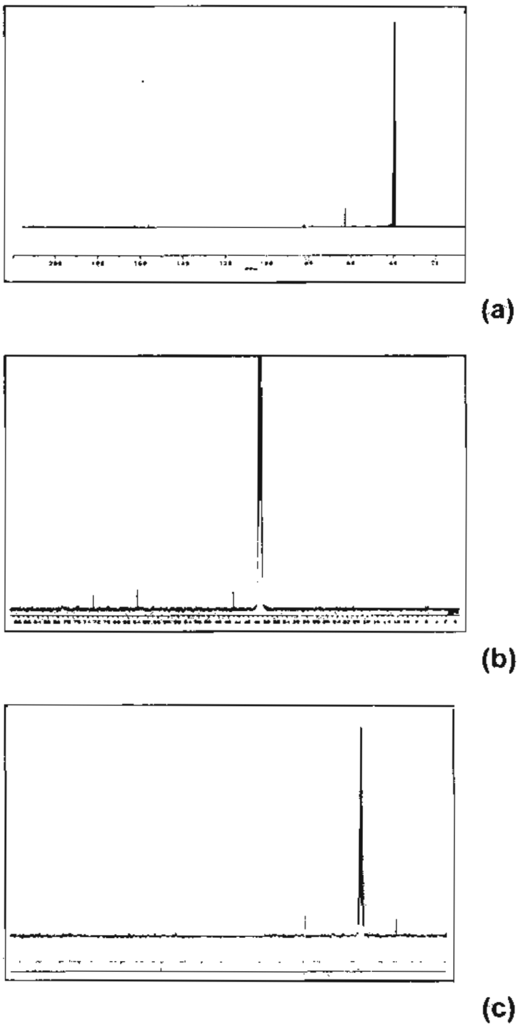


Figure 4.7 ^{13}C-NMR spectra of cured spirosilicate (a) *A*, (b) *B* and (c) *C*

To be certain whether the cured products are the expected ones, ^{13}C-Solid state NMR was employed, see Figure 4.8. The results clearly show the desired product structures.

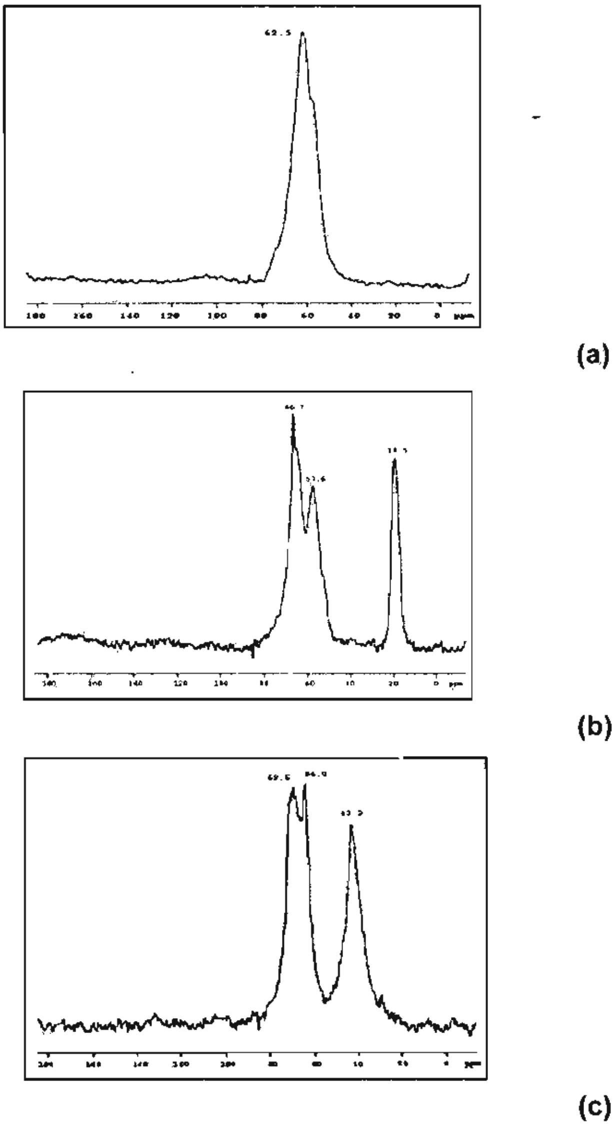
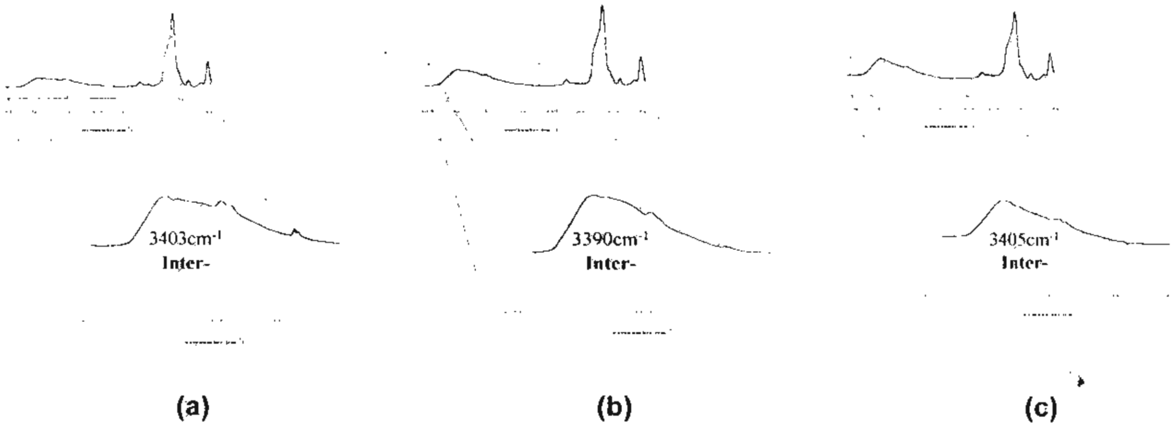


Figure 4.8 ^{13}C-Solid State NMR spectra of cured spirosilicate (a) A, (b) B and (c) C

The FTIR spectra (Figure 4.9) intensively showed the band around 1080 cm^{-1}, corresponding to the Si-O-C stretching. Unsurprisingly, the OH stretching around 3390-3400 cm^{-1} which was from water absorbed was much smaller, as compared with FTIR spectra of monomers. However, the intensity of this peak was bigger in the order of polymers A < B < C due to the steric effect of the cured products. The bulkier the product, the loser the network, as a result, the more hydrogen bonding between water-product and product-product, as studied by Cairn[16]. Cairn studied the hydrogen bonding in phenol structure and found that Infrared spectroscopy (FTIR) technique can distinguish between inter- and intramolecular hydrogen bonding. As can be seen in Figure 4.10, it can be concluded that free hydroxyl group appears as a sharp peak around 3600 cm^{-1}, the intramolecular hydrogen bonding is present as a broad band around 3500 cm^{-1} and intermolecular hydrogen bonding shows a broad band around 3400 cm^{-1}. That means, our cured polymers contained intermolecular hydrogen bonding because of the presence of the peak at 3390-3400 cm^{-1}.



(a) (b) (c)

Figure 4.9 FTIR spectra of cured spirosilicate (a) _A_, (b) _B_ and (c) _C_

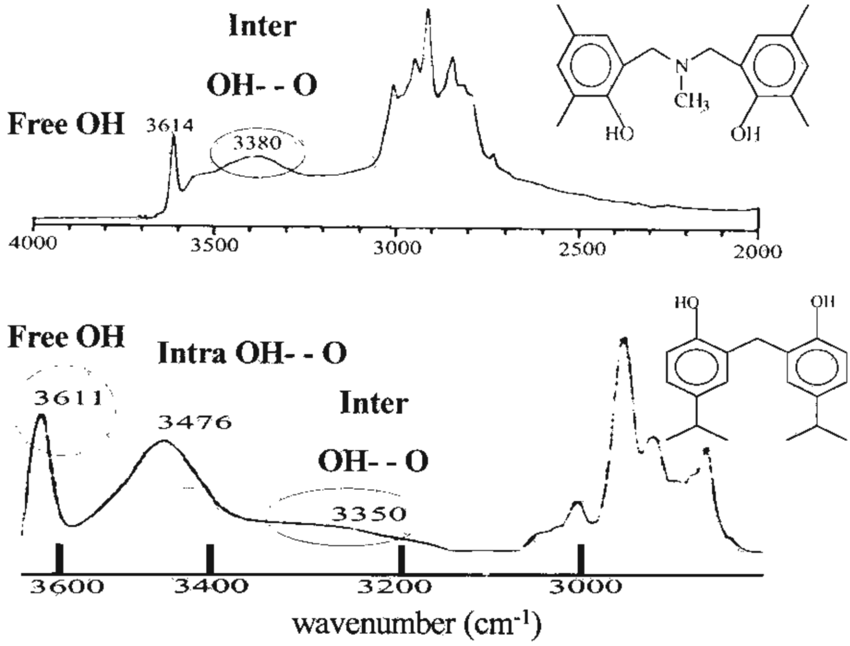


Figure 4.10 FTIR spectra of a) Methylamine based dimers and b) Novolak.

(Cairn, T., Eglinton, G , Journal of Chemical Society, **1965**, 5906-5913)

After polymerizing the purified monomers, the volumetric change of polymers as compared to their corresponding monomers were studied and found that all materials showed small amount of volumetric shrinkage property, as summarized in Table 4.5. As discussed previously, intermolecular hydrogen bonding had significant effect on the volumetric shrinkage property of all products. The more hydrogen bonding in the structure caused the higher shrinkage and the closer the molecule[17]. In the case of cured spirosilicate C, due to the steric hindrance in the structure, it has more effect to occur hydrogen bonding, resulting in smaller volumetric change as compared to A and B spirosilicate products, which B has free amino group that can move easily to form hydrogen bonding.

Table 4.5 The volumetric property of spirosilicates A, B and C

Sample	**Density (g/cm^3) ***		**Result (%)****
	Monomer	**Polymer**	
A	1.7342	1.7517	-1.01
B	1.6111	1.6329	-1.35
C	1.5537	1.5638	-0.65

** (-) Shrinkage; (+) Expansion

* The data was averaged from 3 repeatedly experimental values.

Conclusions

The volumetric property of purified spirosilicate and aminospirosilicate derivative products showed near-zero shrinkage property. It was reported to be an important parameter of the molecular packing. This packing has been caused from intermolecular hydrogen bonding between hydroxyl group and hydroxyl group or hydroxyl group and amino group of curing structures. Moreover, the hydrogen bonding is also influenced from the steric hindrance of its attaching group. The higher steric hindrance, the less hydrogen bonding is, resulting in the less shrinkage property. In addition, aminospirosilicate derivatives are expected to use further as a starting material in benzoxazine synthesis. The products would decrease or minimize the non-dimensional stability, which makes the materials have a high potential to use in engineering industry applications.

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CHAPTER V

SYNTHESIS OF SPIROSILICATE/BENZOXAZINE COMONOMER

Abstract

Benzoxazine, a novel phenolic resin, undergoes polymerization via ring-opening polymerization. Polybenzoxazine shows good properties, such as no production of by-products upon curing, and exhibition of near-zero shrinkage, whereas spirosilicate compounds, obtained by reacting silica with ethylene glycol or ethylene glycol derivatives, also show a near zero shrinkage. The spirosilicate/benzoxazine comonomers were synthesized to obtain the materials which are expected to have a near zero shrinkage property. The new benzoxazines would be synthesized from protecting hydroxyl groups of 2-amino-2-methyl-1,3-propanediol by using cyclohexanone to form ketal product. The ketal was reacted with formaldehyde and phenol to give benzoxazines. The as-synthesized spirosilicate/ benzoxazine comonomer was characterized using TGA, FTIR, FAB^+-MS, ^1H- and ^{13}C-NMR.

Introduction

Synthetic polymers are important in the modern life, especially phenolic resins which are the oldest synthetic polymers. Phenolic resins are produced by the reaction of phenol with aldehyde which are raw materials from petrochemical supply, quite versatile and inexpensive. In most applications, phenolics are combined with reinforcing fillers or fibers to give a function as the adherent or the critical binder of the composition. These phenolic resins bonded materials, i.e. particleboards, molding materials, fiber insulation products, foundry cores, grinding wheels, friction elements, represent the largest consumption. Phenolics can also be copolymerised with other condensation polymers having attractive features, such as high temperature resistance, infusibility and flame retardance. Their applications involve several fields, for example, aerospace, appliance, automotive, construction, clothing and also medical.

While phenolics have many advantages, they do have disadvantages. They release the volatiles, such as H_2O, CH_2O, and NH_3 during curing process, which makes fabrication of void free materials extremely difficult. Due to their brittleness, they are usually used with fillers. Phenolics can be cured with strong acids to produce novolac or bases to yield resole materials. These processes cause the corrosion effect. In addition, phenolic materials have poor molecular design flexibility since the main structures; phenol, and formaldehyde, cannot be changed much. Thus, if these problems can be overcome, it will be greatly useful in commercial applications, and benzoxazines based phenolic resins have been developed as a new alternative to overcome the shortcomings.

Benzoxazine

A phenolic derivative, a ring compound formed from a primary amine and formaldehyde via Mannich reaction, is termed benzoxazine. Benzoxazines based phenolic resins overcome those drawbacks of the traditional phenolics. They were found to react with the ortho position of a phenolic compound to form a dimer with methylene-amine-methylene bridge structure. The process has no volatiles during curing because it proceeds by ring opening polymerization. Due to the synthesis by Mannich condensation of a phenol, formaldehyde and an amine, they do have much more molecular design flexibility than novolac and resole materials. Based on the main chain structure and the properties, polyoxazines provide tremendous freedom in design which can modify products based on the structure-property relationships.

The formation of benzoxazine compounds proceeds according to the reaction in figure 5.1.

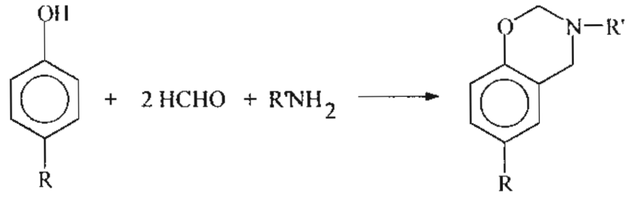


Figure 5.1 The formation of benzoxazine compounds.

The ring opening reaction of a monofunctional benzoxazine initiated by a para-substituted phenol is shown in figure 5.2.

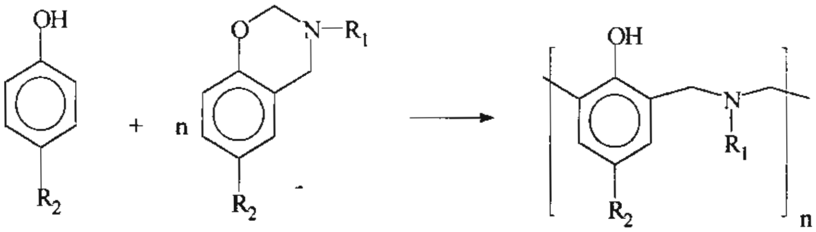


Figure 5.2 Ring opening reaction of a monofunctional benzoxazine initiated by a para-substituted phenol.

Spirosilicate Compounds

For phenolic resins, they require fillers, such as, cellulose flour, wood flour, and more commonly mineral fillers to reduce shrinkage, but these fillers can be abrasive to the mold surface. Various fillers are incorporated into the matrix and molding conditions are modified to reduce resin shrinkage. However, they can not delete this problem, only reduce it.

Bailey and co-worker (1973) introduced a series of spiroortho compounds which are spiroorthoesters and spiroorthocarbonates that expand upon curing[1].

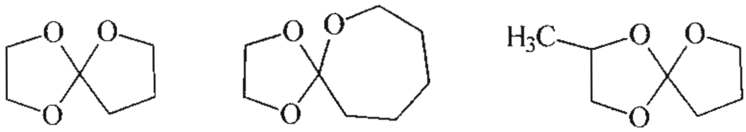
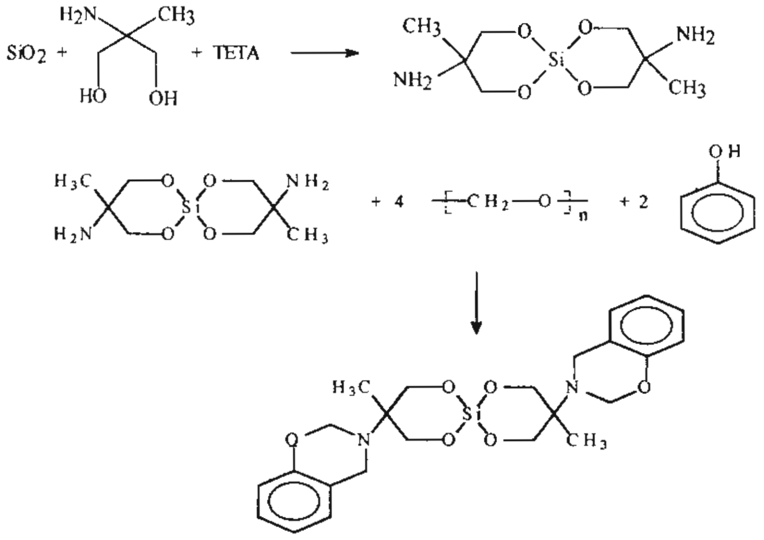


Figure 5.3 Examples of spiroorthoesters

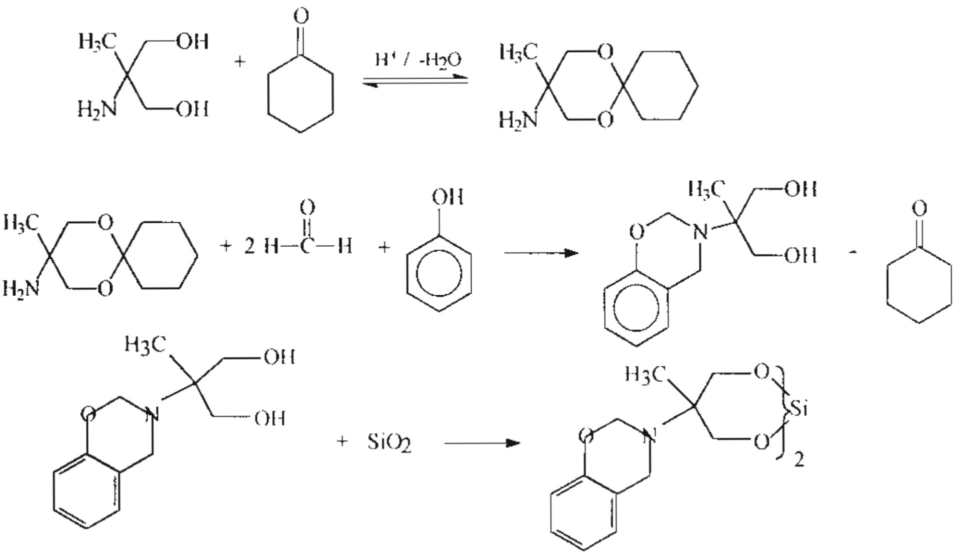
The author's group successfully synthesized spirosilicate compounds directly from silica and ethylene glycol/ethylene glycol derivatives. Spirosilicate C3 is synthesized from silica and 3-amino-1,2-propanediol, while spirosilicate C4 is from silica with 2-amino-2-methyl-1,3-propanediol. Both are produced in the presence of TETA as both catalyst and solvent. We also investigated the volumetric property of aminospirosilicate compounds, and found that the spirosilicates C3 and C4 show near zero shrinkage upon curing.

The aim of this research is to synthesize benzoxazine/spirosilicate comonomer via the following schemes.



Spirosilicate/benzoxazine C4

Scheme 5.1 The reactions of benzoxazine/spirosilicate comonomers starting from the synthesis of spirosilicate.



Scheme 5.2 The reactions of benzoxazine/spirosilicate comonomers starting from the synthesis of benzoxazine.

Experimental

Materials

Fumed silica, 2-amino-2-methyl-1,3-propanediol and 3-amino-1,2-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 purified by distillation under vacuum at 120°C. It was used as a base catalyst and solvent. Potassium hydroxide (KOH) was purchased from J.T. Baker Company Co., Ltd., and sodium hydroxide (NaOH) was purchased from EKA Chemicals Company Co., Ltd., used as catalyst and as received. Acetonitrile and methanol were purchased from Labscan Asia Company Co., Ltd., and J.T. Baker Company Co., Ltd., and were purified by fractional distillation under nitrogen gas over calcium hydride and magnesium activated with iodine, respectively. Both were stored over molecular sieves under nitrogen gas and were used as precipitation agents. Cyclohexanone was purchased from Ajax Laboratory Chemical Company Co., Ltd., and was purified by fractional distillation under nitrogen gas over calcium hydride. It was stored over molecular sieves under nitrogen gas and was used as protecting agent. Hydrochloric acid solution (36%wt) was purchased from Ajax Laboratory Chemical Company Co., Ltd., and used as acid catalyst in ketal formation and as received. Phenol was purchased from Ajax Laboratory Chemical Company Co., Ltd., and used as received. Formaldehyde solution (37%wt) and paraformaldehyde were purchased from Merck Company Co., Ltd., and used as received. They were used as starting materials for benzoxazine synthesis. 1,4-Dioxane was purchased from Ajax Laboratory Chemical Company Co., Ltd. It was purified by distialltion over calcium hydride and kept in sealed container. Diethyl ether was purchased from J.T. Baker Company Co., Ltd., and it was stored over magnesium sulfate. UHP grade nitrogen gas with 99.99% purity was purchased from Thai Industrial Gases Public Company Limited (TIG).

Equipment

FTIR spectra were obtained by using a VECTOR 3.0 BRUKER spectrometer with 32 scans at a resolution of 2 cm^{-1}. A frequency range of 4000-400 cm^{-1} was observed using a deuterated triglycinesulfate detector (DTGS) with specific detectivity of D^{*}, of 1×10^{9} $cm \times Hz^{1/2} \times W^{-1}$. Both neat techniques on ZnSe plate and KBr pellet were used. ^{1}H-NMR and ^{13}C-NMR spectra were performed on a Bruker 500 MHz spectrometer at room temperature. The samples were pulsed at 500 MHz for proton and 200 MHz for carbon NMR with a spin rate of 21 rpm. A relaxation delay time was 1 sec with a sweep width of 3105 Hz or about 15 ppm, using a pulse of 45 µsec. Deuterated dimethyl sulfoxide (DMSO-d_6), deuterated chloroform, and deuterated methanol were used as solvents. 16 scans were run for proton NMR while carbon NMR samples were pulsed for more than 2 hours or more than 400 scans. Tetramethylsilane (TMS) was used as the reference for chemical shift measurements in both proton and carbon NMR. Thermograms were conducted using Thermogravimetric Analysis (TGA) mode. They were carried out on a Netzsch instrument, TA 209 cell, respectively, with TASC 414/3 controller in nitrogen gas, N_2. Sample weights were typically from 5-10 mg. For TGA measurements, the purge flow rate of nitrogen was set at 60 ml/min and 40 ml/min for the balance. The temperature analysis range in the TGA using a ramp rate of 10°C/min was from 30°C to 750°C. Mass spectra were obtained using a VG Autospec model 7070E from Fison Instruments with VG data system. Samples were run in the positive fast atomic bombardment ($FAB\text{-}MS^{+}$) mode using glycerol as the matrix. Cesium gun was used as an initiator and cesium iodine (CsI) was used as a reference.

Methodology

Starting from benzoxazine

Protecting Hydroxyl Groups of 2-Amino-2-methyl-1,3-Propanediol (C4)

To obtain optimum conditions for synthesis of ketal C4, 2 variations, reaction time and temperature, in the reaction were studied.

A mixture of 0.02 mmol (2.10g) 2-amino-2-methyl-1,3-propanediol, 0.02 mmol (1.963g) cyclohexanone and 5% by vol of 1 M HCl was placed into a 50 mL two-neck round bottomed flask equipped with a simple distillation set. The mixture was heated to the temperature 100° and 110°C under nitrogen atmosphere to distill off water produced during the reaction. The reaction time was varied from 0-5 hours.

Synthesis of Benzoxazine from Formaldyhyde, Phenol and Ketal C4

A mixture of 0.01 mmol (1.8515g) of ketal C4 and 0.023 mmol (1.86g) of formaldehyde solution was placed into 50 mL two-neck round bottomed flask equipped with a simple distillation set. The reaction mixture was left at 20°C for 2 hours. 0.01 mmol (0.9411g) phenol was then added, and the reaction was heated to 110°C for 2 hours. The as-product, benzoxazine C4, was obtained.

Synthesis of Spirosilicate C4/benzoxazine Comonomer from Silica and Benzoxazine C4

By following the synthesis of the spirosilicate C4, the as-product, benzoxazine C4, was reacted with fumed silica at the approximate ratio of 2:1. The reaction mixture was heated at 160 °C under vacuum (1 torr) for 10-16 hours.

Starting from spirosilicate

Synthesis of Spirosilicate C4 from Silica and 2-Amino-2-methyl-1,3-propanediol

The aminospirosilicate product (C4) was synthesized followed Sun's method from fumed silica and 2-amino-2-methyl-1,3-propanediol, using triethylenetetramine (TETA) as both catalyst and solvent and small amount of potassium hydroxide as a co-catalyst. The reaction was done under vacuum (1 torr) at 160°C for 14 hours. The product was precipitated using trace amount of methanol in acetonitrile. It was then kept under nitrogen atmosphere to use as a starting material in the step of benzoxazine derivative synthesis.

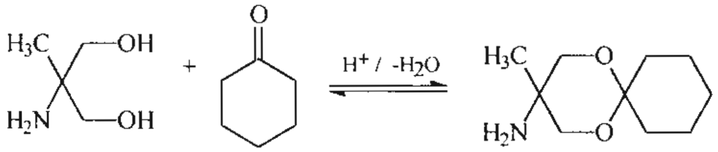
Synthesis of Spirosilicate C4/benzoxazine Comonomer

A mixture of 0.01 mmol (2.34g) spirosilicate C4, 0.043 mmol (1.29g) paraformaldehyde was placed into a 50 mL two-neck round bottomed flask equipped with a simple distillation set under nitrogen atmosphere. The mixture was heated at 80°C for 3 hours. Then 0.02 mmol (1.882g) phenol was added and the reaction mixture was heated to 110°C for 3 hours.

Results and Discussion

Protecting Hydroxyl Groups of 2-Amino-2-methyl-1,3-propanediol

In this study, ketal C4 product was synthesized directly from a mixture of 2-amino-2-methyl-1,3-propanediol and cyclohexanone in the presence of hydrochloric acid as a catalyst. Since water produced during the equilibrium reaction hydrolyzed the product, it must be removed out from the system to push the reaction forward, as illustrated in equation (5.1).



(5.1)

Effect of Reaction Time and Temperature on the Ketal C4 Synthesis

The mixture of 2-amino-2-methyl-1,3-propanediol and cyclohexanone in the presence of hydrochloric acid was heated to 100°C and 110°C for a variation of time, 0-5 hours. Sampling of the mixture was done every hour to follow the reaction, using FTIR.

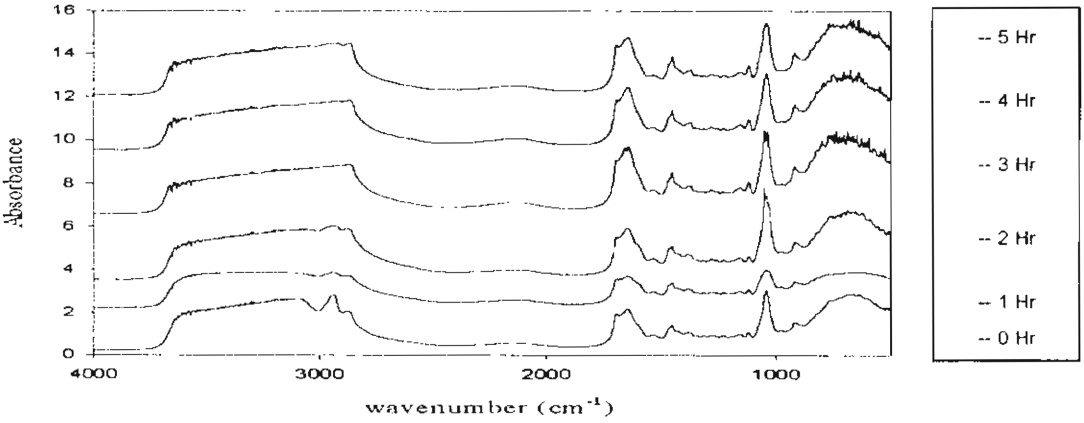


Figure 5.1 FTIR spectra of the crude product of ketal C4 at 100°C from 0-5 hours.

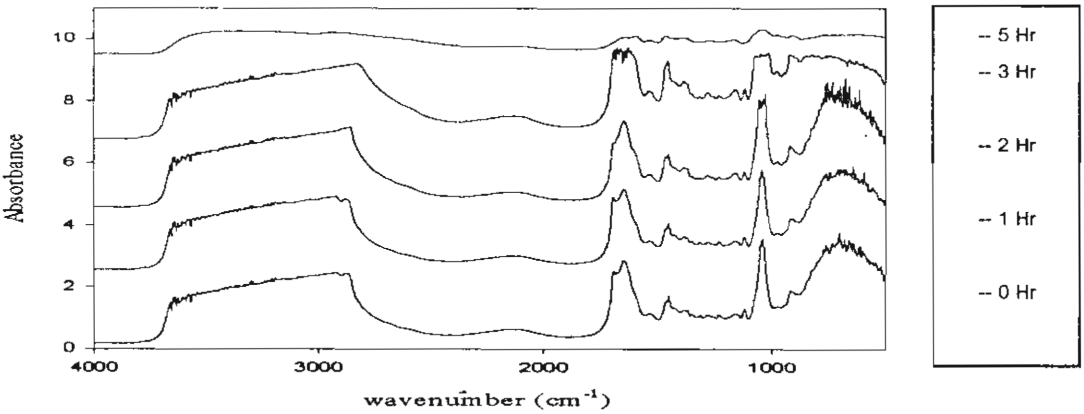


Figure 5.2 FTIR spectra of the crude product ketal C4 at 110°C from 0-5 hours.

From FTIR spectra in figures 5.1 and 5.2, as the reaction went on, the peak at 1693 cm^{-1} representing C=O in cyclohexanone was decreased whereas the peaks at 1044 cm^{-1} and 915 cm^{-1} representing C-O-C in ketal structure were increased. As compared with the results from both temperatures, the suitable condition for ketal C4 synthesis is at temperature 100°C for 2 hours.

The product was separated by using column chromatography packed with silica gel as a stationary phase and a mixture of acetonitrile and methanol was used as a mobile phase. The solvents in the selected fractions were evaporated out to obtain powder product.

Figure 5.3 shows a broad band at 3274-3165 cm^{-1} corresponding to $-NH_2$ stretching, whereas, the band at 2933-2860 cm^{-1} results from C-H stretching. The C-O-C functional group in the ketal product is assigned by the bands at 1046 and 927 cm^{-1}.

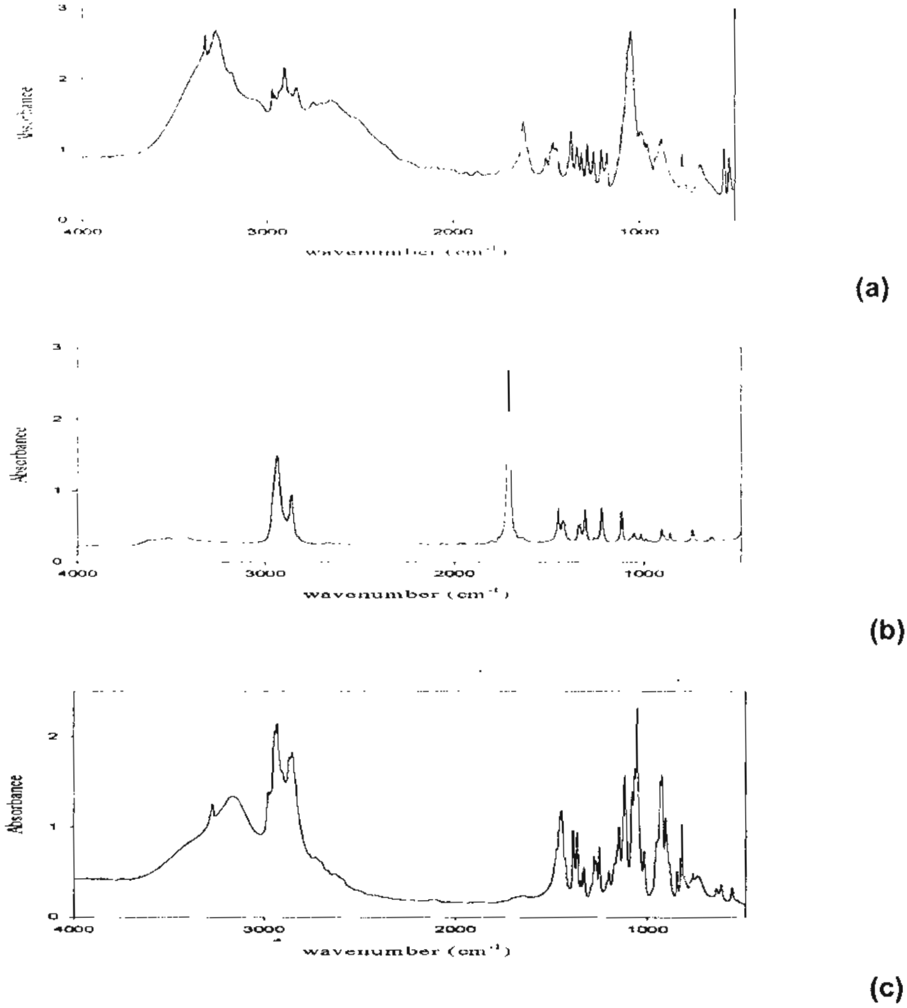


Figure 5.3 FTIR spectra of (a) 2-amino-2-methyl-1,3-propanediol, (b) cyclohexanone, and (c) ketal C4 product.

The spectra of ^{1}H- and ^{13}C-NMR of ketal C4 are shown in figures 5.4 and 5.5, respectively. From the results, it is clearly showed the expected ketal product.

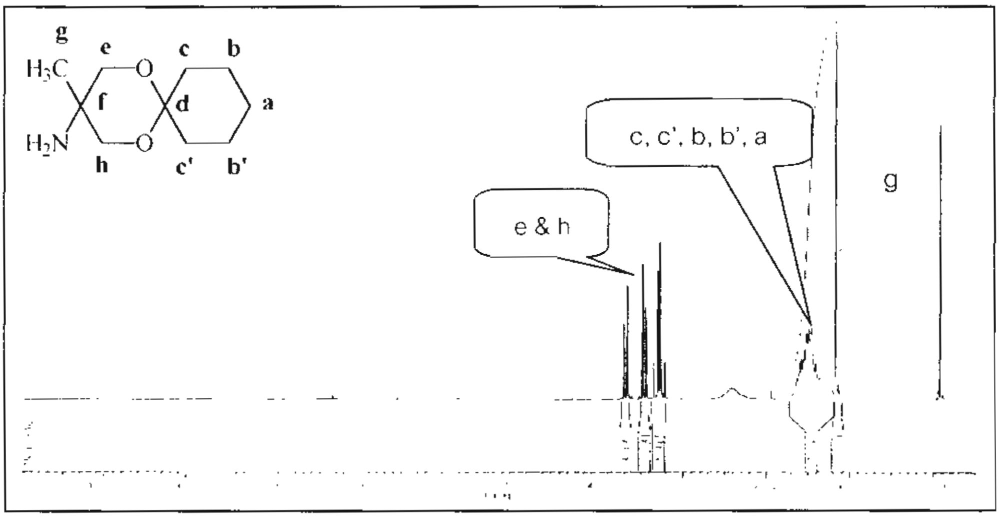


Figure 5.4 ^{1}H-NMR of ketal C4.

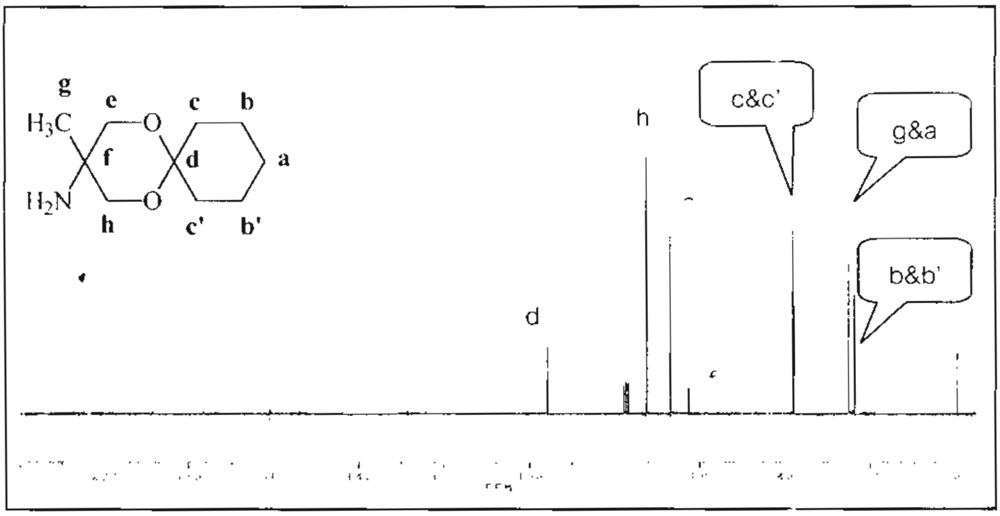
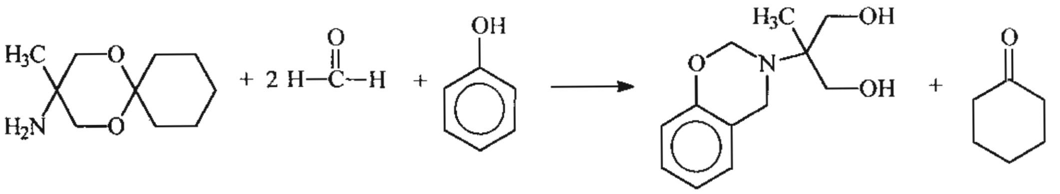


Figure 5.5 ^{13}C-NMR of ketal C4.

Synthesis of Benzoxazine from Ketal C4

In this study, benzoxazine C4 product was synthesized directly from a mixture of ketal C4, formaldehyde and phenol, as illustrated in equation 5.2.



(5.2)

This reaction gave cyclohexanone, the protecting agent, as a by-product due to the decomposition of ketal structure since phenol acted as acid catalyst and the reaction was heated.

The product was separated by liquid extraction using ether and 1N NaOH solution. Further separation was done by neutralizing the NaOH layer and then ether was used in liquid extraction. The ether layer was selected and evaporated out to obtain the final product.

Figure 5.6 shows FTIR spctrum of the as-synthesized benzoxazine C4. The peak at 1500 cm^{-1} represents the di-substituted benzene ring-mode in the oxazine structure, while the peak at 1475 cm^{-1} represents the di-substituted benzene ring-mode in the ortho-substituted (methylene-amine-methylene bridge) phenolic structure formed by the reaction between the oxazine ring and the free ortho position of phenol. Moreover, the bands at 755 and 692 cm^{-1} represent the 1,2-disubstituted benzene ring in the benzoxazine structures.

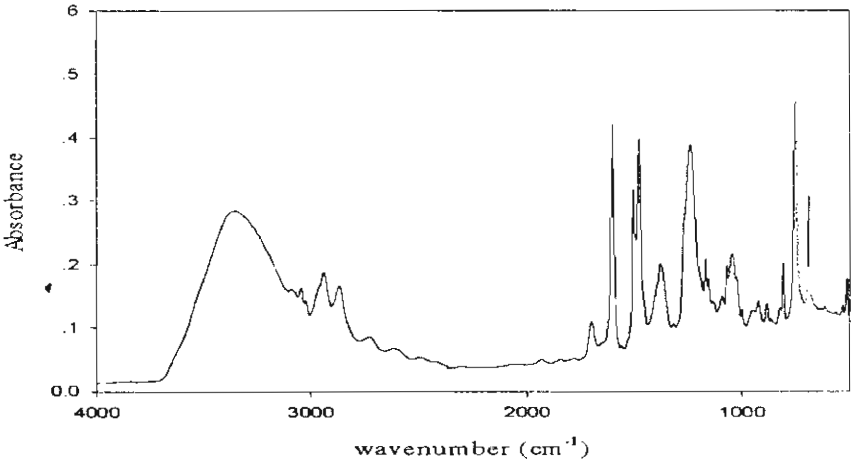


Figure 5.6 FTIR spctrum of benzoxazine C4.

Figure 5.7 illustrates the FAB^+-mass spectrum of benzoxazine C4. The fragmentation of the proposed product is shown in table 5.1. Interestingly, the mass spectrum also shows some amounts of phenolic dimer (m/e=212), meaning that the benzoxazine synthesis also gave phenolic oligomers as by products.

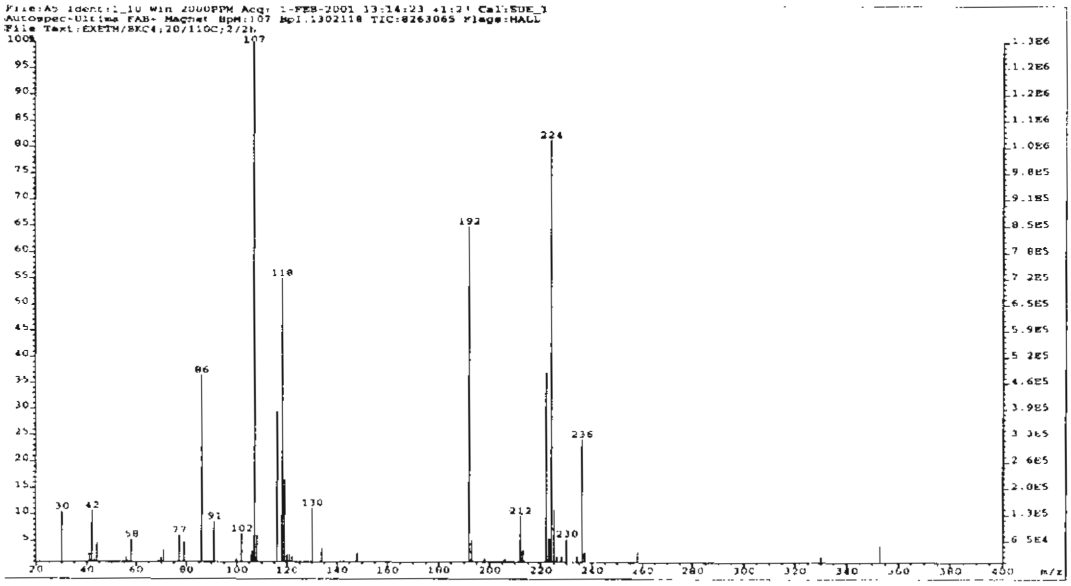
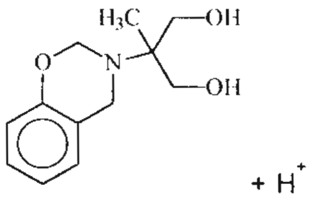
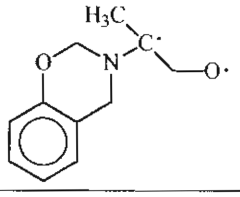
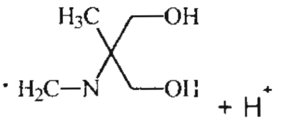
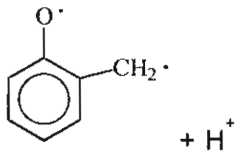


Figure 5.7 The mass spectrum of benzoxazine C4.

Table 5.1 The proposed structure and fragmentations of the product.

m/e	Intensities	Proposed structure
224	81.43	
192	65.00	
118	55.13	
107	100	

The ^{1}H- and ^{13}C-NMR spectra of benzoxazine C4 are shown in figures 5.8 and 5.9, respectively. Both spectra are in agreement with the result of FAB^{+}-MS spectrum. That is, the obtaining product contains both benzoxazine and phenolic products.

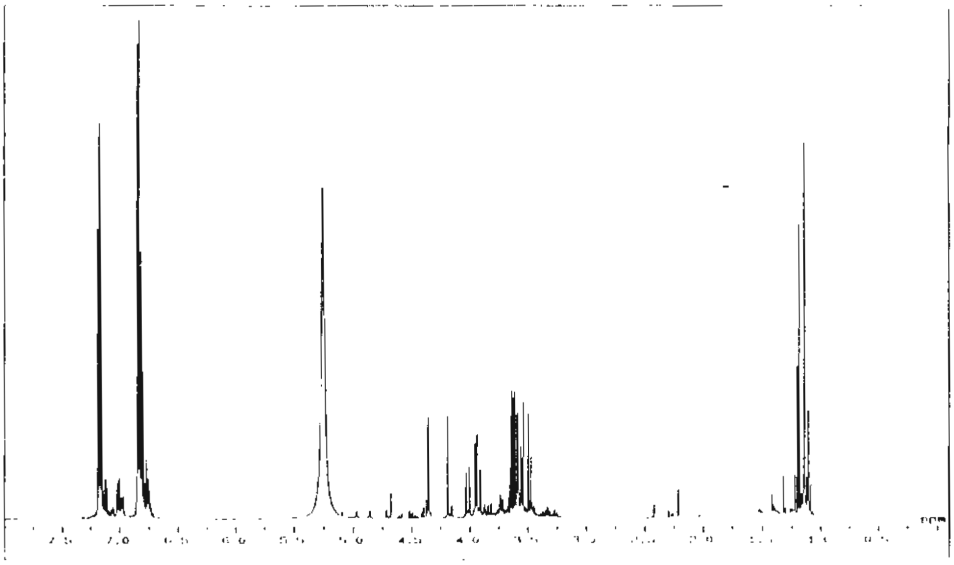


Figure 5.8 ^{1}H-NMR of benzoxazine C4.

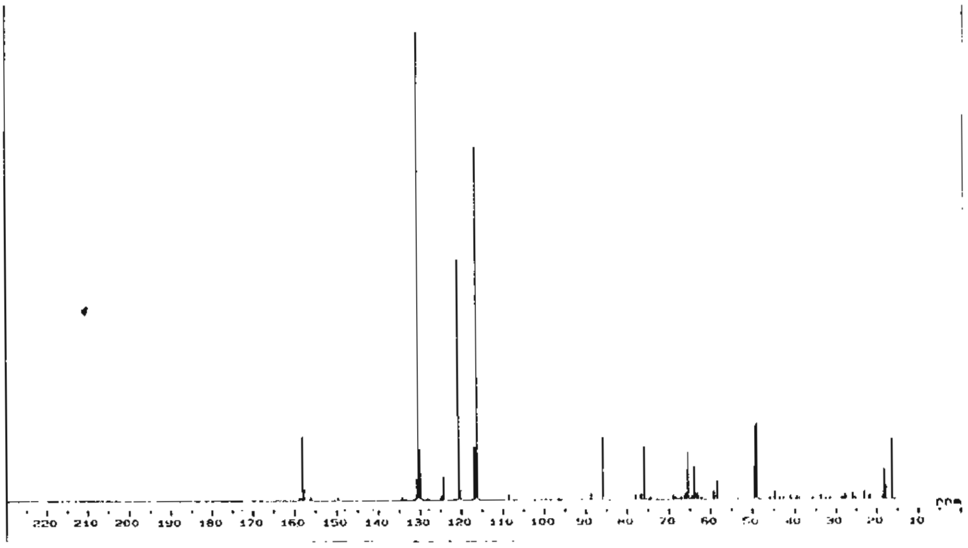
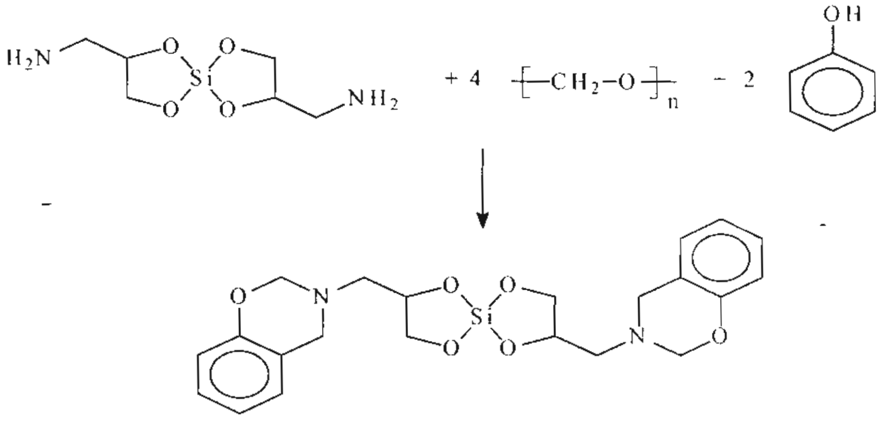


Figure 5.9 ^{13}C-NMR of benzoxazine C4.

Synthesis of Spirosilicate/benzoxazine C3 Comonomer

In this study, spirosilicate/benzoxazine C3 product was synthesized directly from a mixture of aminospirosilicate C3, paraformaldehyde and phenol, as illustrated in equation 5.3.



Spirosilicate/benzoxazine C3 comonomer

(5.3)

Figure 5.10 shows FTIR spectrum of the spirosilicate/benzoxazine C3 comonomer. The peak at 1511 cm^{-1} represents the oxazine ring structure. The band at 1092-1214 cm^{-1} represents the Si-O and Si-O-C peaks. The peak at 759 cm^{-1} refers to the benzene ring in the comonomer structure. By comparing the intensities of oxazine ring to the Si-O and Si-O-C peaks, it was found that the product was not pure. It may contain silica, the starting material, and need to be purified.

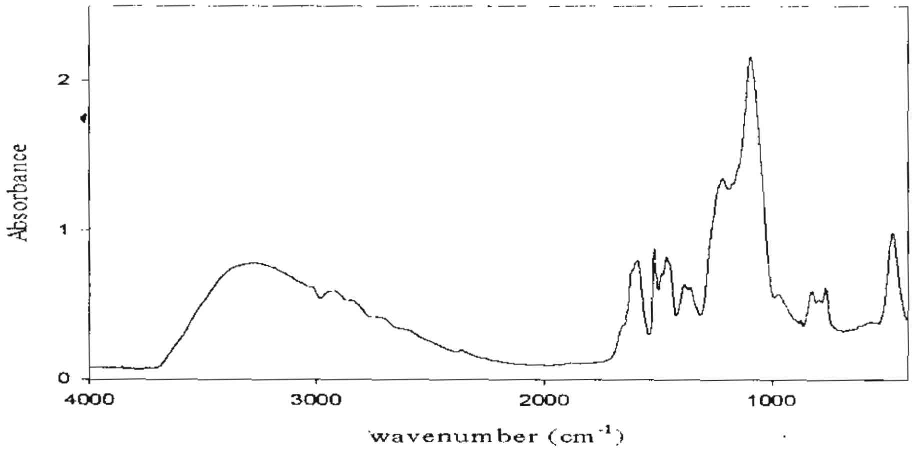


Figure 5.10 FTIR spectrum of spirosilicate/benzoxazine C3 comonomer.

The mass spectrum of spirosilicate/benzoxazine C3 comonomer is illustrated in figure 5.11. The fragmentation of the product is shown in table 5.2.

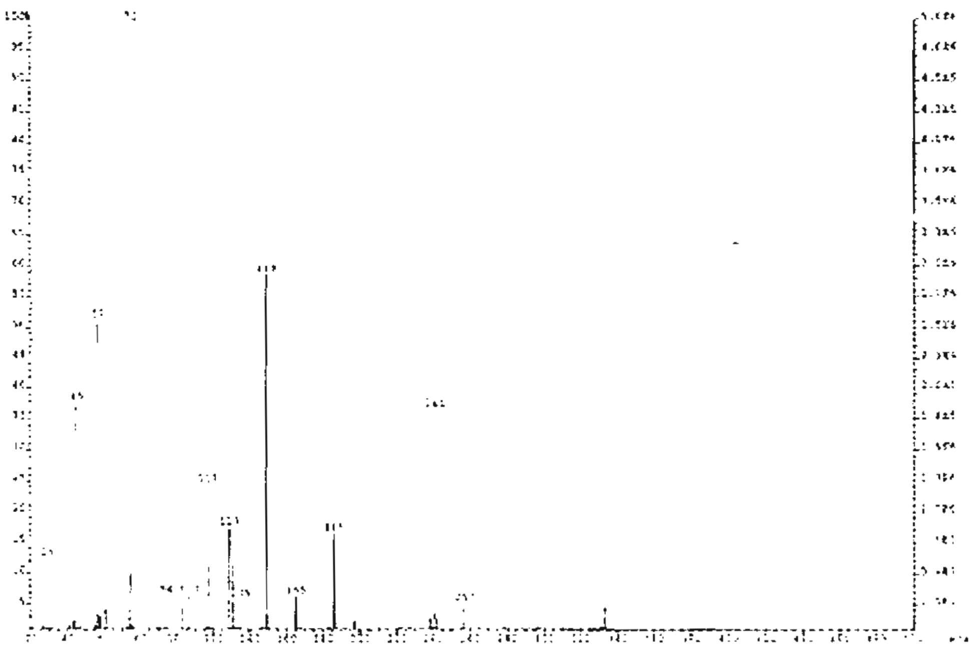
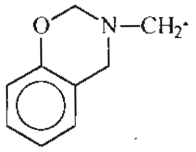
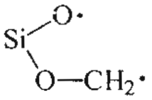
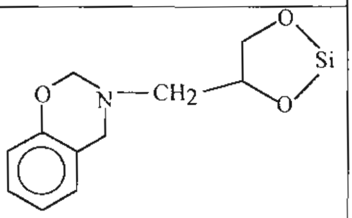
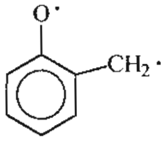
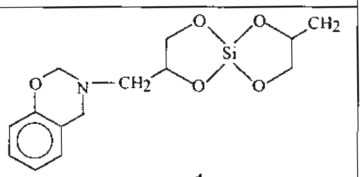
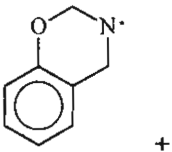


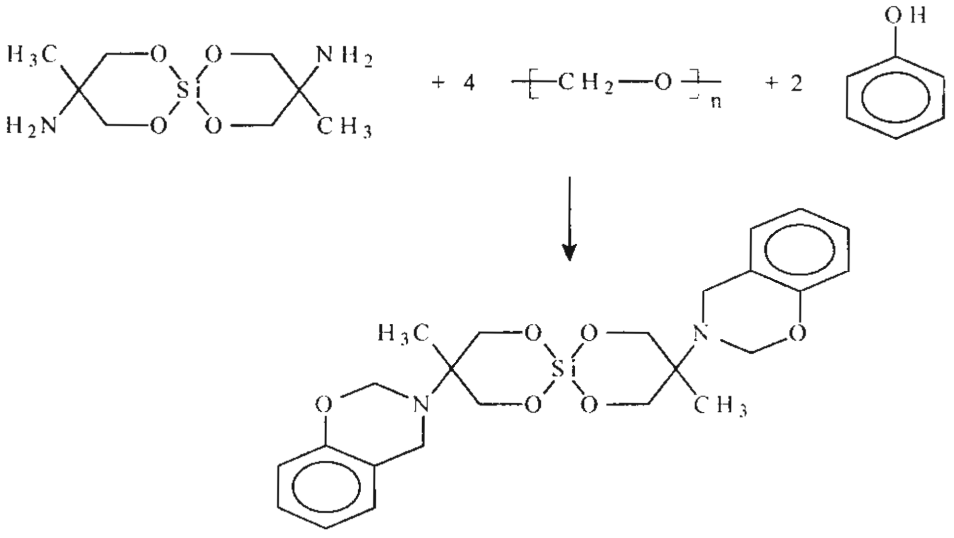
Figure 5.11 The mass spectrum of spirosilicate/benzoxazine C3 comonomer.

Table 5.2 The proposed structure and fragmentations of the product.

m/e	Intensity	Proposed structrue	m/e	Intensity	Proposed structrue
45	38	Si-O + H^+	149	59	 + H^+
75	100	 + H^+	251	5	 + H^+
107	6	 + H^+	309	4	 + H^+
135	6	 + H^+			

Synthesis of Spirosilicate/benzoxazine C4 Comonomer

In this study, spirosilicate/benzoxazine C4 comonomer was synthesized directly from a mixture of aminospirosilicate C4, paraformaldehyde and phenol, as illustrated in equation 5.4.



Spirosilicate/benzoxazine C4

(5.4)

Figure 5.12 shows FTIR spectrum of the spirosilicate/benzoxazine C4 comonomer. The weak peak at 1511 cm^{-1} represents the oxazine ring structure. The band at 1092-1214 cm^{-1} represents the Si-O and Si-O-C peaks. The peak at 759 cm^{-1} refers to the benzene ring in the comonomer structure. By comparing the intensities of oxazine ring to Si-O and Si-O-C peaks, it was found that the product was not pure. This was confirmed using FAB^{+}-MS and the result showed some amount of fragments belonging to the desired product.

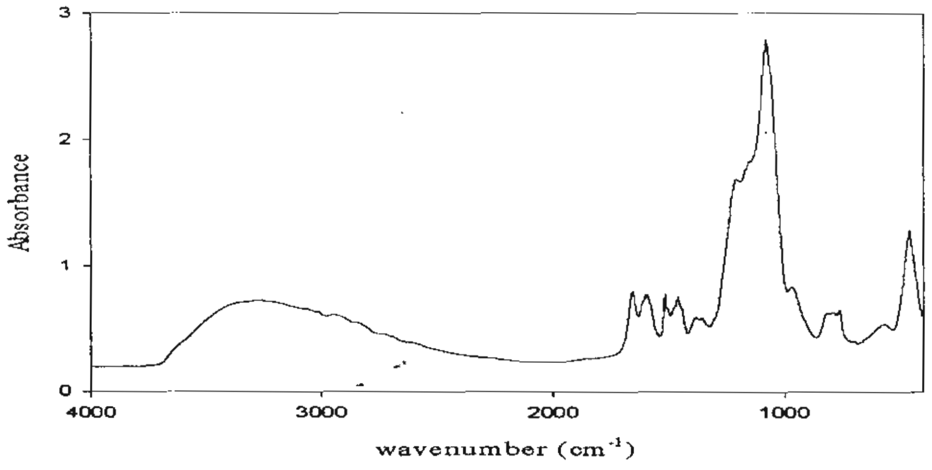


Figure 5.12 FTIR spectrum of spirosilicate/benzoxazine C4 comonomer.

Conclusions

In this work, spirosilicate/benzoxazine comonomers were synthesized as crude products directly from aminospirosilicates, paraformaldehyde and phenol. From the results, they showed that the obtained products contain silica and starting material. So the products need to be purified.

In addition, the new benzoxazine was synthesized from 2-amino-2-methyl-1,3-propanediol by protecting hydroxyl groups to form ketals. The suitable conditions to protect the hydroxyl groups of 2-amino-2-methyl-1,3-propanediol are at temperature 100°C, 2 hours reaction time. Benzoxazine C4 was further synthesized by reacting ketal C4 with formaldehyde and phenol.

PROJECT OUTPUT

- This research project results in two international publications and three submitted papers, as follows;

1. Varangkana Jitchum, Chivin Sun, Sujitra Wongkasemjit[*] and Hatsuo Ishida, “Synthesis of spirosilicates directly from silica and ethylene glycol/ethylene glycol derivatives”, *Tetrahedron*, 57(18), 3997-4003 (2001).
2. Srisuda Thitinun, Nopporn Thanabodeekij, Alex. M. Jamieson and Sujitra Wongkasemjit[*], “Sol-gel processing of spirosilicates”, *J. Eur. Cer. Soc.*, 23/3, 417-427 (2003).
3. Sujitra Wongkasemjit[a*], Varangkana Jitchum[a] and Hatsuo Ishida[b], “Ring-Opening Polymerization with Near-Zero Shrinkage in Volume of Spirosilicates”, submitted to Chemistry of Materials.
4. นพพร ธนบดีกิจ และ สุจิตรา วงศ์เกษมจิตต์ “สารประกอบสไปโรซิลิเคต” ส่งไปที่วารสารวิจัยวิทยาศาสตร์ (ฉบับภาษาไทย) คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
5. นพพร ธนบดีกิจ และ สุจิตรา วงศ์เกษมจิตต์ “การเตรียมสารรองรับคะตะลิสต์ที่มีพื้นที่ผิวสูงจากสารสไปโรซิลิเคต” ส่งไปที่วารสารวิจัยวิทยาศาสตร์ (ฉบับภาษาไทย) คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX A

Reprint of Synthesis of Spirosilicate and Spirosilicate Derivatives Directly from Silica and Ethylene Glycol/Ethylene Glycol Derivatives

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Tetrahedron 57 (2001) 3997–4003

TETRAHEDRON

Synthesis of spirosilicates directly from silica and ethylene glycol/ethylene glycol derivatives

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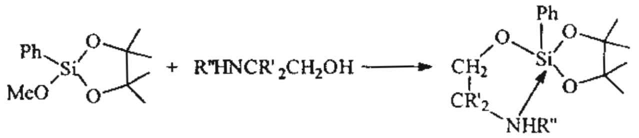
act—Tetracoordinated spirosilicates have been synthesized directly from the reaction of a very inexpensive and plentiful material, nd ethylene glycol in the presence of triethylenetetramine (TETA), as catalyst with and without potassium hydroxide as co-catalyst. reactions are run under nitrogen gas with constant stirring at 200°C, and complete in a reaction time of 10–18 h depending on the lysts. The reactions using only TETA are complete in 18 h, while with potassium hydroxide the reactions occur much more quickly. 3-amino-1,2-propanediol, or 2-amino-2-methyl-1,3-propanediol is employed, the reaction must run under vacuum at 0.1mmHg, and is complete in 14 and 24 h, respectively. The structures of spirosilicates are fully characterized using FTIR, ^{1}H, ^{13}C, ^{29}Si R, FAB^{+}-MS, and TGA. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

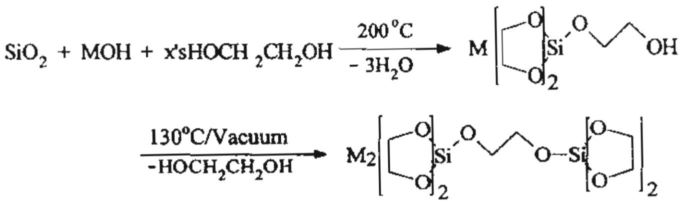
ally, thermosetting resins undergo a volumetric age (3–15%) during polymerization even using the system.[1–3] However, resins without shrinkage would dvantageous for such applications as precision castings, composites, rock cracking materials, and high th composites. The superior mechanical interlocking substrate that would be possible with zero shrinkage or nding materials makes them ideally suited for higher mance adhesives, sealants and coatings.[4–7] Most of piroorthocarbonate and spiroorthoester monomers 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 (Scheme 1).[14–16]

Laine *et al.* synthesized pentacoordinated and hexacoordinated spiro-silicates directly from silica and ethylene glycol



me 1.



2.

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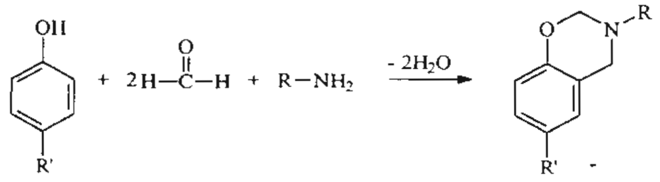
rds: silica; tetracoordinated spirosilicates; aminospirosilicates.

ponding author. Tel.: +66-2-218-4133; fax: +66-2-215-4459; e-mail: dsujitra@chula.ac.th

0040-4020(01)00275-7



eme 3.

ı the presence of group I metal hydroxides and II metal des.[17–18] These strong bases are expensive and have low ironmental stability (Scheme 2).

hida, H. et al. synthesized benzoxazine monomers from nol derivatives, paraformaldehyde, and primary amine ivatives.[19] Benzoxazines have good heat resistant, flame- etardant, and dielectric properties and reduce environ- ntal and health risks. Polybenzoxazines, the ring-opening ymerization phenolic resins, as compared to epoxy resins conventional phenolics, have indicated excellent glass ansition temperatures (T_g), and moduli, low water absorp- values, in addition to near-zero shrinkage or slight ansion upon curing (Scheme 3).[20–21]

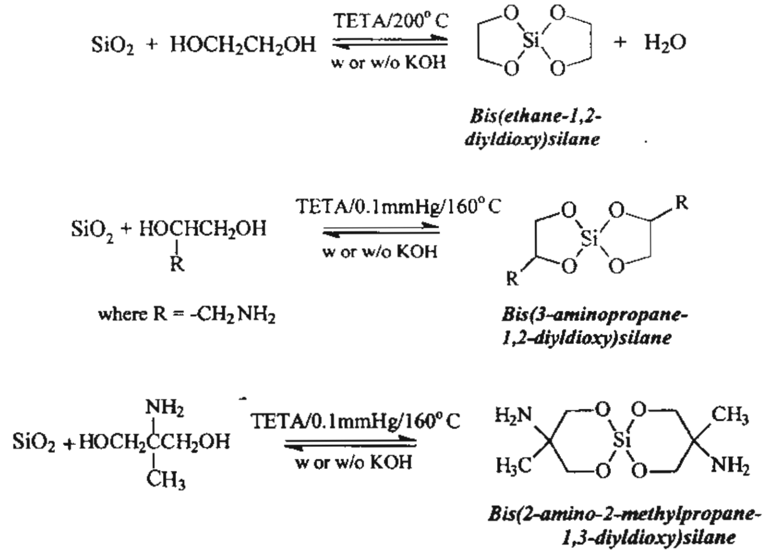
espite the position of silicon directly below carbon roup IV, the properties of the two elements are entirely erent, for example, Si–O bonds are 22 kCal/mol more able than C–O bonds. As a result, polymers having recur- ng Si–O linkages are of interest and importance, because offer good thermal, oxidative stability, and chemical stance.[22] We report herein an extension of silicon chem- try by the synthesis of neutral alkoxysilanes, tetracoordi- ated spirosilicates. In particular, we focus on synthesis ting from an inexpensive and abundant material, silica, ethylene glycol or 3-amino-1,2-propanediol or -amino-2-methyl-1,3-propanediol. Ethylene glycol is of ticular interest because it is the prototypical 1,2-diol the expected product has the same structure as spiro- ocarbonate and spiroorthoester, which give little hrinkage in volume on polymerization. We thus investi- d 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.

2. Results and Discussion

2.1. 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 reactions in Scheme 4.

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,



Bis(ethane-1,2-diyldioxy)silane

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

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

cheme 4.

1. FTIR assignments of bis(ethane-1,2-diyldioxy)silane, **1**, bis-aminopropane-1,2-diyldioxy)silane, **2**, and bis(2-amino-2-methylpro-ne-1,3-diyldioxy)silane, **3**

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

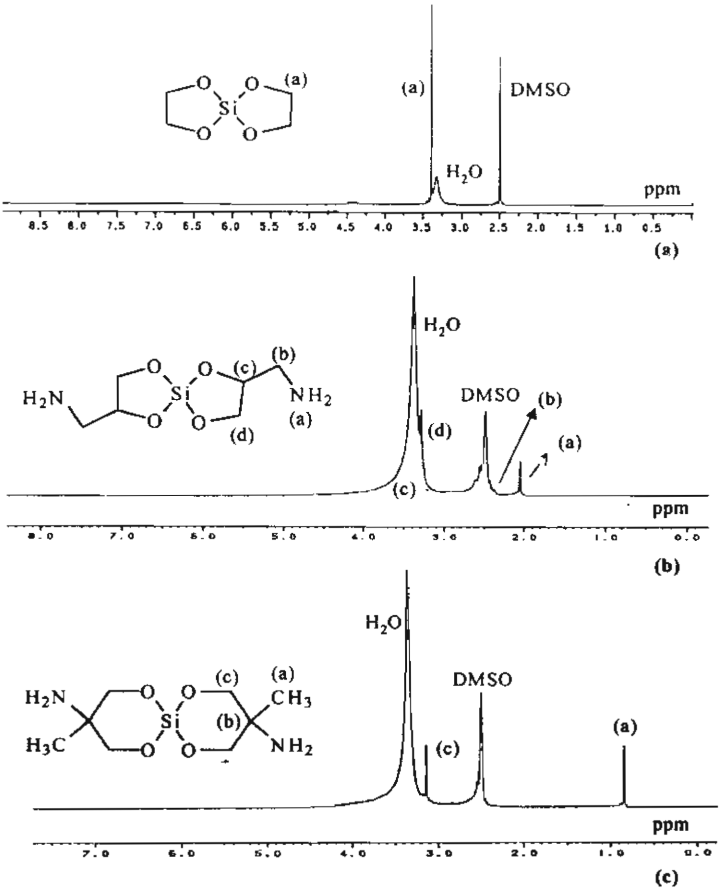
ding to Laine et al.'s work,[17–18] pentacoordinated silicates were resulted.

s for the aminospirosilicate products of bis(3-aminopro- 1,2-diyldioxy)silane and bis(2-amino-2-methylpro- 1,3-diyl dioxy)silane, the reactions need to be carried under vacuum at high temperature owing to the high oiling points of starting materials, 3-amino-1,2-propane- 264°C/739 mmHg) and 2-amino-2-methyl-1,3-propane- 151°C/10 mm Hg). TETA, which has the boiling point 6°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.

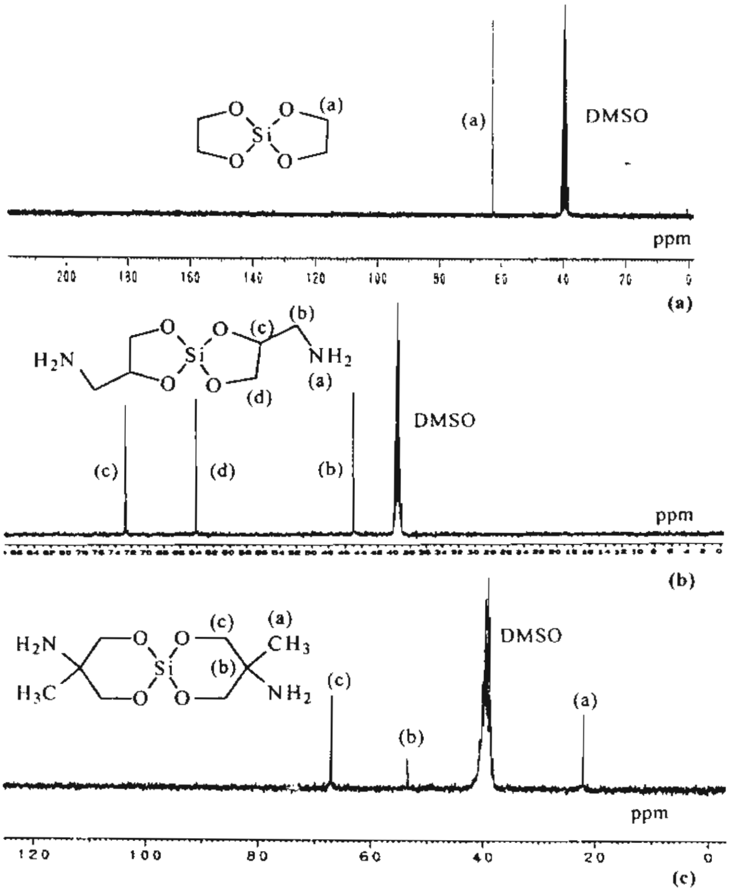
2.2. Characterization

The structures of spirosilicate products were identified by FTIR, ^1H, ^{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 1).



re 1. ^1H 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- ldioxy)silane.



re 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-ioxy)silane.

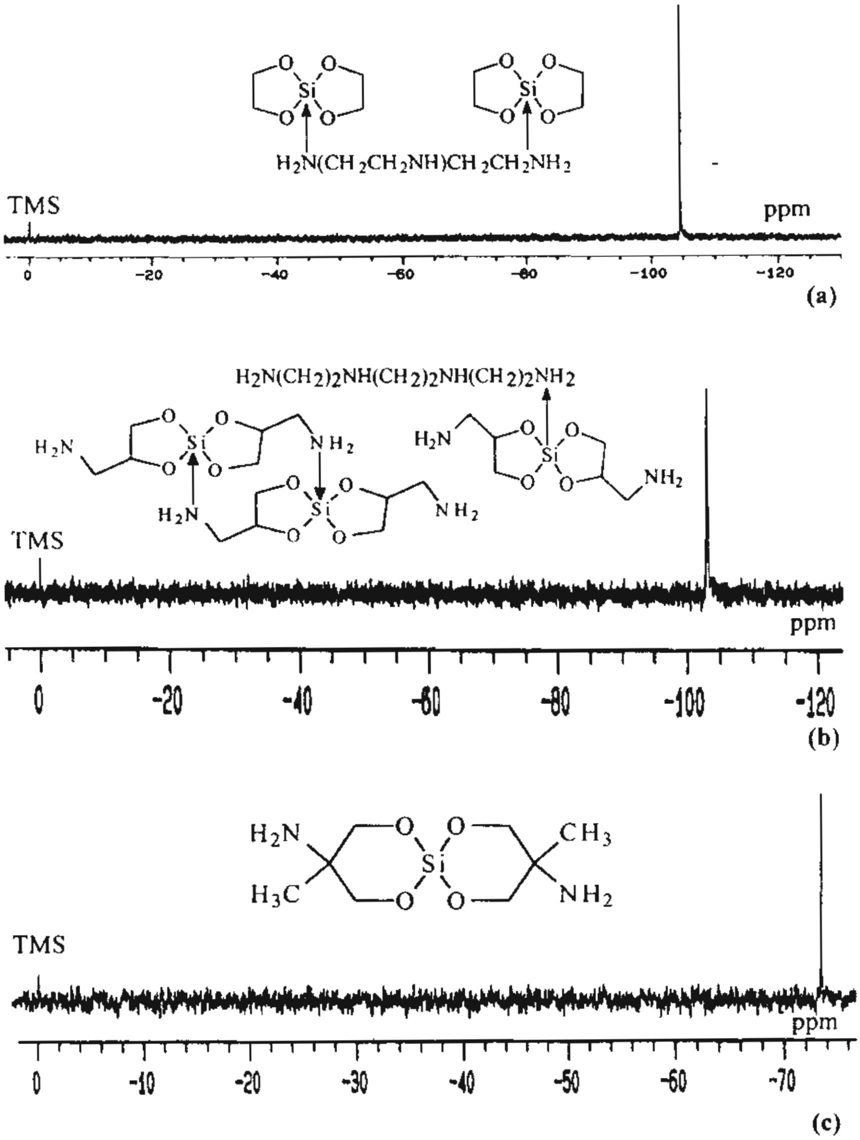
^1H NMR spectra, as illustrated in Fig. 1, show reso-es that belong to the corresponding products. They all the H_2O contained in deuterated DMSO and absorbed the product at $\delta=3.27$ ppm, in agreement with the FTIR ts. For bis(ethane-1,2-diyldioxy)silane, there appears to singlet at $\delta=3.38$ ppm, resulting from the four hydro-atoms (4H) of CH_2–O–Si. For bis(3-aminopropane-1,2-ldioxy)silane, the ^1H NMR spectrum shows a singlet at 05 ppm corresponding to the 4H of $-NH_2$, multiplet =2.45 ppm belonging to the 4H of CH_2–N, doublet at 3.29 ppm referring to the 4H of CH_2–O–Si. The 2H of –O–Si is unfortunately overlapped with the H_2O peak. however, can be confirmed by ^{13}C NMR data. The ^1H spectrum of bis(2-amino-2-methylpropane-1,3-diyl-xy)silane shows clearer chemical shifts at $\delta=0.83$ ppm onging to $-CH_3$ and $\delta=3.13$ ppm corresponding to -O–Si.

sides the deuterated DMSO peak, the ^{13}C NMR spectra, hown in Fig. 2, show only one resonance at $\delta=62.7$ ppm –O–Si) for bis(ethane-1,2-diyldioxy)silane; chemical for bis(3-aminopropane-1,2-diyldioxy)silane at $\delta=$ 9 ppm (CH_2–N), $\delta=64.0$ ppm (CH_2–O–Si) and $\delta=$ ppm (CH–O–Si); and also 3 resonances for bis-nino-2-methylpropane-1,3-diyldioxy)silane at $\delta=$ ppm ($-CH_3$), $\delta=53.5$ ppm (C) and $\delta=67.1$ ppm H_2–O–Si).

The results of ^{29}Si NMR spectra (Fig. 3) support that we have obtained tetracoordinated spirosilicate products, although the first two products showed the resonances at $\delta=-104$ 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 $\delta=-77$ 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.

FAB^+-MS results are shown in Tables 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.

The other results, which support that the synthesized spiro-silicates are truly the tetracoordinated not pentacoordinated species, were obtained by TGA (Table 5). They gave ceramic yields in close agreement with the calculated values based on the tetracoordinated species.



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-y)silane.

3. Conclusions

licates have been successfully synthesized directly an one step process from very inexpensive materials, nd ethylene glycol/its derivatives in the presence of

The proposed structure and fragmentation of bis(ethane-1,2-diyl-y) silane

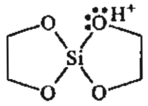
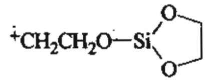
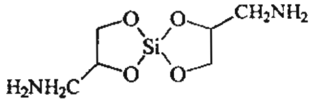
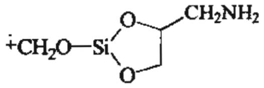
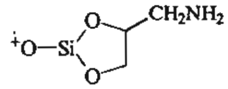
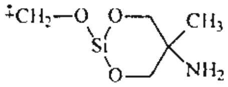
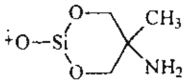
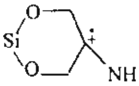
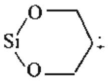
Intensities	Proposed Structure
7.00	
31.57	
9.11	$^{\cdot+}CH_2CH_2O\text{–}Si$
100	$^{\cdot+}CH_2O\text{–}Si$
80.94	$^{\cdot+}O\text{–}Si$

Table 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	$^{\cdot+}CH_2O\text{–}Si$
44	42.28	$^{\cdot+}O\text{–}Si$

ble **4.** The proposed structure and fragmentation of bis(2-amino-2-hylpropane-1,3-diyldioxy)silane

Intensities	Proposed Structure
0.8	
1.2	
13	
28	
46	${}^{\cdot+}CH_2O{-}Si$
54	${}^{\cdot+}CH_2O{-}Si$
100	${}^{\cdot+}O{-}Si$

e **5.** % Ceramic yields of bis(ethane-1,2-diyldioxy)silane, **1**, bis(3-opropane-1,2-diyldioxy)silane, **2**, and bis(2-amino-2-methylpropane--diyldioxy)silane, **3**

	% Ceramic yield	
ct	Calculation	Experiment
	40.5	40.8
	29.1	30.4
	25.4	26.9

thylenetetramine, as catalyst/solvent with/without potas- hydroxide, as co-catalyst. The reactions are much r when the co-catalyst and silica with a higher surface a are employed.

4. Experimental

Materials

 reactions were equilibrium reactions and products were nsitive to either moisture or air. Thus, all glassware used hese experiments was dried in an oven at 100°C over-. All reactions were carried out in an inert atmosphere trogen gas).

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

4.2. 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 ($FAB\text{-}MS^+$) 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.

4.3. Syntheses

4.3.1. 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.

4.3.2. 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°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.

Acknowledgements

This research project was funded by the Thailand Research Fund and partially supported by the Development and Technology of Economics and Cooperation.

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APPENDIX B

Reprint of Sol-Gel Processing of Spirosilicates

Journal of the European Ceramic Society □ (□□□□) □–□
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Sol-gel processing of spirosilicates

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stract

he sol-gel transition of tetra-coordinated spirosilicate via hydrolysis and condensation under acidic and basic conditions is ned to elucidate the effect of catalyst, reaction time and temperature on the properties of obtained gel. The main advantage of rocess is the low temperature employed, producing a solid network with a high specific surface area. FTIR spectroscopy and A analysis were used to characterize the formation of siloxane bonds (Si–O–Si). It is found that spirosilicate can be hydrolyzed both acid and base catalyzed conditions. The condensation rate to silicates is shown to be at a minimum in 0.001M HCl, which iso-electric point of silica. The prepared xerogel has a low-density and is an amorphous material with a specific surface area of ^{2}/g. Besides the catalyst media, the type of precursor also has a strong influence on the gel formation. An aminospirosilicate, six-mbered ring, containing methyl and amino groups as substituents, was chosen for this study. The resulting xerogel is determined fact that to obtain the Si–O–Si bonds, a higher concentration of solvent and higher temperature are more favorable, due to ngth and branching of alkyl portion. © 2002 Elsevier Science Ltd. All rights reserved.

words: Aminospirosilicate; Siloxane; SiO_2; Sol-gel processing; Spirosilicate; Xerogel

Introduction

limited number of simple silicon containing rting materials restricts the potential role of inorganic d organometallic silicon compounds in the develop- of new polymeric glasses and ceramics. The main n is that silicon-containing chemicals are almost clusively prepared from element silicon, obtained from arbothermal reduction of silica around 1200 °C, is energy-intensive.[1] Organosilicate compounds are interest for their potential as precursors in sol-gel processing to form complex preceramic shapes and structures, adily accessible by melt processing.[2,3]

gel chemistry of silicon alkoxides is rather simple, mpared to that of complexes of transition metal alk- in which metal atoms may exhibit several coordi- states.[4] Molecular precursors of silicon alkoxides 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] The 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 as 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 pyrotlyzed 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.

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Experimental

Materials

used silicon dioxide or HI-SIL 927 silica (SiO_2), with rface area of 168 m^2/g, by BET, was donated by Siam Silica Co., Ltd., and dried in oven at 100 °C 10 h. 2-Amino-2-methyl-1,3-propanediol [$HOCH_2C$ $H_3xNH_2)CH_2OH$] was purchased from Aldrich Che- l Company, used without purification and kept r nitrogen atmosphere. Ethylene glycol (EG, CH_2CH_2OH), purchased from Labscan, was used as tion solvent. Triethylenetetramine [TETA, H_2N $CH_2NH)_3$] was purchased from Facai Polytech Ltd., and used as a catalytic base. Potassium roxide (KOH) was purchased from Baker Analyzed ent, and used as co-catalyst. Methanol (CH_3OH) acetonitrile (CH_3CN) were purchased from Baker alyzed Reagent and Lab-scan Analytical Science, ctively. Each was distilled using standard method e as precipitating agents. UHP grade nitrogen gas 99.99% purity was purchased from Thai Industrial ses Public Company Limited (TIG). Hydrochloric (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.

2.2. *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 35–20,000×. 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.

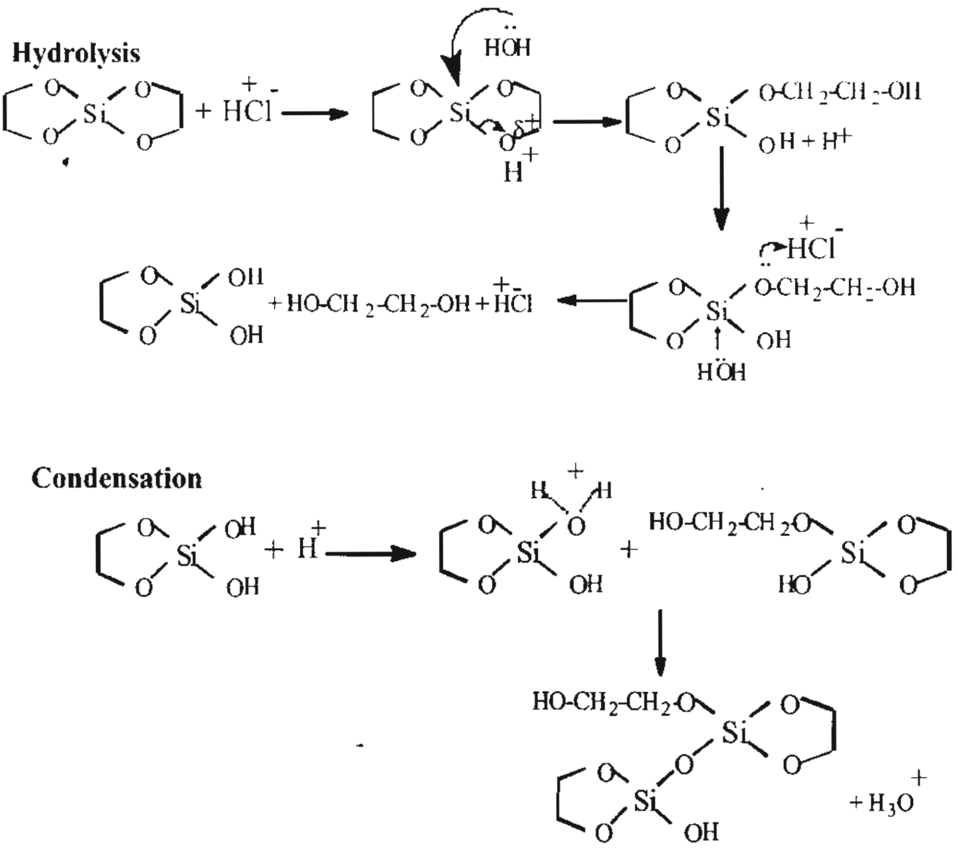
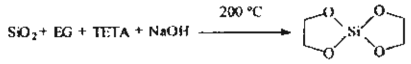


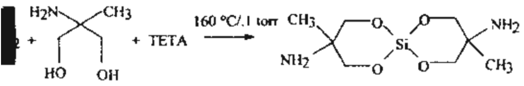
Fig. 1. Schematic of hydrolysis and condensation under hydrochloric acid solution.

3. Methodology

3.1. Synthesis method

Following the synthetic methods described by Wongasemjit et al.,[18] spirosilicates were synthesized, as own in Eqs. (1) and (2).


(1)


(2)

3.2. Sol-gel transition study

Hydrolysis of the spirosilicate products was carried ut by addition of either HCl or NH_4OH solution at arious concentrations. The mixture was prepared ectly in a crucible at room temperature, resulting in a med-gel product. The gel was aged at room temerature. To study the sol-gel transition, at each hour e aliquots of mixture were deducted and dried using h vacuum (0.1 mm Hg) to remove solvent. The ydrolysis reaction also carried out was at 40 and 0 °C.

2.3.3. 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.

2.3.4. 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.

3. Results and discussion

It is well known that the catalyst used in a gelation reaction can have large effects on the microstructure of

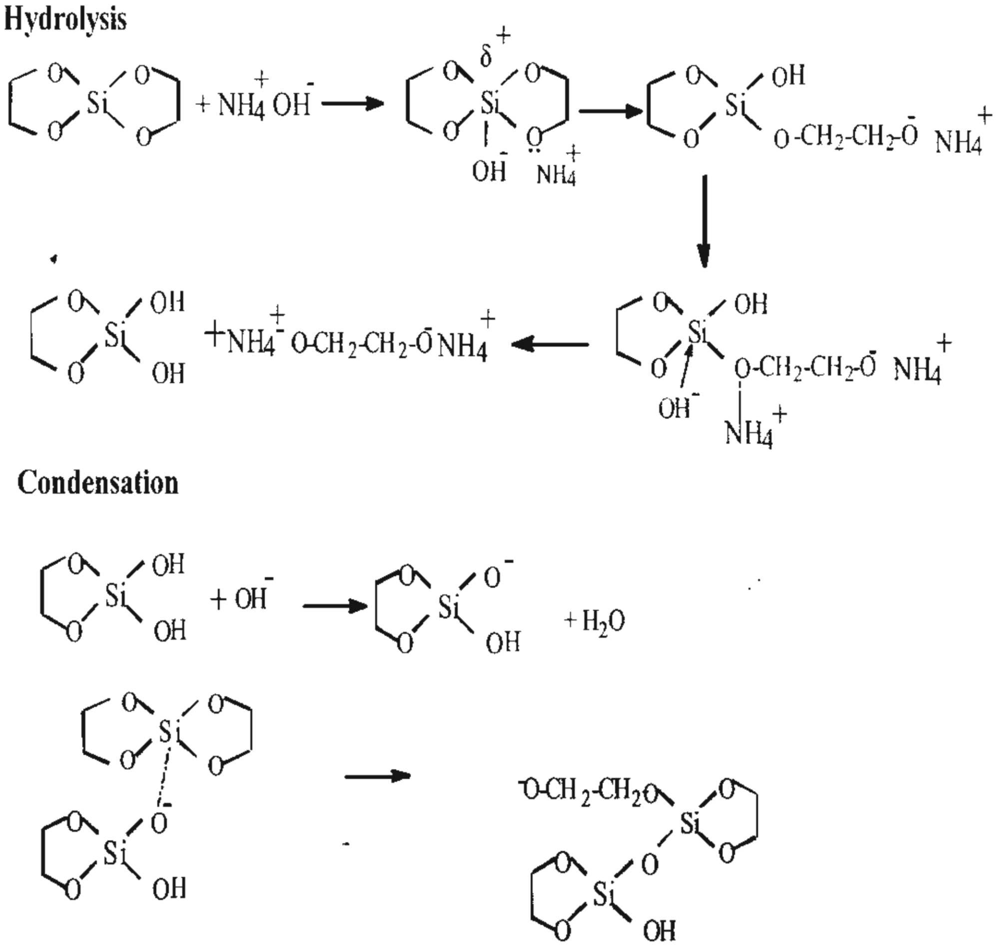


Fig. 2. Schematic of hydrolysis and condensation under ammonium hydroxide solution.

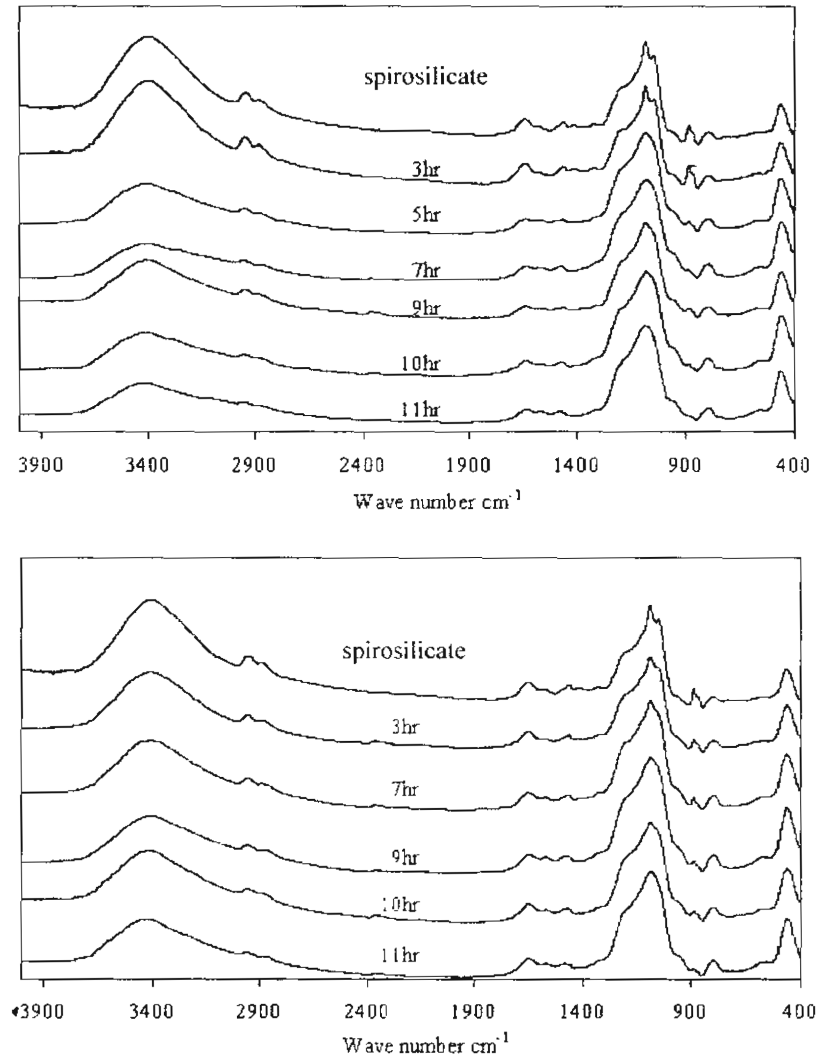


Fig. 3. FTIR spectra of hydrolyzed spirosilicate with (a) 0.001 and (b) 0.002 M HCl at room temperature.

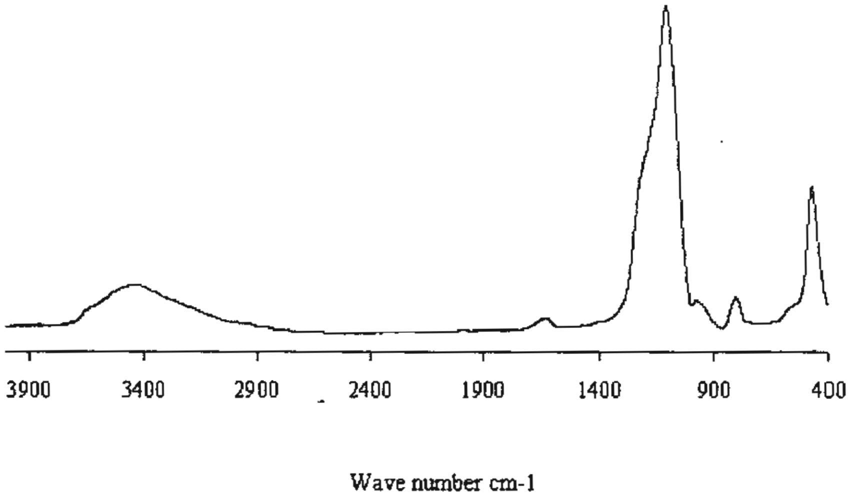


Fig. 4. FTIR spectrum of fused silica starting material.

els formed as well as on the rapidity of the gelation ess.[20] During the sol to gel transition induced by ing solvent, the polymerization occurs via hydro- and polycondensation reaction. Figs. 1 and 2 show proposed mechanisms of hydrolysis and condensa- for tetracoordinated spirosilicates under acidic and conditions.

3.1. Spirosilicate

FTIR spectra of products obtained using 0.001 M HCl, see Fig. 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

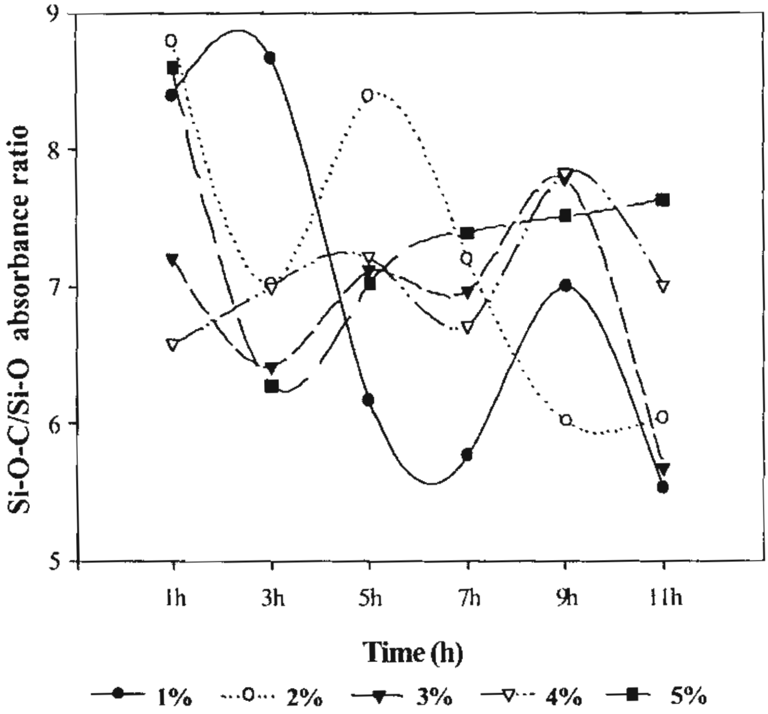


Fig. 5. The time-dependence of hydrolyzed spirosilicate with 0.001–0.005 M HCl at room temperature.

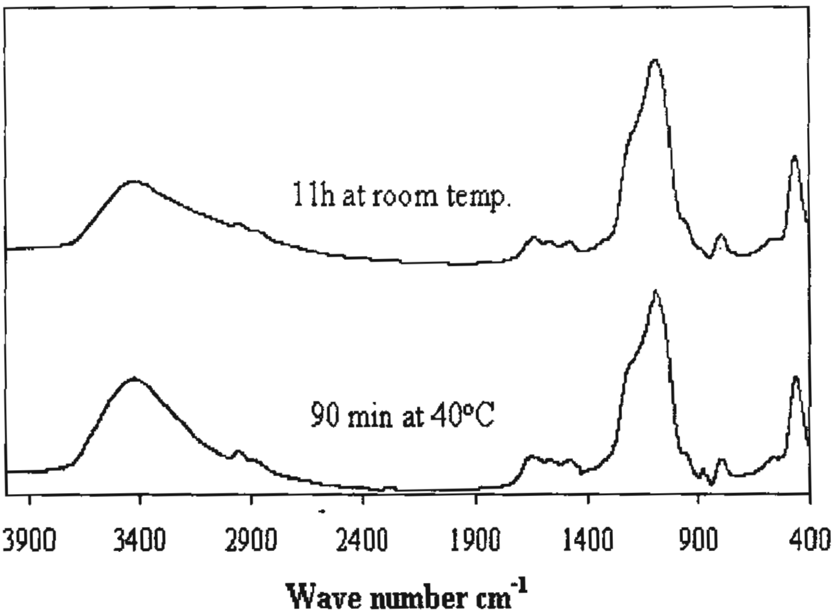


Fig. 6. FTIR spectra showing the effect of temperature on the hydrolyzed product.

ue to the condensation of silanols.[21] At the same time, ne peak around 1648 cm^{-1}, which was assigned to the H bending,[22] also decreased in the same manner. The crease in the absorption peak at 1086 cm^{-1} suggested hat crosslinking of Si–O–Si bonds occurred via hydrois and condensation. This was confirmed by comparn with the disappearance of absorption peaks at 405, 2951 and 2883 cm^{-1}, indicating a decrease of rganic ligands. It should be noted that, at 9 h, the aks at 3405, 2951, 2883 and 1086 cm^{-1} change in the verse direction. This phenomenon was also detected y Brinker et al. that when hydroxyl groups on the sure of the particles condense to form siloxane bonds, particles coalesce in an irreversible sol-gel transition, nd when coalescence occurs without forming siloxane onds, the sol-gel transition may be reversible.[23,24] The ucture obtained at 11 h of hydrolysis was very close to t of silica (Fig. 4). Using a higher concentration of atalyst, 0.002M HCl, the obtained results were essentially ntical [Fig. 3(b)]. However, the change of absorption ks at 3405, 2951, 2883 and 1086 cm^{-1} decreased faster s compared to a lower concentration of HCl.

The overall results are summarized in Fig. 5, which plays the relationship between the ratio of Si–O–C/Si–Si (the peaks at 1086 and 463 cm^{-1}) plotted against me for hydrolysis of the spirosilicate at various acid centrations at room temperature. Fig. 5 indicates t the optimum condition, showing more effective hydrolysis occurs when 0.001 M 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 Fig. 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 1 h for spirosilicate to become silica while more than 10 h was needed to obtain silica at room temperature.

Changing the catalyst from acid to base using 1M ammonium hydroxide solution gave different results, as shown in Fig. 7. 0.001M NH_4OH gave little change in the structure of Si–O–C and Si–O–Si during the time period of 1-8 h. After 9 h, a substantial decrease of the peak ratio was observed. Subsequently, however, after 11 h, the ratio increased again.

Table 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

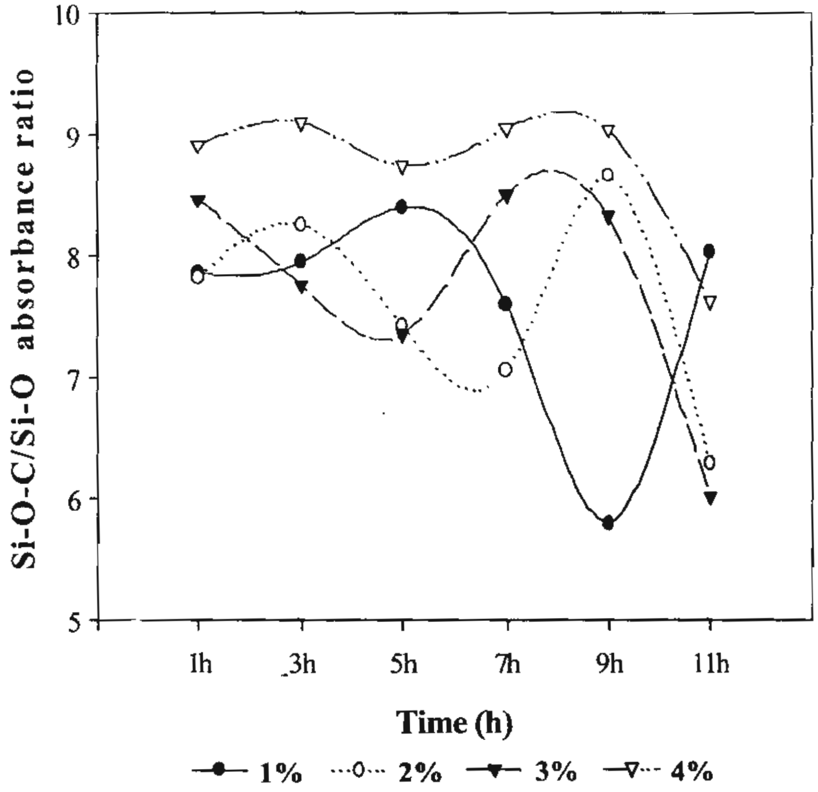


Fig.7. The time-dependence of hydrolyzed products of spirosilicate with 0.001–0.004M NH_4OH at room temperature.

In summary, the kinetics of the sol-gel transition of spirosilicate are slowest at 0.001 and 0.002 M HCl, for hich pH≈2, due to the absence of ionized hydroxyl oups [Si–O$^-$ or Si–(OH$_2$)$^+$],[26] see Table 1, as monitored y a decrease of the peaks at 3405, 2951, 2883 and 1086 m^{-1}. This result is consistent with experimental studies Brinker and coworkers,[24] who determined the opti-al gel time of TEOS to be at pH near 2.

TGA analysis of spirosilicate (Fig. 8) after hydrolysis th 0.001 and 0.002 M HCl were used to confirm the TIR results shown in Figs. 3 and 5. Evidently, the kinetic data obtained from FTIR spectra and the cera-ic yields obtained from TGA are in agreement. A

Table 2
The BET surface area measurement of spirosilicate after hydrolysis with 0.001M HCl and NH$_4$OH at various time, followed by pyrolysis at 750 °C for 7 h, as compared to fused-silica starting material

Time (h)	Surface area (m^2/g)	
	1% of 1M HCl	1% of 1M NH$_4$OH
3	307	296
5	354	278
7	369	307
9	339	347
11	596	280
Fused silica	167	168

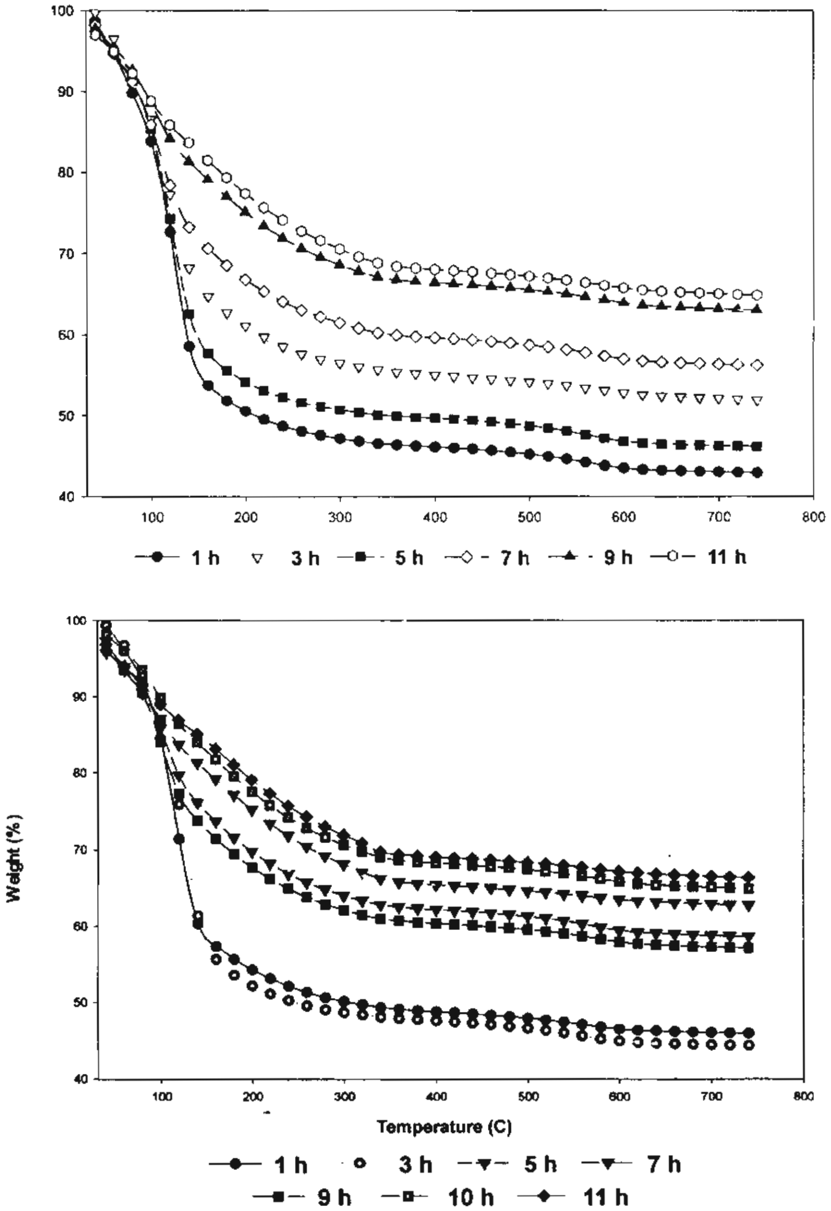


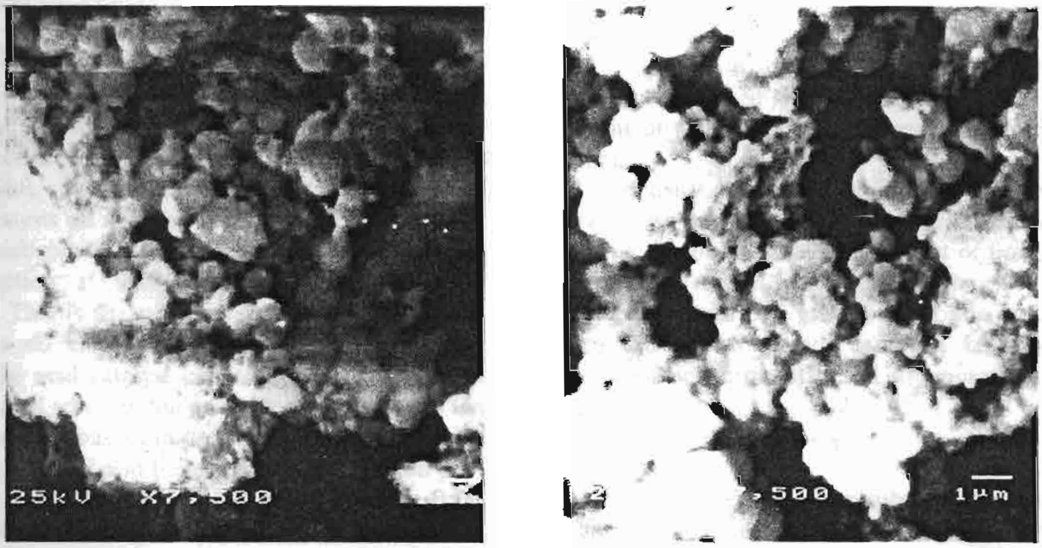
Fig. 8. TGA thermograms showing percent ceramic yields at various time after hydrolysis with HCl at (a) 0.001M and (b) 0.002M.

ecrease in the Si–O–C peak long with an increase in Si–O–Si peak correlates to an increase in ceramic yield. otably, the increase of Si–O–C peak at 9 h compared 7 and 10 h using 0.001M HCl, correlates with a decrease of ceramic yield obtained from TGA.

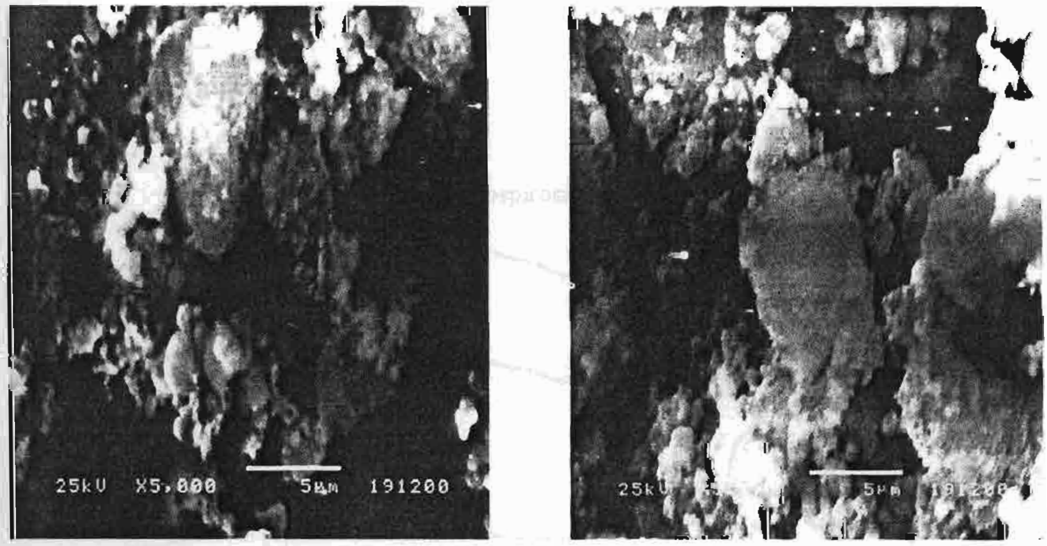
Thus, these surprisingly suggest that the reaction can oceed in the reverse direction, so called "reesterifica-ion", in which an alcohol molecule displaces a hydroxyl group to produce an alkoxide ligand and water as a by oduct.[24]

The BET surface area study of pyrolyzed product obtained from hydrolysis of spirosilicate at 750 °C for 7 h is shown in Table 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.

The morphology of the hydrolyzed aggregates was observed by scanning electron microscopy, as shown in Fig. 9. Fig. 9(a) and (b) show the characteristics of the dried gel, under acidic and basic conditions, respec-



(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.

Fig. 9. SEM of hydrolyzed (a) and (b) and pyrolzed (c) and (d) spirosilicate.

tively. Certain differences in morphology are evident, which can be traced to the effect of the different catalyst ed.

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

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

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

$$\text{-}OH + OH^- \rightarrow SiO^- + H_2O$$

Obviously, each condition has a distinct influence on rate of condensation ans 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, ich gives no electrostatic particle repulsion.[26] By reasing 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 leophilic attack,[21] and the condensation reaction provides SiO^-, resulting in faster condensation before complete hydrolysis. Furthermore, with the base catalysis, ulsion of the sol structure gives more time for the pares 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 Fig. 9(b), showing that the porosity of the sol structure is greater than that in Fig. 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 Fig. 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 Fig. 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]

3.2. *Aminospirosilicate C4*

In the case of the six-membered cyclic aminospirosilicate, ring is more stable than the five-membered spirosilicate ring. Moreover, the aminospirosilicate has bulkier substituents. As a result, hydrolysis of the

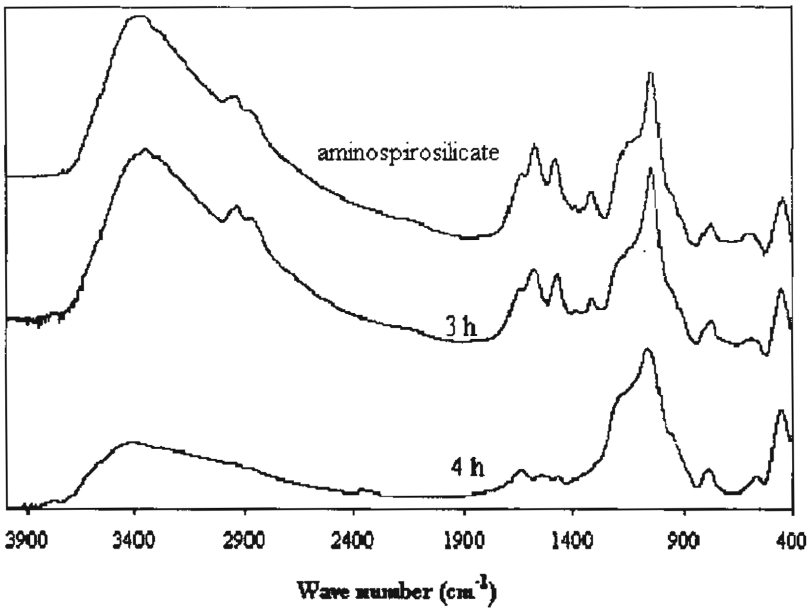


Fig. 10. FTIR spectra showing the effect of time on the hydrolyzed aminospirosilicate product at 60 °C.

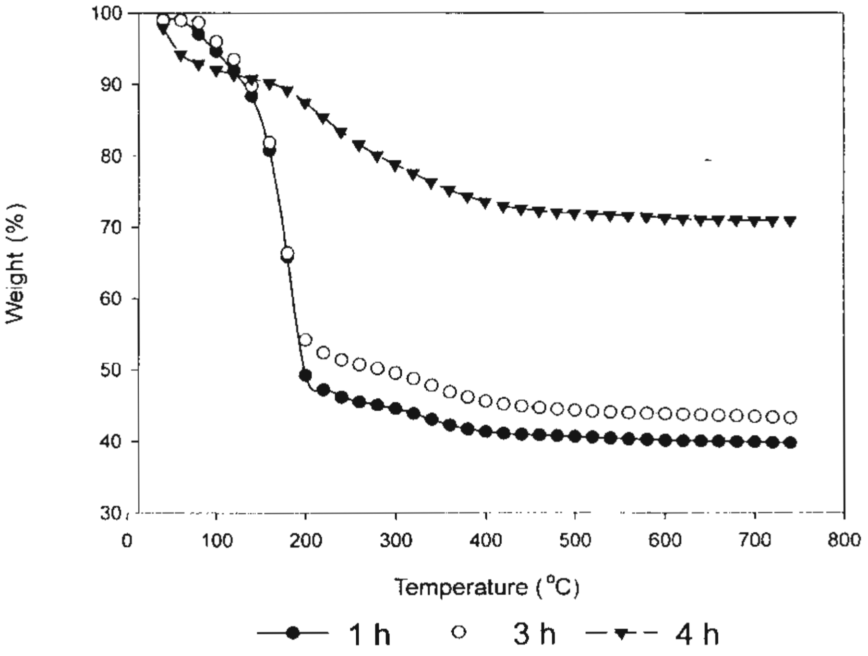


Fig. 11. TGA thermograms showing percent ceramic yields of hydrolyzed aminospirosilicate at 60 °C for 1, 3 and 4 h.

inospirosilicate with either 1M HCl or 1M NH_4OH ows no significant reaction at room temperature and °C. 1M HCl also shows no reaction on hydrolysis n at 60 °C. Thus, under acidic condition, protona- n of alkoxy group is retarded due to the more stable ng structure, more steric hindrance, and the presence amino group in the structure. This thus resulted in no ictural change during hydrolysis of the products der acid condition.

Fig. 10 shows only the results of C4 hydrolyzed using NH_4OH at 60 °C. Inspection of the decrease in the sorption peaks at 3405, 2951, 2883, 1086 cm^{-1} indi- ites a slower hydrolysis rate. This is confirmed by the that the aminospirosilicate hydrolyzed at 60 °C for gives the highest ceramic yield, 70.89%, as shown in ig. 11. The increased ceramic yield is due to a high centration of reactive groups under base-catalysis high temperature, allowing less time for the lecules to rearrange to form a crosslinked Si–O–Si twork.

he BET analysis of aminospirosilicate sol-gel pro- t pyrolyzed at 750 °C for 7 h indicated a surface area 82.93 m^2/g, reflecting the increase of reaction rate use of the increase in concentration of catalyst and perature.[26]

Conclusions

Spirosilicate can function as a reactive metal alkoxide up allowing sol-gel processing at room temperature lightly 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.

Acknowledgements

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APPENDIX C

Manuscript of Ring-opening Polymerization with Near-zero Shrinkage in Volume of spirosilicates

Ring-Opening Polymerization with Near-Zero Shrinkage in Volume of Spirosilicates

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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, ^1H- and ^{13}C-NMR.

Key words : Spirosilicate, Aminospirosilicates, Near-zero shrinkage and Ring-opening polymerization

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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 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].

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.1-2, 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.

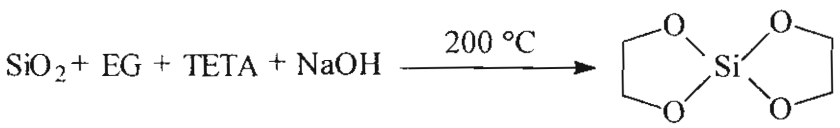
Characterization

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). ^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.

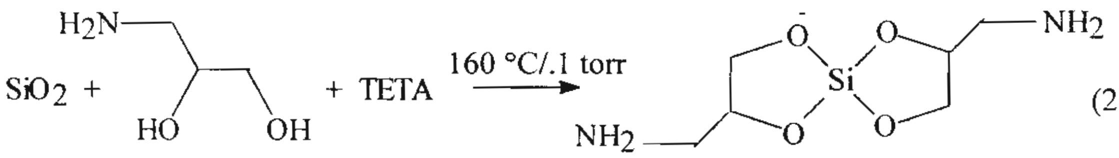
Procedure

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.1-3.



(1)



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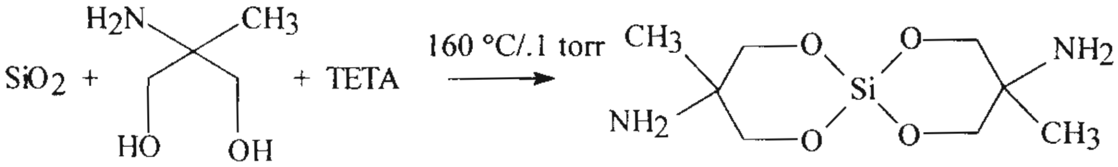

(3)

Determination of Curing Conditions

To determine the density of monomers in order to compare with their corresponding polymers, the suitable time and temperature for curing monomers to obtain fully crosslinked polymers were first investigated. The optimum curing temperature was obtained by fixing curing time at 1 hr and varying temperature from 80° to 180°C in a vacuum oven. %Ceramic yield data from TGA was used to clarify the amount of crosslinking, meaning that the higher %ceramic yield, the higher crosslinking. The suitable curing temperature was the point that the % ceramic yield started to approach constant. Like-wise, the optimum curing time was obtained by fixing the selected temperature and varying the time in range of 1 to 5 h. in a vacuum oven. The suitable time was again the point that the %ceramic yield started to approach constant.

Density Measurement

The volumetric property of each product was obtained by comparing the densities of monomer and its corresponding polymer. The density measurements were performed according to ASTM D792 (Method A), using a 25 mL pycnometer (for powder form product) and distilled isooctane as media. In the process, the pycnometer bottle was first weighed and tarred. The purified product in the bottle was weighed in the range of 0.5-1.0 g. The media was added to the bottle until covering the product. The bottle-containing sample and media was then sonicated in an ultrasonic bath to eliminate bubbles. The sample was then incubated at 25°C for 2 h. The media was then added to the bottle until it reached the marked point. The bottle was wiped and covered with the cap having a thermometer. The weight was measured and the density of the sample was finally calculated. The steps of density measurement are followed;

the weight of sample = (A) g.
the weight of sample + isooctane = (B) g.
the density of isooctane at the set temperature obtaining from reference = (C) g/cm^3
the weight of isooctane = (B) - (A) = D g.
the volume of isooctane = D / (C) = E cm^3
the volume of sample = the volume of the bottle - E = G cm^3
then the density of sample = (A) / G g/cm^3

RESULTS AND DISCUSSION

The synthesized products of spirosilicate, *A*, aminospirosilicates from 3-amino-1,2-propanediol and 2-amino-2-methyl-1,3-propanediol, *B* and *C*, respectively, were used further in the density measurement to compare with their corresponding polymers thermally obtained from ring-opening polymerization. Finding the optimum conditions for polymerizing each monomer was first conducted by studying the variation of curing temperature and time.

For spirosilicate *A*, the product was cured by first varying temperature and fixing the time at 1 h. and 1 torr. The %ceramic yield obtained from the TGA result was approaching constant when the temperature reached 120°C (Figure 2a). This temperature was thus selected to find the optimum time. The curing time studied was ranged from half an hour to 5 h. It was found that the 1 h. curing time gave the highest %ceramic yield (Figure 2b). As a result, the optimum curing condition for the spirosilicate *A* was 1 h. at 120°C, 1 torr.

As for aminospirosilicates *B* and *C*, the optimum curing conditions were carried out in the same manner. The results are shown in Figures 3-4. The optimum conditions at 1 torr for curing *B* and *C* products were at 140°C for 1 h. and 160°C, 2 h., respectively. Clearly, spirosilicate *C* product needs higher temperature and longer time for curing as compared to spirosilicates *A* and *B.* This is due to the fact that stability of six- membered ring structure of spirosilicate *C* is higher than those of five-membered ring spirosilicates *A* and *B*.

The cured spirosilicates were characterized using FTIR, DSC, TGA, FAB$^+$-MS, ^{1}H- and ^{13}C-NMR. Interestingly, the DSC results of all polymers, as shown in Figure 5, indicated that the first endothermic peak occurred approximately 10 °C lower as the monomer became to its corresponding polymer. Generally, the product showed one major endothermic peak on heating, and no exotherm appeared on cooling. It is due to the degradation of the product at elevated temperatures with slow heating rate. Thus a second heating cycle (after the first heat-cool cycle) revealed no endothermic transition as the material had undergone degradation. In case of aminospirosilicates, there was also one small endotherm occurring next to the major one. Probably, this peak was from the cleavage of the hydrogen bondings between amino groups and alkoxy groups since it became smaller when it was a polymer. It is owing to the steric effect of network structure in polymer, resulting in less hydrogen bondings. All DSC results of both monomers and polymers showed one small exotherm around 350 °C corresponding to the oxidative reaction.

The TGA profiles of both monomers polymers gave two regions of mass loss during heating process from room temperature to 950 °C, as shown in Table 1. The decomposition temperatures of monomers were higher than those of polymers. The first mass loss resulted from oxidative decomposition of organic ligands. The other mass loss corresponded to the oxidative decomposition of remaining organic residue in the product. The final ashes obtained from pyrolysis of polymers were dark-gray while for monomers they were almost white. This is also another indication of being network structure in polymer products.

As for the results of FAB^+-MS (Tables 2-4), it is certain that the products had become polymers having network structure since there was no evidence of having monomer molecule or spirosilicate ring part in the spectra, as found in the spectra of monomers [1].

Both ^1H- and ^{13}C-NMR spectra (Figures 6 and 7) gave similar results to those of monomer although the peaks were weaker due to the less solubility of polymers in deuterated dimethylsulfoxide. This is not unsurprising since it is often found in thermosetting polymers. All spectra showed the H_2O contained in deuterated DMSO and absorbed by the product at $\delta = 3.3$ ppm, in agreement with the FTIR results (Figure 8). Polymer <u>*A*</u> showed one singlet at $\delta = 3.4$ ppm, corresponding to the four hydrogen atoms (2H) of CH_2-O-Si. Polymer <u>*B*</u> gave three peaks at $\delta = 2.45$ and 2.55 ppm (doublets) belonging to the 2H of CH_2-N being influenced from the adjacent chiral carbon atom, $\delta = 3.3$ ppm (doublet) referring to the 2H of CH_2-O-Si. Again, the 1H of CH-O-Si was unfortunately overlapped with the H_2O peak. However, this missing peak can be confirmed by ^{13}C-NMR data. The ^{1}H-NMR spectrum of polymer C showed clearer chemical shifts at $\delta = 0.8$ ppm belonging to $-CH_3$ and $\delta = 3.2$ ppm corresponding to CH_2-O-Si.

The ^{13}C-NMR spectra, as shown in Figure 7, can confirm the structures of polymer products. Polymer *A* showed only one peak at $\delta = 63$ ppm (CH_2-O-Si) while polymer *B* gave three peaks at $\delta = 45$ ppm (CH_2-N), $\delta = 64$ ppm (CH_2-O-Si) and $\delta = 73$ ppm (CH-O-Si). Polymer C showed 3 corresponding peaks at $\delta = 23$ ppm ($-CH_3$), $\delta = 54$ ppm (C) and $\delta = 67$ ppm (CH_2-O-Si).

To be certain whether the cured products are the expected ones, ^{13}C-Solid state NMR was employed, see Figure 8. The results clearly show the desired product structures.

The FTIR spectra (Figure 9) intensively showed the band around 1080 cm^{-1}, corresponding to the Si-O-C stretching. Unsurprisingly, the OH stretching around 3390-3400 cm^{-1} which was from water absorbed was much smaller, as compared with FTIR spectra of monomers. However, the intensity of this peak was bigger in the order of polymers *A* < *B* < C due to the steric effect of the cured products. The bulkier the product, the loser the network, as a result, the more hydrogen bonding between water-product and product-product, as studied by Cairn [16]. Cairn studied the hydrogen bonding in phenol structure and found that Infrared spectroscopy (FTIR) technique can distinguish between inter- and intramolecular hydrogen bonding. As can be seen in Figure 10, it can be concluded that free hydroxyl group appears as a sharp peak around 3600 cm^{-1}, the intramolecular hydrogen bonding is present as a broad band around 3500 cm^{-1} and intermolecular hydrogen bonding shows a broad band around 3400 cm^{-1}. That means, our cured polymers contained intermolecular hydrogen bonding because of the presence of the peak at 3390-3400 cm^{-1} (Figure 9).

After polymerizing the purified monomers, the volumetric change of polymers as compared to their corresponding monomers were studied and found that all materials showed small amount of volumetric shrinkage property, as summarized in Table 5. As discussed previously, intermolecular hydrogen bonding had significant effect on the volumetric shrinkage property of all products. The more hydrogen bonding in the structure caused the higher shrinkage and the closer the molecule [17]. In the case of cured spirosilicate *C*, due to the steric hindrance in the structure, it has more effect to occur hydrogen bonding, resulting in smaller volumetric change as compared to *A* and *B* spirosilicate products, which *B* has free amino group that can move easily to form hydrogen bonding.

CONCLUSIONS

The volumetric property of purified spirosilicate and aminospirosilicate derivative products showed near-zero shrinkage property. It was reported to be an important parameter of the molecular packing. This packing has been caused from intermolecular hydrogen bonding between hydroxyl group and hydroxyl group or hydroxyl group and amino group of curing structures. Moreover, the hydrogen bonding is also influenced from the steric hindrance of its attaching group. The higher steric hindrance, the less hydrogen bonding is, resulting in the less shrinkage property. In addition, aminospirosilicate derivatives are expected to use further as a starting material in benzoxazine synthesis. The products would decrease or minimize the non-dimensional stability, which makes the materials have a high potential to use in engineering industry applications.

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ACKNOWLEDGEMENT

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CAPTIONS OF TABLES AND FIGURES

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Table 2 : The proposed structure and fragmentation of polymer _A_

Table 3 : The proposed structure and fragmentation of polymer _B_

Table 4 : The proposed structure and fragmentation of polymer _C_

Table 5 : The volumetric property of spirosilicates _A_, _B_ and _C_

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Figure 2: %Ceramic yields of cured spirosilicate _A_ at a). various temperatures and b). various times

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Figure 8: ^{13}C-Solid State NMR spectra of cured spirosilicate (a) _A_, (b) _B_ and (c) _C_

Figure 9: FTIR spectra of cured spirosilicate (a) _A_, (b) _B_ and (c) _C_

Figure 10: FTIR spectra of a) Methylamine based dimers and b) Novolak.

(Cairn, T., Eglinton, G , Journal of Chemical Society, **1965**, 5906-5913)

Table 1

Sample	Monomer (°C)		Polymer (°C)	
	1st transition	2nd transition	1st transition	2nd transition
_A_	160-250	250-550	100-220	220-600
_B_	120-250	250-500	90-220	220-500
_C_	120-230	230-320	120-220	220-400

Table 2

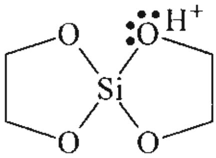
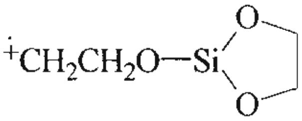
m/e	Intensities		Proposed Structure
	Polymer	Monomer	
149	-	7.0	
132	-	31.6	
72	41.7	9.1	$\overset{\cdot}{+}CH_2CH_2O-Si$
58	71.9	100	$\overset{\cdot}{+}CH_2O-Si$
44	100	80.9	$\overset{\cdot}{+}O-Si$ and $\overset{+}{\cdot}CH_2CH_2O$

Table 3

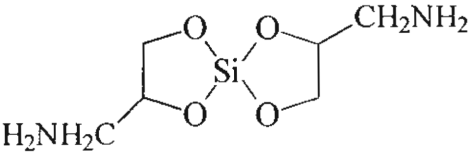
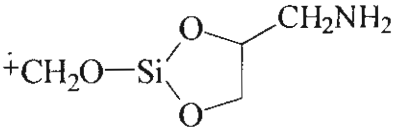
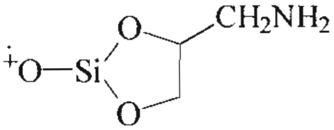
m/e	Intensities		Proposed Structure
	Polymer	Monomer	
206	-	0.8	
147	-	17.6	
133	-	100	
71	100	-	$^{+\cdot}CHCH_2O - Si$
58	17.9	4.9	$^{\dot{+}}CH_2O—Si$
44	43.5	42.3	$^{\dot{+}}O—Si$
43	31.5	-	$^{+\cdot}CHCH_2O$

Table 4

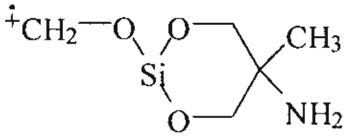
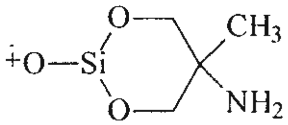
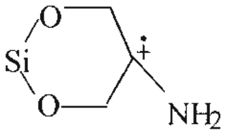
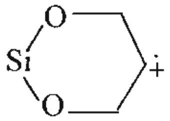
m/e	Intensities		Proposed Structure
	Polymer	Monomer	
161	-	0.8	
147	-	1.2	
116	-	13	
100	-	28	
74	-	46	$\dot{+}CH_2O{-}Si{-}O$
70	42.9	-	$\overset{+}{\cdot}CCH_2O$ - Si
58	12.8	54	$\dot{+}CH_2O{-}Si$
56	100	-	$\overset{+}{\cdot}CH_2CCH_2O$
44	62.9	100	$\dot{+}O{-}Si$
42	32	-	$\overset{+}{\cdot}CCH_2O$

Table 5

Sample	Density (g/cm^3) *		Result (%)**
	Monomer	Polymer	
A	1.7342	1.7517	-1.01
B	1.6111	1.6329	-1.35
C	1.5537	1.5638	-0.65

** (-) Shrinkage; (+) Expansion

* The data was averaged from 3 repeatedly experimental values.

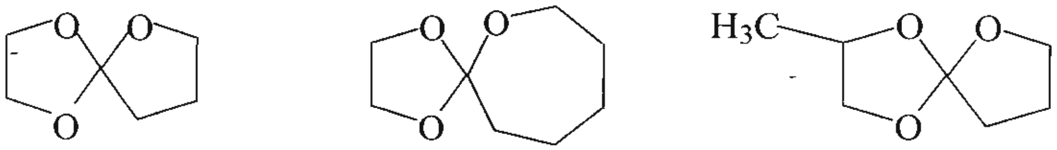
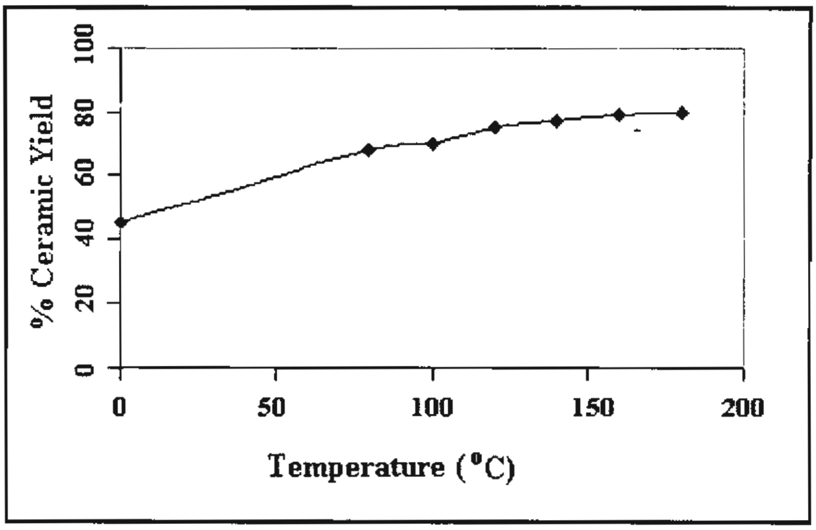
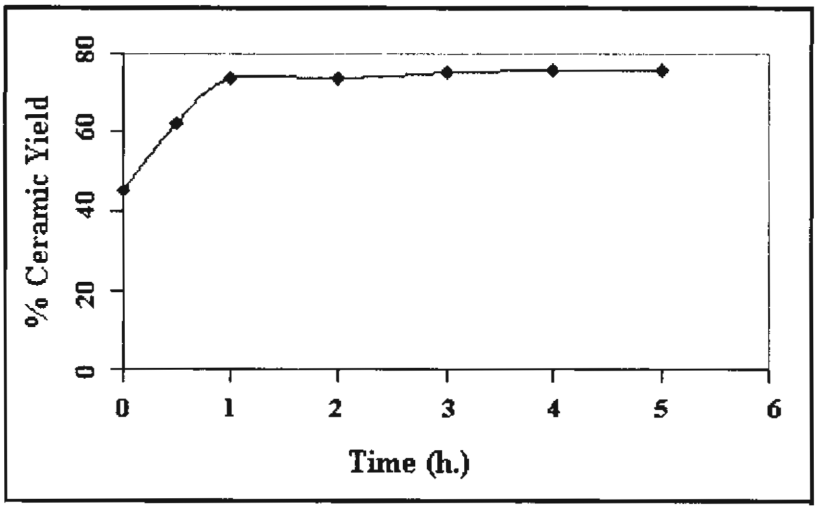


Figure 1

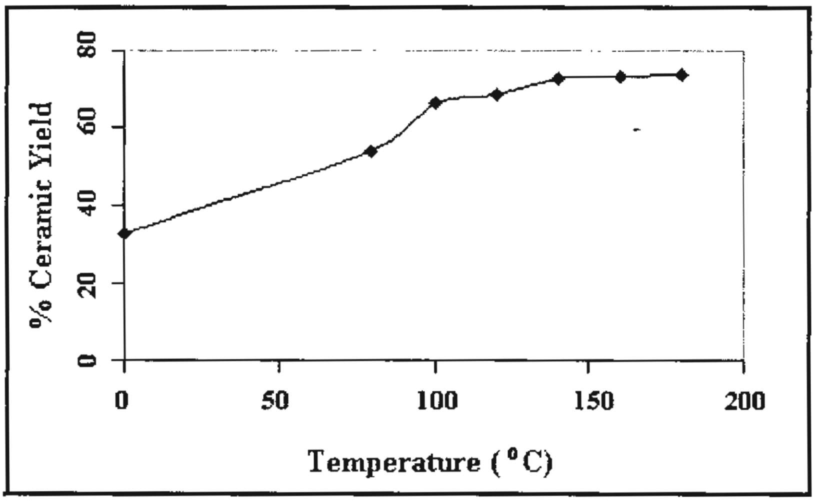

% Ceramic Yield
0
20
40
60
80
100
0
50
100
150
200
Temperature (°C)

(a)

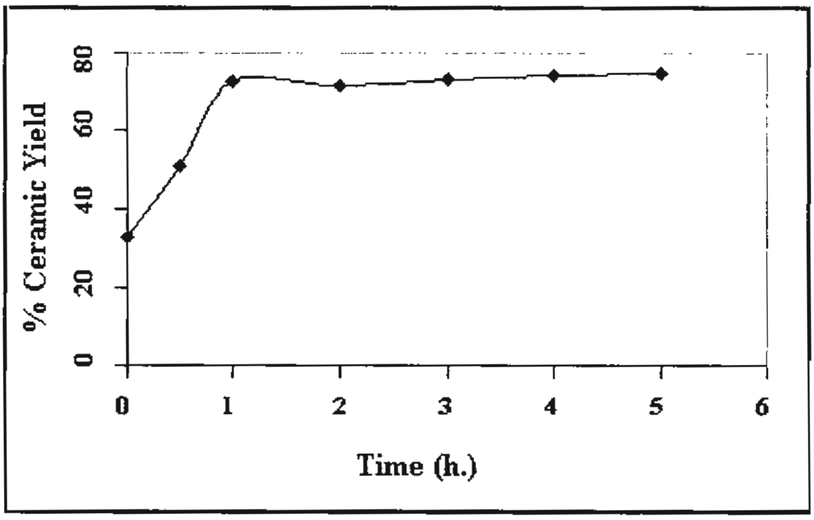

% Ceramic Yield
0
20
40
60
80
0
1
2
3
4
5
6
Time (h.)

(b)

Figure 2

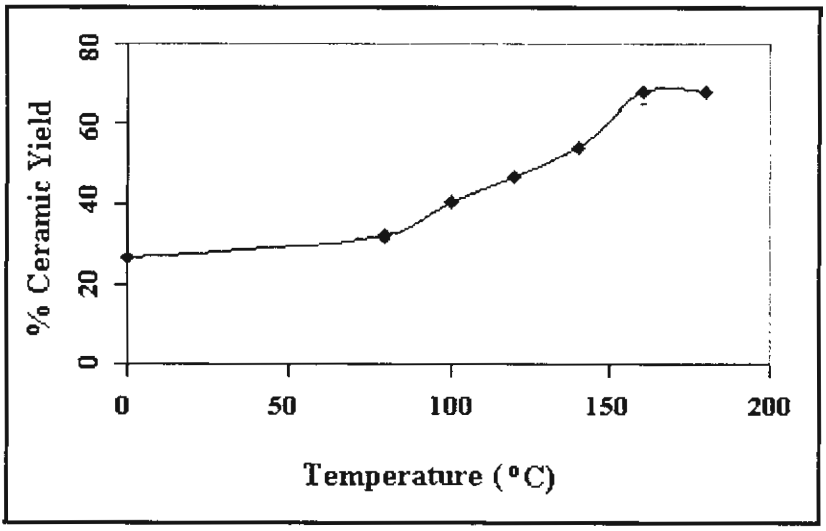

% Ceramic Yield
0
20
40
60
80
0
50
100
150
200
Temperature (°C)

(a)

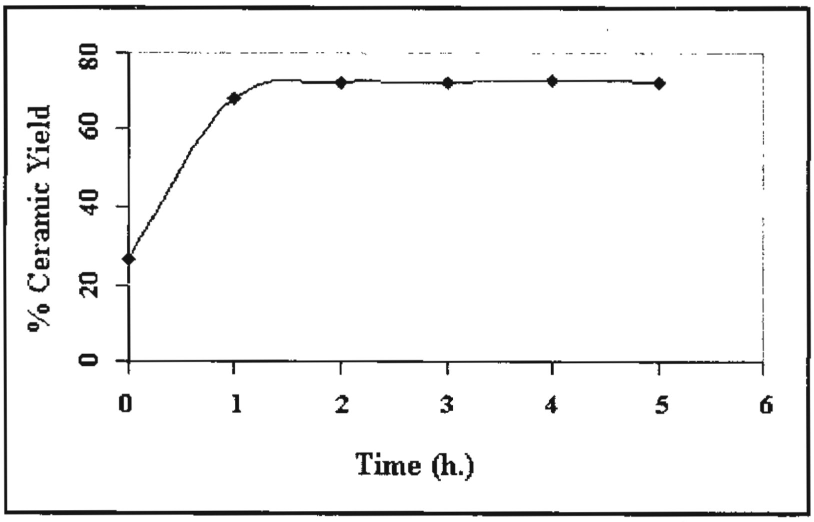

% Ceramic Yield
0
20
40
60
80
0
1
2
3
4
5
6
Time (h.)

(b)

Figure 3

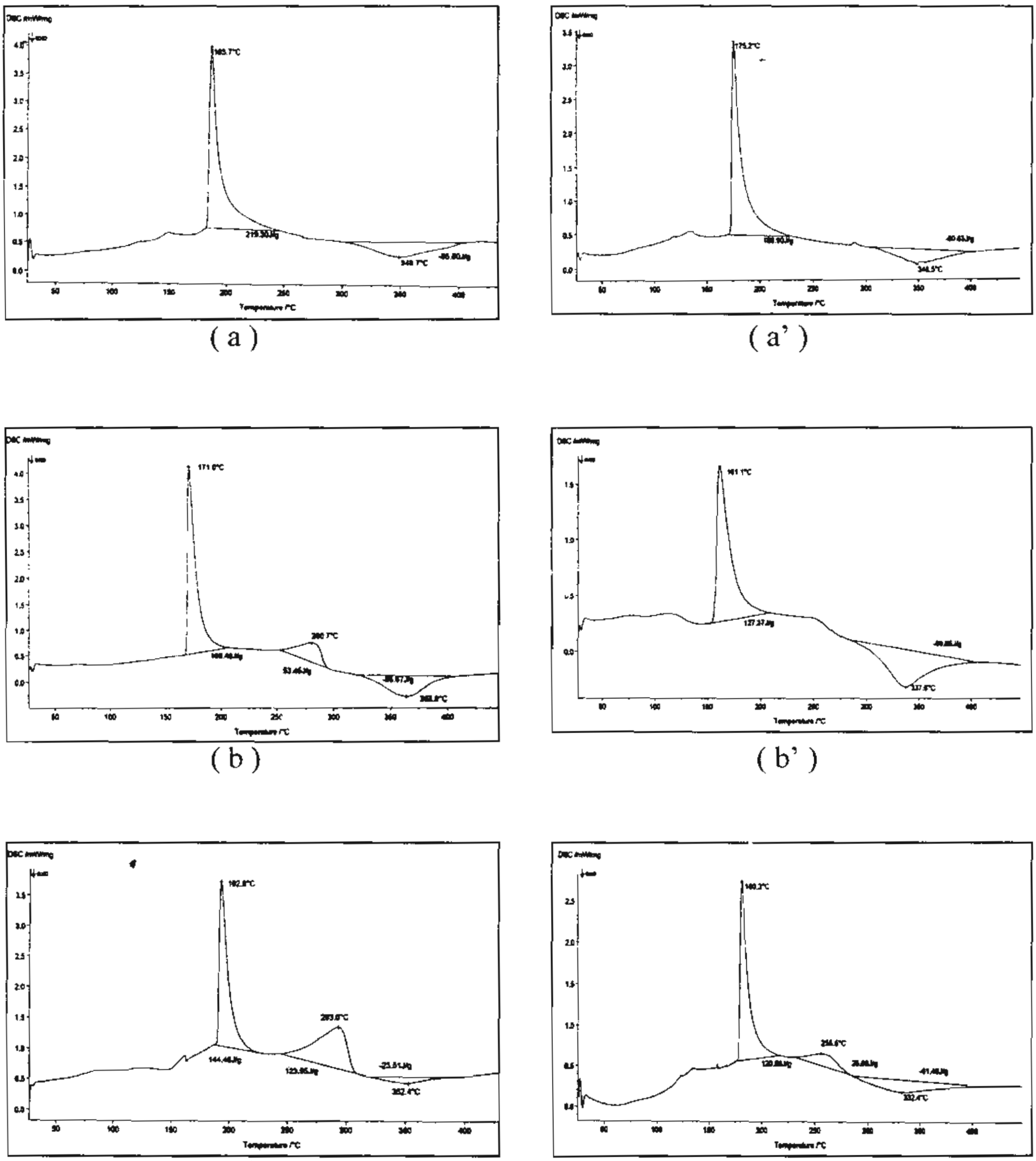

% Ceramic Yield
0
20
40
60
80
0
50
100
150
200
Temperature (°C)

(a)


% Ceramic Yield
0
20
40
60
80
0
1
2
3
4
5
6
Time (h.)

(b)

Figure 4



(a) (a')

(b) (b')

(c) (c')

Figure 5

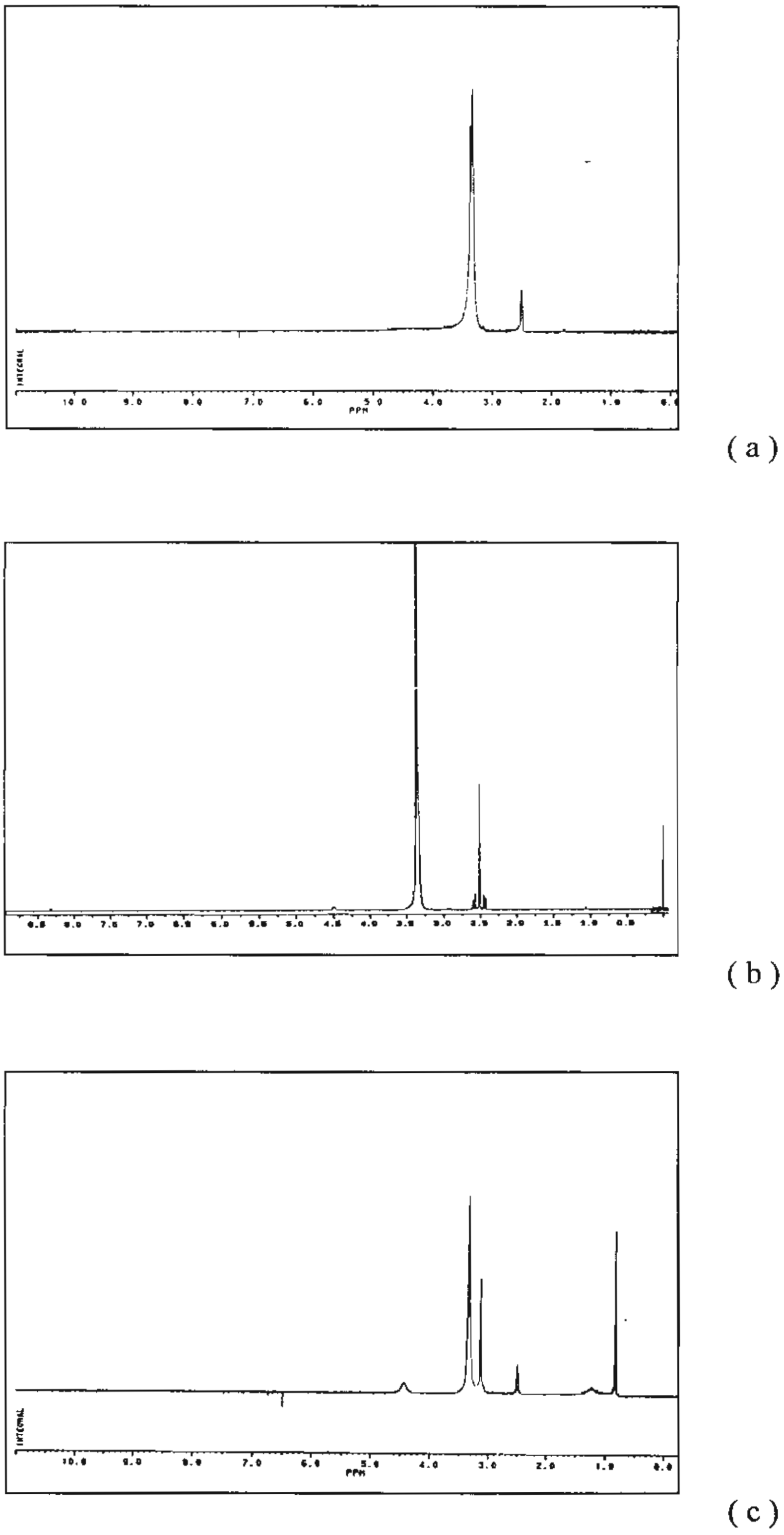

INTEGRAL
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
PPM
(a)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(b)
INTEGRAL
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
PPM
(c)

Figure 6

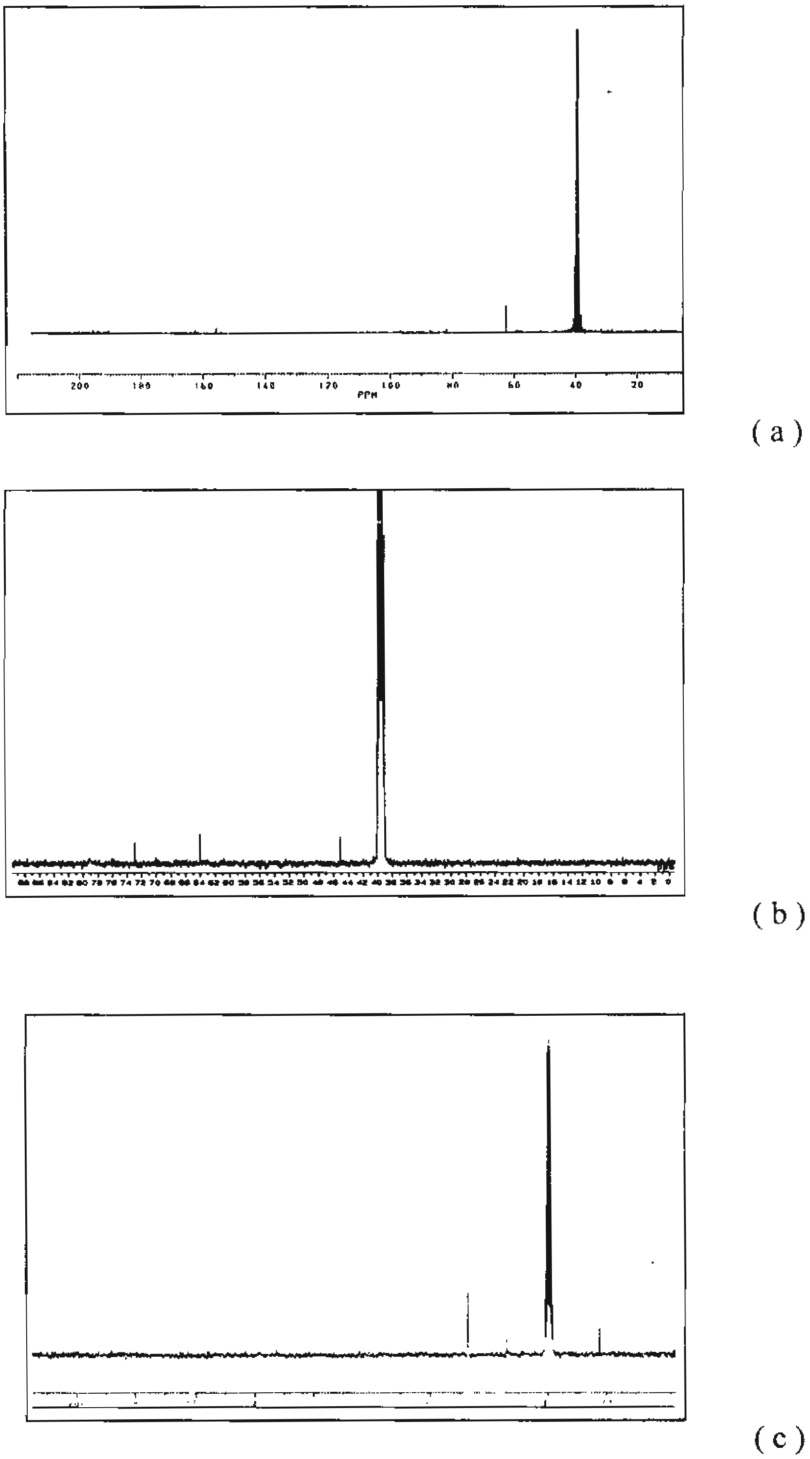
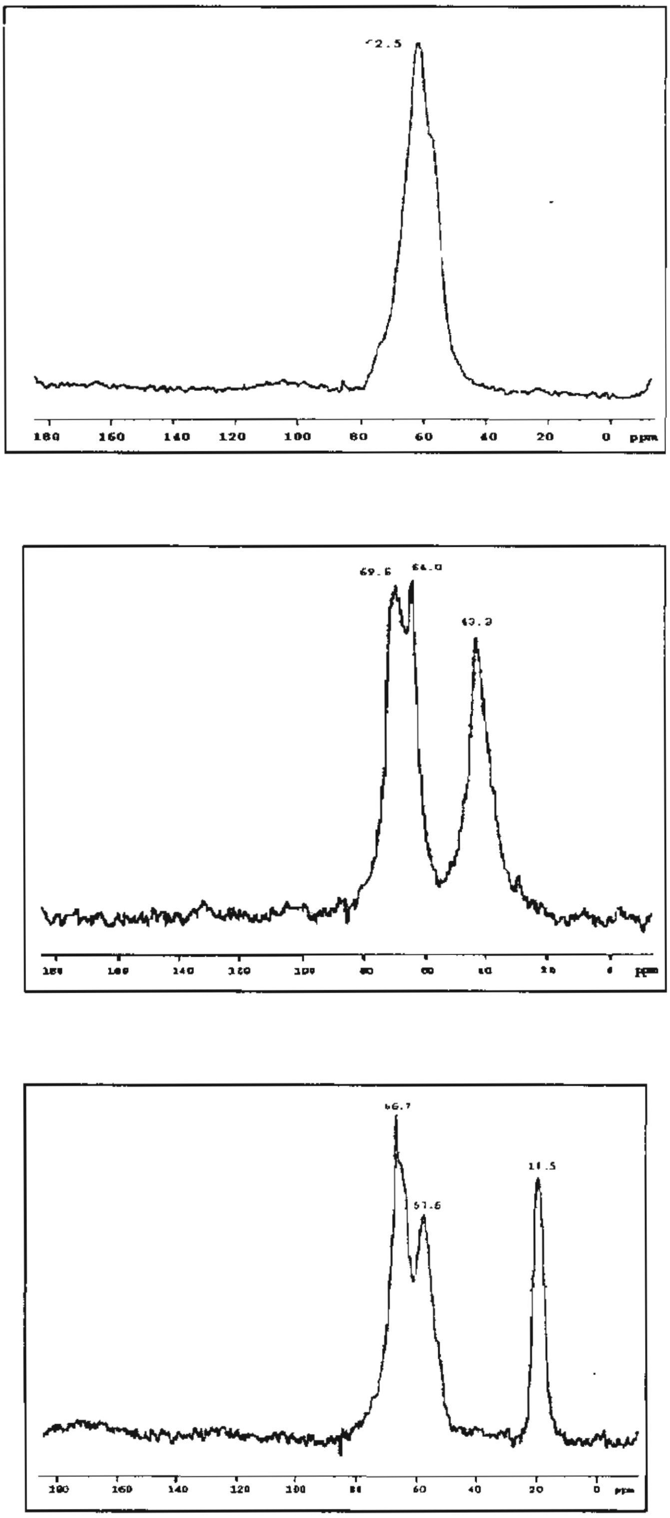

200
180
160
140
120
PPM
100
80
60
40
20
(a)
88 86 84 82 80 78 76 74 72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
ppm
(b)
(c)

Figure 7


62.5
180
160
140
120
100
80
60
40
20
0
ppm
69.6
64.0
43.2
180
160
140
120
100
80
60
40
20
0
ppm
66.7
57.6
19.5
180
160
140
120
100
80
60
40
20
0
ppm

(a)

(b)

(c)

Figure 8

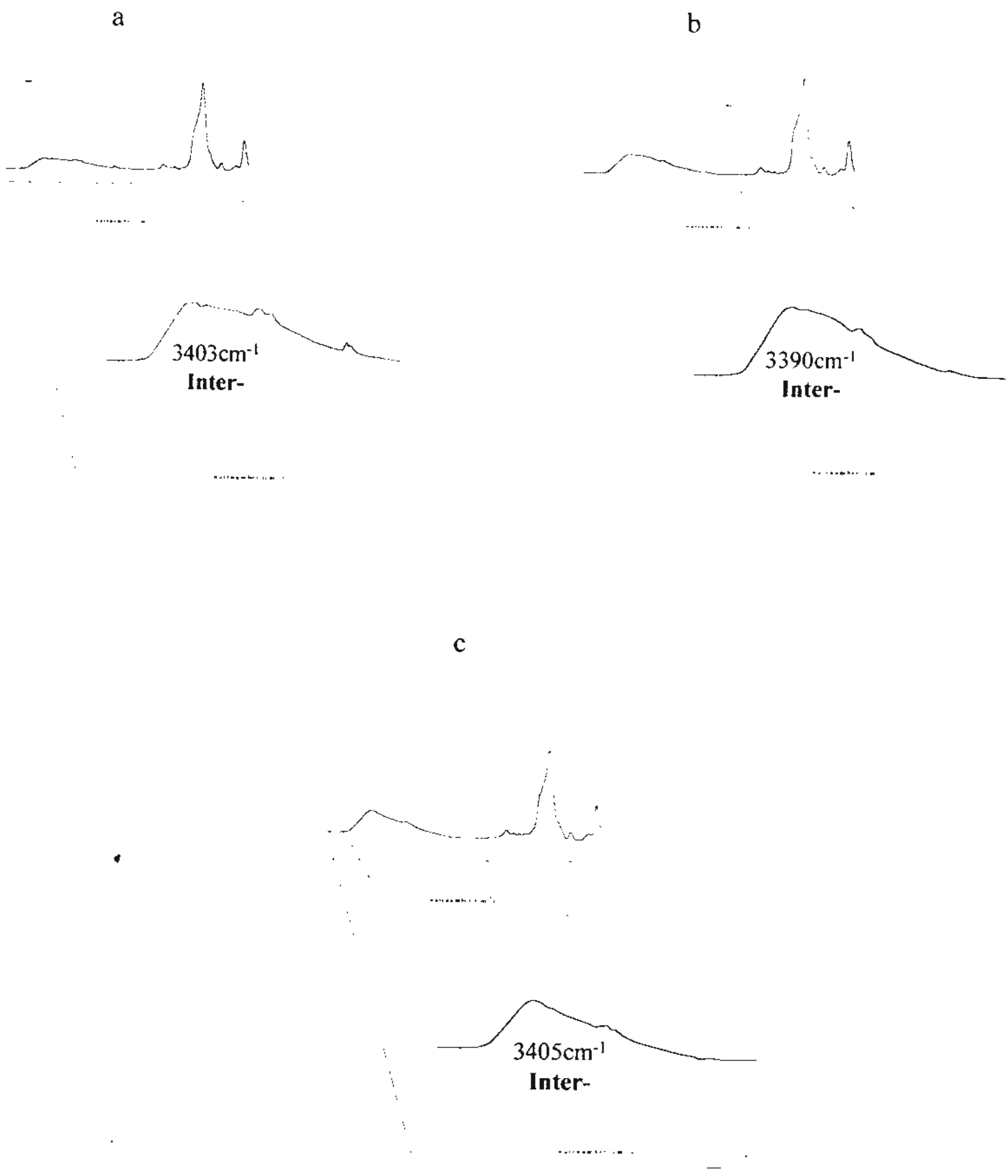


Figure 9

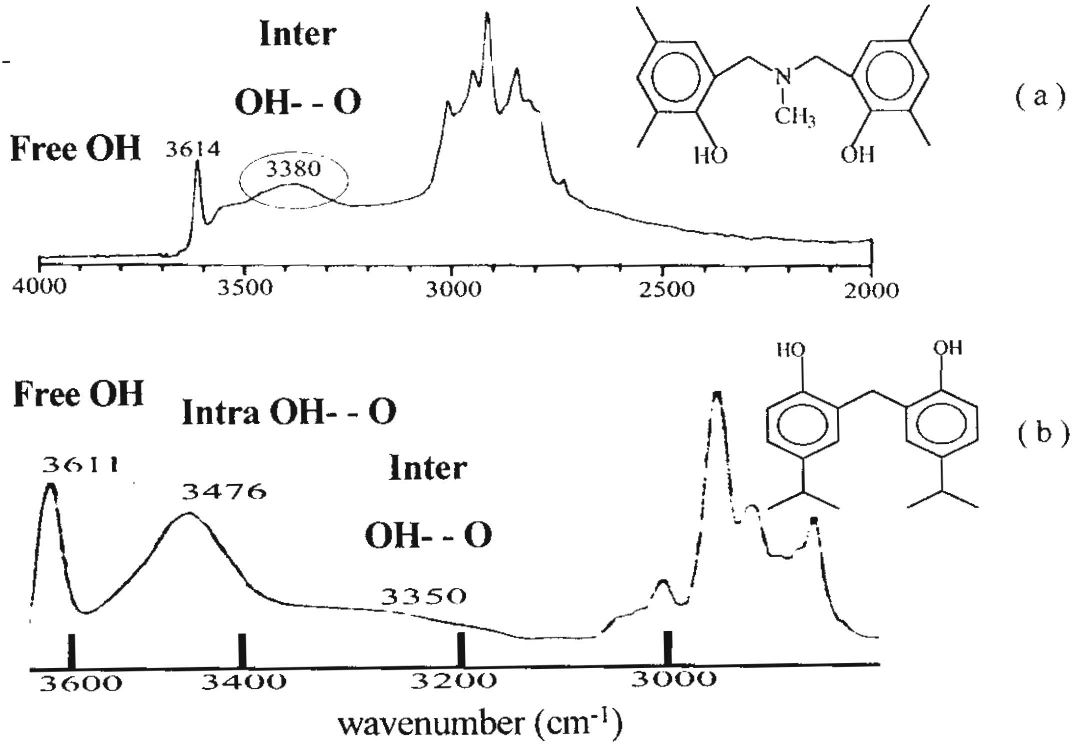

Inter
OH- - O
Free OH
3614
3380
CH3
HO
OH
(a)
4000
3500
3000
2500
2000
HO
OH
Free OH
Intra OH- - O
(b)
3611
3476
Inter
OH- - O
3350
3600
3400
3200
3000
wavenumber (cm-1)

Figure 10

APPENDIX D

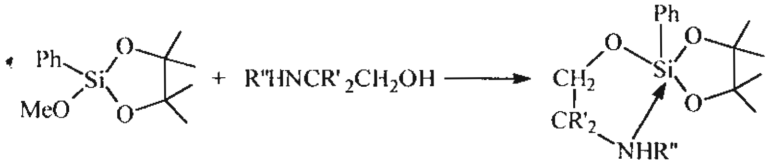
Thai Manuscript of Spirosilicate Compounds

สารประกอบสไปโรซิลิเคต

นพพร ธนบดีกิจ และ สุจิตรา วงศ์เกษมจิตต์*
วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย พญาไท กรุงเทพฯ 10330

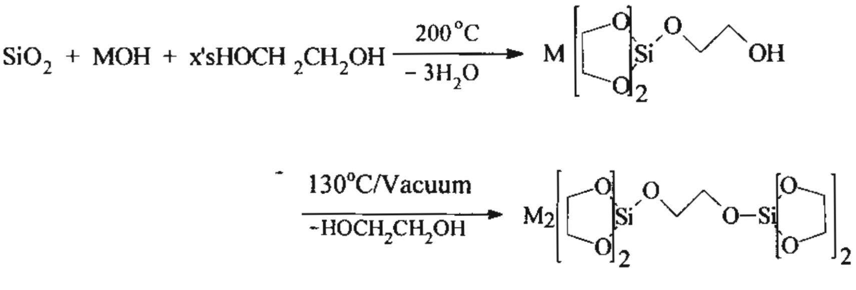
โดยทั่วไป เรซิ่นประเภทเทอร์โมเซตจะมีการหดตัวประมาณ 3-15% ระหว่างขั้นตอนการพอลิเมอไรซ์(1-3) ดังนั้น เรซิ่นที่ไม่มีการหดตัวจะมีข้อดีในการนำไปใช้ทำองค์ประกอบในอุตสาหกรรมที่ต้องการความแม่นยำสูง ตัวอย่างเช่น อุตสาหกรรมทางด้านทันตกรรม หรือนำไปใช้เป็นสารที่ต้องการความแข็งแรงสูง เช่น การทำกาว หรือ สารเคลือบผิว(4-7) ตั้งแต่อดีตจนถึงปัจจุบัน มีการนำสารประเภทสไปโรออโธคาร์บอเนต และสไปโรออโธเอสเทอร์โมโนเมอร์ ไปประยุกต์โดยนำไปผ่านกระบวนการพอลิเมอไรเซชันพบว่า มีการหดตัว หรือขยายตัวเพียงเล็กน้อย อย่างไรก็ตาม Tg (glass transition temperature) ของสารเหล่านี้ค่อนข้างต่ำ ทำให้นำไปใช้งานได้น้อย ยิ่งไปกว่านี้ การสังเคราะห์สไปโรคาร์บอเนต และสไปโรเอสเทอร์มีขั้นตอนค่อนข้างสลับซับซ้อนอีกด้วย(8-13)

จากการรายงานของ Frye ในการเตรียมสไปโรไซลอกเซนจากซิลิกอนเตตระเอธอกไซด์ ($Si(OEt_4)$) กับ เอททีลีนไกลคอล ในสารละลายผสมระหว่างเมธานอล และโซเดียมเมธอกไซด์ที่มีปริมาณเล็กน้อย พบว่า สารผลิตภัณฑ์ที่ได้เป็นประเภทพอลิเมอร์ และยังพบอีกว่า ในกรณีที่มีเอมีนเบสเข้ามาในระบบจะได้สารที่มีจำนวนโคออดิเนชันเท่ากับ 5 (penta-coordinated compound) (แผนภาพที่ 1)(14-16)



แผนภาพที่ 1

จากการศึกษาของ Laine และผู้ร่วมงาน ในการสังเคราะห์เพนตะโคออดิเนตและเฮกซะโคออดิเนตสไปโรซิลิเคตจากซิลิกาและเอททีลีนไกลคอล โดยมีโลหะไฮดรอกไซด์ของธาตุหมู่ 1 และโลหะออกไซด์ของธาตุหมู่ 2 เป็นคะตะลิสต์(17-18) ข้อเสียของการศึกษานี้ คือ เบสแก่เหล่านี้มีราคาแพงและไม่เสถียรต่อสิ่งแวดล้อม (แผนภาพที่ 2)



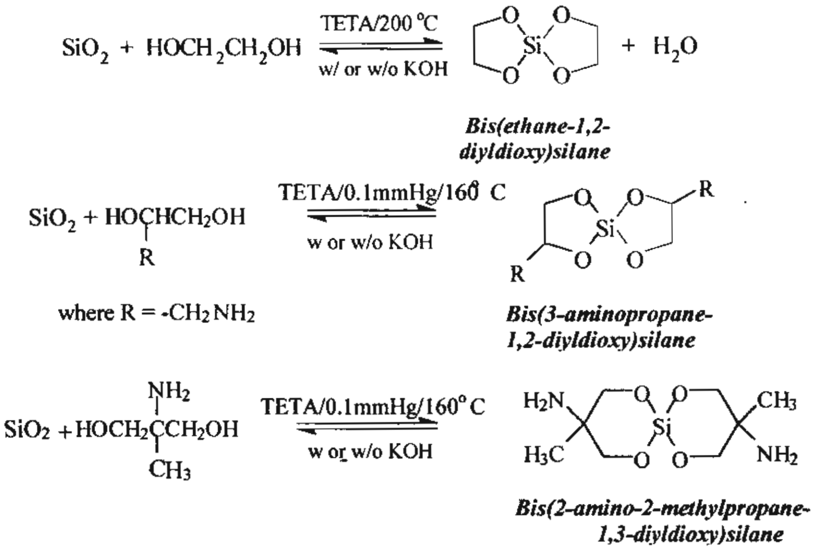
แผนภาพที่ 2

เมื่อพิจารณาจากตารางธาตุ พบว่า แม้ว่าตำแหน่งของซิลิกอนและคาร์บอนจะอยู่ในหมู่ IV เดียวกัน แต่สมบัติของธาตุทั้ง 2 ตัว กลับแตกต่างกัน ตัวอย่างเช่น พลังงานพันธะระหว่างซิลิกอนและออกซิเจน (Si-O) สูงกว่าพลังงานพันธะระหว่างคาร์บอนและออกซิเจน (C-O) 22 กิโลแคลอรี่ต่อโมล ทำให้พอลิเมอร์ที่เกิดจากการสร้างพันธะกับ Si-O เป็นสารที่น่าสนใจ และมีความสำคัญ เนื่องจาก สารเหล่านี้จะสามารถทนต่อความร้อน การออกซิเดชัน และสารเคมีอื่นๆ ได้ดี(19)

ในบทความฉบับนี้ ได้บรรยายถึงการสังเคราะห์สไปโรซิลิเคต ซึ่งเป็นสารซิลิกอนแอลคอกไซด์ประเภทที่มีจำนวนโคออดิเนชันเท่ากับ 4 (tetra-coordinated spirosilicates) โดยใช้สารซิลิกาเป็นสารตั้งต้นที่มีราคาถูกและมีอยู่มากในธรรมชาติ และสารเอธิลีนไกลคอลที่สามารถผลิตได้เองภายในประเทศ นอกจากนี้ ยังได้กล่าวถึงการสังเคราะห์อนุพันธ์ของสารประกอบสไปโรซิลิเคตที่เกิดจากการทำปฏิกิริยาระหว่างซิลิกากับ 3-อะมิโน-1,2-โพรเพนไดออล (3-amino-1,2-propanediol) หรือ 2-อะมิโน-2-เมธิล-1,3-โพรเพนไดออล (2-amino-2-methyl-1,3-propanediol) การเลือกใช้เอธิลีนไกลคอลเป็นสารตั้งต้นตัวหนึ่ง เนื่องจากเป็นสารประเภท 1,2 ไดออล ซึ่งคาดว่าจะให้โครงสร้างเหมือนกับสไปโรออโธคาร์บอเนต หรือสไปโรออโธเอสเทอร์ ซึ่งมีการหดตัวเพียงเล็กน้อยในขั้นตอนการพอลิเมอไรซ์ นอกจากนี้ อนุพันธ์ของสไปโรซิลิเคตที่ใช้ 3-อะมิโน-1,2-โพรเพนไดออล หรือ 2-อะมิโน-2-เมททิล-1,3-โพรเพนไดออล เป็นสารตั้งต้น ยังสามารถนำไปพัฒนาต่อไปได้

วิธีการสังเคราะห์สารประกอบสไปโรซิลิเคต

วงศ์เกษมจิตต์ และคณะ(20) พบว่า ไตรเอธิลีนเตเตระมีน (triethylenetetramine, TETA) สามารถใช้เป็นตัวเร่งปฏิกิริยาการละลายของสารตั้งต้นซิลิกา ดังนั้น การสังเคราะห์สไปโรซิลิเคตจึงควรจะเตรียมได้โดยตรงจากซิลิกาและเอธิลีนไกลคอล หรือ 3-อะมิโน-1,2-โพรเพนไดออล หรือ 2-อะมิโน-2-เมททิล-1,3-โพรเพนไดออล และใช้ ไตรเอธิลีนเตเตระมีน เป็นตัวเร่งปฏิกิริยา อย่างไรก็ตาม อัตราการเกิดปฏิกิริยาที่มีเฉพาะไตรเอธิลีนเตเตระมีน เป็นตัวเร่งปฏิกิริยา ค่อนข้างช้า ดังนั้น เพื่อเป็นการเพิ่มอัตราการเกิดปฏิกิริยา จำเป็นต้องใช้โปแทสเซียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยาร่วมด้วย ดังแสดงในแผนภาพที่ 3



แผนภาพที่ 3.

บิส(เอเธน-1,2-ไดอิลไดออกซี)ไซเลน เตรียมได้จากการทำปฏิกิริยาระหว่างซิลิกาและเอธิลีนไกลคอล ณ อุณหภูมิที่ประมาณจุดเดือดของเอธิลีนไกลคอล ปฏิกิริยาที่เกิดขึ้นเป็นปฏิกิริยาการควบแน่น (condensation reaction) ดังนั้น น้ำจะเป็นผลพลอยได้จากการเกิดปฏิกิริยา และเพื่อให้ปฏิกิริยาดำเนินไปข้างหน้าอย่างต่อเนื่อง การกำจัดน้ำออกขณะเกิดปฏิกิริยาจึงเป็นสิ่งจำเป็นอย่างยิ่ง อย่างไรก็ตาม เมื่อปฏิกิริยาโดยมีแต่ไตรเอธิลีนเตเตระมีนเป็นตัวเร่ง การสังเคราะห์ต้องใช้เวลานานถึง 18 ชั่วโมง ขณะที่ปฏิกิริยาที่มีโปแทสเซียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยาร่วมด้วยสามารถประหยัดเวลาในการสังเคราะห์ได้ถึง 8 ชั่วโมง ในกรณีที่ใช้ซิลิกาที่มีพื้นที่ผิวสูง เช่น ฟูมซิลิกา (fumed silica) ซึ่งมีพื้นที่ผิวเท่ากับ 280 ตารางเมตร ต่อ กรัม ความว่องไวต่อปฏิกิริยาจะมีมากกว่าซิลิกาที่เกิดจากการหลอมตัว (fused silica) ซึ่งมีพื้นที่ผิว 182 ตารางเมตร ต่อ กรัม มาก หมายความว่า พื้นที่ผิวสูงขึ้น ความว่องไวต่อการเกิดปฏิกิริยามากขึ้น และเมื่อใช้โปแทสเซียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยาร่วมในระบบด้วย ปฏิกิริยาของฟูมซิลิกาเกิดอย่างสมบูรณ์ภายในระยะเวลาเพียง 4 ชั่วโมง เท่านั้น ในขณะที่ซิลิกาที่เกิดจากการหลอมตัวใช้เวลา 10 ชั่วโมง ในการเกิดปฏิกิริยาสมบูรณ์ เหตุผลก็คือ โปแทสเซียมไฮดรอกไซด์เป็นด่างที่แรง สามารถดึงโปรตอนจากเอธิลีนไกลคอลได้เร็วกว่าไตรเอธิลีนเตเตระมีนมาก แต่ในกรณีที่ใช้เพียงโปแทสเซียมไฮดรอกไซด์เพียงอย่างเดียว จากการรายงานของ Laine และผู้ร่วมงาน(17-18) พบว่า จะได้เพนตะโคออดิเนตสไปโรซิลิเคตเท่านั้น

สำหรับอะมิโนสไปโรซิลิเคตของ บิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน และ บิส(2-อะมิโน-2-เมททิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน ปฏิกิริยาต้องดำเนินไปภายใต้ระบบสุญญากาศ อุณหภูมิที่ใช้จะเท่ากับจุดเดือดของสารตั้งต้นเอมีน นั่นคือ ที่ 264 องศาเซลเซียส ต่อ 739 มิลลิเมตรปรอท สำหรับ 3-อะมิโน-1,2-โพรเพนไดออล และ 151 องศาเซลเซียส ต่อ 10 มิลลิเมตรปรอท สำหรับ 2-อะมิโน-2-เมททิล-1,3-โพรเพนไดออล สำหรับไตรเอธิลีนเตเตระมีน ซึ่งมีจุดเดือดใกล้เคียงกับจุดเดือดของสารตั้งต้นเอมีนดังกล่าว คือ 266 องศาเซลเซียส ต่อ 760 มิลลิเมตรปรอท ถูกนำมาใช้เป็นทั้งตัวเร่งปฏิกิริยาและตัวทำละลาย ดังนั้น เพื่อที่จะได้สารผลิตภัณฑ์ปริมาณมาก ระหว่างการเกิดปฏิกิริยา จำเป็นต้องกลั่นน้ำและไตรเอธิลีนเตตระมีนออกเพื่อให้ปฏิกิริยาดำเนินไปข้างหน้า ขณะเดียวกัน สารตั้งต้นเอมีนจะถูกกลั่นออกมาด้วย ดังนั้น จึงจำเป็นต้องใช้อะมิโนไดออลทั้งสองชนิดในปริมาณมาก เพื่อให้ได้ปริมาณสารผลิตภัณฑ์สูง โดยเปอร์เซ็นต์ที่ได้ของสารผลิตภัณฑ์ทั้งสองจากการสังเคราะห์ที่ใช้ฟูมซิลิกา คือ >70% และ >80% ตามลำดับ เวลาที่ใช้ในการเกิดปฏิกิริยาสมบูรณ์สำหรับสารผลิตภัณฑ์ชนิดแรกคือ 10 และ 14 ชั่วโมงในระบบที่มีและไม่มีโปแทสเซียมไฮดรอกไซด์ ตามลำดับ สารผลิตภัณฑ์เอมีนชนิดที่สองใช้เวลา 14 ชั่วโมงในระบบที่มีโปแทสเซียมไฮดรอกไซด์เป็นตัวเร่ง และ 24 ชั่วโมง ในระบบที่ไม่มีโปแทสเซียมไฮดรอกไซด์ สาเหตุเช่นเดียวกับที่ได้กล่าวมาแล้วข้างต้น และเนื่องมาจากจุดเดือดที่สูงกว่าของ 2-อะมิโน-2-เมททิล-1,3-โพรเพนไดออล ทำให้ต้องใช้เวลามากกว่าในการเกิดปฏิกิริยาให้สมบูรณ์

การตรวจสอบโครงสร้างผลิตภัณฑ์

การวิเคราะห์โครงสร้างของผลิตภัณฑ์สไปโรซิลิเคตทำเช่นเดียวกับการตรวจสอบโครงสร้างของสารตัวใหม่ทั่วไป นั่นคือ การใช้ ฟูเรียร์ทรานสฟอร์ม อินฟราเรดสเปกโตรมิเตอร์ (FTIR) เพื่อศึกษาหมู่ฟังก์ชันแนลที่สำคัญ โปรตอน คาร์บอน และ ซิลิกอน นิวเคลียร์แมกเนติกเรโซแนนซ์ (^{1}H-, ^{13}C- และ ^{29}Si-NMR) ใช้ศึกษาชนิดของโปรตอน คาร์บอน และซิลิกอนในผลิตภัณฑ์ สำหรับเครื่องฟาสต์อะตอมิกบอมบาดเมนท์ แมสสเปกโตรเมตรี (FAB^{+}-MS) ใช้หาน้ำหนักโมเลกุล และการแตกตัวเป็นอิออนเล็กๆ ส่วนทางด้านการทนต่อความร้อนของสาร ใช้เครื่องเทอร์โมกราวิเมตรี (TGA) วิเคราะห์

FTIR สเปกตรัมของสารสไปโรซิลิเคตทุกชนิด แสดงตำแหน่งพีคที่ 3386 ซม$^{-1}$ ซึ่งเป็นการยืดหยุ่นของพันธะระหว่างไนโตรเจน และไฮโดรเจน (N-H) และพันธะระหว่างออกซิเจน และไฮโดรเจน (O-H)(21) พีคที่ตำแหน่ง 2949-2882 ซม$^{-1}$ คือ พันธะคาร์บอน และไฮโดรเจน (C-H) ส่วนที่ 1085, 966 และ 883 ซม$^{-1}$ เป็นการยืดหยุ่นของพันธะซิลิกอน-ออกซิเจน-คาร์บอน (Si-O-C) ผลของ FTIR สเปกตรัมสรุปอยู่ในตารางที่ 1

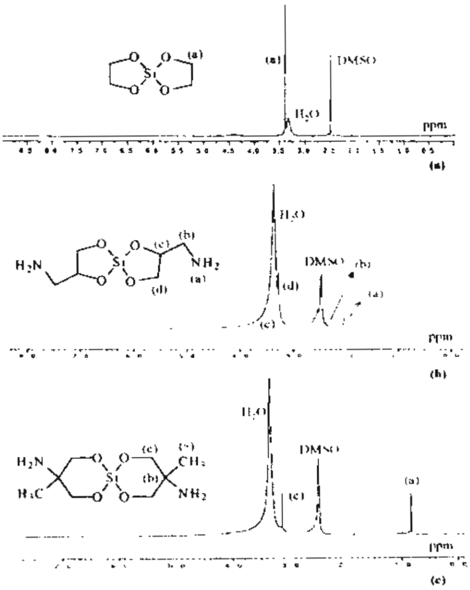
ตารางที่ 1 ผล FTIR ของ บิส(อีเทน-1,2-ไดอิลไดออกซี)ไซเลน (1) บิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน (2) และ บิส(2-อะมิโน-2-เมทิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน (3)

สารผลิตภัณฑ์	ช่วงความยาวคลื่น (ซม$^{-1}$)	ชนิดของพันธะเคมี
1	3386	-OH (น้ำที่ถูกดูดซับในสารผลิตภัณฑ์)
	2949-2882	C-H บอนด์
	1085 966 และ 883	Si-O-C บอนด์
2	3406	-OH :น้ำที่ดูดซับในสารผลิตภัณฑ์; -NH$_2$
	2955-2889	C-H ยืด
	1060 966 และ 872	Si-O-C ยืด
3	3379	-OH :น้ำที่ดูดซับในสารผลิตภัณฑ์; -NH$_2$
	2953-2868	C-H ยืด
	1082 962 และ 883	Si-O-C ยืด

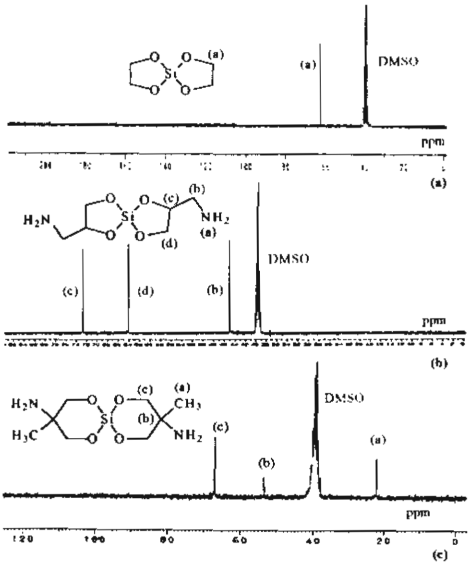
ผลของ ^{1}H-NMR (รูปที่ 1) แสดงตำแหน่งของน้ำที่ตำแหน่ง 3.27 ppm น้ำเหล่านี้มาจากตัวทำละลายที่ใช้ในการวิเคราะห์ NMR คือ ดิวทีเรตไดเมธิลซัลฟอกไซด์ และจากการดูดซึมซับของผลิตภัณฑ์ ซึ่งตรงกับผลที่ได้จาก FTIR สำหรับ บิส(อีเทน-1,2-ไดอิลไดออกซี)ไซเลน ปรากฏพีคเดี่ยว (Singlet) เพียงตำแหน่งเดียว ที่ 3.38 ppm ซึ่งเป็นผลมาจากไฮโดรเจนอะตอมที่ต่อกับคาร์บอนใกล้ออกซิเจนและซิลิกอน (CH$_2$-O-Si) ผลของบิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน ปรากฏพีคเดี่ยว ที่ 2.05 ppm ซึ่งเป็นผลมาจากไฮโดรเจนอะตอมของหมู่เอมีน พีคหัวแตกหลายพีค (multiplet) ที่ตำแหน่ง 2.45 ppm ซึ่งเป็นสัญญาณของหมู่เมธิลีนที่ต่ออยู่กับอะตอมไนโตรเจน (CH$_2$-N) พีคหัวแตกเป็น 2 พีค (douplet) ที่ตำแหน่ง 3.29 ppm เป็นตำแหน่งของหมู่เมธิลีนใกล้อะตอมออกซิเจน (CH$_2$-O-Si) อย่างไรก็ตาม อะตอมไฮโดรเจนของ CH-O-Si ซ้อนทับกับตำแหน่งของน้ำ ซึ่งสามารถใช้วิธี ^{13}C-NMR ในการพิสูจน์แทนได้ ^{1}H-NMR ของบิส(2-อะมิโน-2-เมทิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน แสดงตำแน่งชัดเจนของพีคเดี่ยวที่ 0.83 ppm ของ หมู่เมธิล (-CH$_3$) และ ที่ 3.13 ppm ของหมู่เมธิลีนที่ต่อกับอะตอมออกซิเจน (CH$_2$-O-Si)

ผล ^{13}C-NMR ซึ่งแสดงในรูปที่ 2 ให้ผลสอดคล้องกับผลของ FTIR และ^{1}H-NMR คือ บิส(อีเทน-1,2-ไดอิลไดออกซี)ไซเลน แสดงสัญญาณของคาร์ชนิดเดียวที่ตำแหน่ง 62.7 ppm (CH$_2$-O-Si) ขณะที่ บิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน แสดงชนิดของคาร์บอนจำนวน 3 ชนิด ที่ตำแหน่ง 44.9 ppm (CH$_2$-N) 64.0 ppm (CH$_2$-O-Si) และ 72.7

ppm (CH_2-O-Si) เช่นเดียวกับบิส(2-อะมิโน-2-เมททิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน ซึ่งแสดงตำแหน่งสัญญาณของคาร์บอน 3 ชนิดที่ 22.0 ppm (CH_3) 53.5 ppm (C) และ 67.1 ppm (CH_2-O-Si)

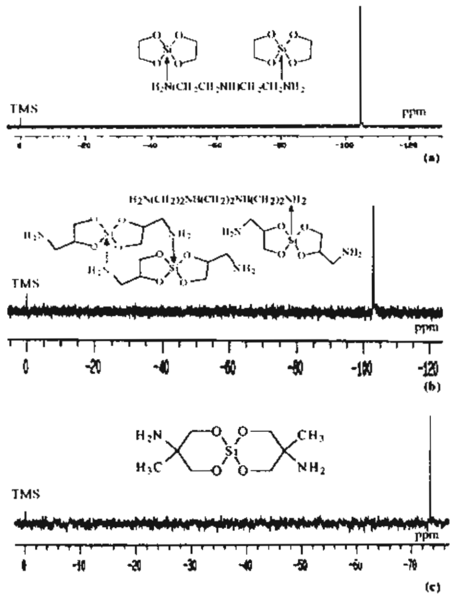


รูปที่ 1 โปรตรอนนิวเคลียแมกเนติกเรโซแนนซ์ของ (a) บิส(อีเทน-1,2-ไดอิลไดออกซี)ไซเลน, (b) บิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน และ (c) บิส(2-อะมิโน-2-เมททิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน



รูปที่ 2 คาร์บอน 13 นิวเคลียแมกเนติกเรโซแนนซ์ของ (a) บิส(อีเทน-1,2-ไดอิลไดออกซี)ไซเลน, (b) บิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน และ (c) บิส(2-อะมิโน-2-เมททิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน

ผลของ ^{29}Si-NMR สเปกตรัม (รูปที่ 3) สามารถยืนยันได้มากขึ้นว่า สารผลิตภัณฑ์ที่ได้เป็นเตตระโคออดิเนตสไปโรซิลิเคต แม้ว่าสารผลิตภัณฑ์สองชนิดแรกแสดงเรโซแนนซ์ที่ -104 และ -103 ppm ซึ่งเป็นเป็นตำแหน่งของสารชนิดเพนตะโคออดิเนต(22) เหตุผล ก็คือ การวิเคราะห์ชนิดของซิลิกอนในผลิตภัณฑ์ ได้ใช้สารละลายจากปฏิกิริยาโดยตรง ซึ่งในการทำปฏิกิริยามีไตรเอธิลีนเตตระมีนเป็นทั้งตัวเร่งปฏิกิริยา และตัวทำละลาย ดังนั้น จึงเกิดพันธะบางส่วนระหว่างซิลิกอนและไนโตรเจนของสารผลิตภัณฑ์และไตรเอธิลีนเตตระมีน หรือพันธะระหว่างผลิตภัณฑ์ด้วยกันเอง ดังเช่นผลิตภัณฑ์ที่สอง ทำให้เกิดเป็นสารประเภทเพนตะโคออดิเนตขึ้น เนื่องจากสารผลิตภัณฑ์ชนิดที่สองมีหมู่อะมิโนเป็นองค์ประกอบตามที่ Frye(15) ได้อธิบายไว้ ส่วน^{29}Si-NMR สเปกตรัม ของสารผลิตภัณฑ์ชนิดสุดท้ายแสดงสัญญาณที่ –77 ppm ซึ่งเป็นตำแหน่งของเตตระโคออดิเนต ในกรณีนี้ ไม่มีพันธะระหว่างสารผลิตภัณฑ์และไตรเอททีลีนเตตระมีน หรือ กับสารผลิตภัณฑ์ด้วยกันเอง เนื่องจากการกีดกั้นของโครงสร้าง มีผลทำให้อีกโมเลกุลหนึ่งไม่สามารถเข้าไปได้ (steric effect)

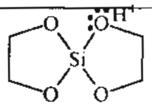
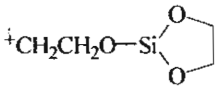


รูปที่ 3 ซิลิกอนนิวเคลียแมกเนติกเรโซแนนซ์ของ (a) บิส(อีเทน-1,2-ไดอิลไดออกซี)ไซเลน, (b) บิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน และ (c) บิส(2-อะมิโน-2-เมททิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน

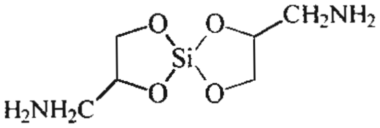
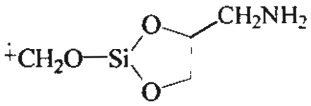
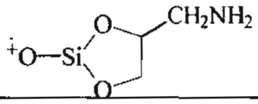
ผลแมสสเปคโตรมิเตอร์ของทั้งสามผลิตภัณฑ์ บิส(อีเทน-1,2-ไดอิลไดออกซี)ไซเลน บิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน และ บิส(2-อะมิโน-2-เมททิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน แสดงในตารางที่ 2-4 ตามลำดับ ผลจากตาราง สามารถบอกได้ว่า ผลิตภัณฑ์ทั้งสาม มีโครงสร้างดังที่ได้คาดไว้

นอกจากนี้ ผลอื่นๆ ที่สามารถยืนยันได้ว่า สารประกอบสไปโรซิลิเคตที่ได้ ไม่ได้มีโครงสร้างเป็นเพนตะโคออดิเนต แต่มีโครงสร้างเป็นเตตระโคออดิเนต คือ ผลจาก TGA (ตารางที่ 5) ซึ่งให้ผลของเปอร์เซ็นต์เซรามิกซ์ที่ได้มีค่าใกล้เคียงกับค่าที่ควรได้จากโครงสร้างแบบเตตระโคออดิเนต

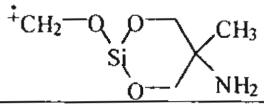
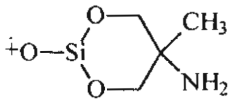
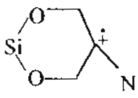
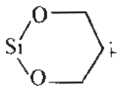
ตารางที่2 สรุปโครงสร้างจากผลแมสเสปคโตรมิเตอร์ของ บิส(อีเทน-1,2-ไดอิลไดออกซี)ไซเลน

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

ตารางที่3 สรุปโครงสร้างจากผลแมสเสปคโตรมิเตอร์ของ บิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน

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

ตารางที่4 สรุปโครงสร้างจากผลแมสเสปคโตรมิเตอร์ของ บิส(2-อะมิโน-2-เมททิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน

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

ตารางที่5 เปอร์เซ็นต์เซรามิกซ์ของ บิส(อีเทน-1,2-ไดอิลไดออกซี)ไซเลน, 1,บิส(3-อะมิโนโพรเพน-1,2-ไดอิลไดออกซี)ไซเลน, 2, และ บิส(2-อะมิโน-2-เมททิลโพรเพน-1,3-ไดอิลไดออกซี)ไซเลน, 3.

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

สรุป

สไปโรซิลิเคตชนิดเตตระโคออดิเนต สามารถสังเคราะห์ได้โดยตรงจากสารตั้งต้นที่มีราคาถูก และหาได้ง่ายในธรรมชาติ คือ ซิลิกา ซึ่งทำปฏิกิริยากับเอธิลีนไกลคอล กระบวนการสังเคราะห์ค่อนข้างง่าย และสะดวก สามารถสังเคราะห์ได้ภายในขั้นตอนเดียว โดยมีไตรเอธิลีนเตตระมีนเป็นตัวเร่ง และ/หรือ เป็นตัวทำละลาย อัตราเร็วในการเกิดปฏิกิริยาจะเพิ่มขึ้นมากในระบบที่ใช้โปแทสเซียมไฮดรอกไซด์เป็นตัวเร่งร่วม และระบบที่ใช้สารตั้งต้นซิลิกาที่มีพื้นที่ผิวสูง

บทความฉบับนี้ ได้มีการตีพิมพ์เป็นฉบับภาษาอังกฤษในวารสารนานาชาติ ดังนี้

> Varangkana Jitchum, Chivin Sun, Sujitra Wongkasemjit* and Hatsuo Ishida, "Synthesis of spirosilicates directly from silica and ethylene glycol/ethylene glycol derivatives", ***Tetrahedron*, 57 (18)**, 3997-4003 (2001).

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APPENDIX E

Thai Manuscript of Preparation High Surface Area Catalyst Support from Spirosilicates

การเตรียมสารรองรับคะตะลิสต์ที่มีพื้นที่ผิวสูงจากสารสไปโรซิลิเคต

นพพร ธนบดีกิจ และ สุจิตรา วงศ์เกษมจิตต์
วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย พญาไท กรุงเทพฯ 10330

สารตั้งต้นที่ใช้ในการพัฒนาผลิตภัณฑ์จากแก้ว และเซรามิกซ์ ซึ่งมีซิลิกอนเป็นองค์ประกอบมีอยู่เพียงไม่กี่ชนิด สาเหตุหลักเนื่องมาจากสารที่มีซิลิกอนเป็นองค์ประกอบจำเป็นต้องใช้อุณหภูมิสูงถึง 1200 องศาเซลเซียส ในการเตรียมขึ้นมา จัดว่าเป็นการสิ้นเปลืองพลังงาน(1) ดังนั้นสารประกอบประเภทออแกนโนซิลิเคตจึงจุดประกายความน่าสนใจในการนำไปใช้เป็นสารตั้งต้นสำหรับกระบวนการโซล-เจล เพื่อเตรียมการขึ้นรูปที่มีลักษณะและโครงสร้างสลับซับซ้อน โดยไม่ต้องใช้กระบวนการหลอมเหลว(2-3)

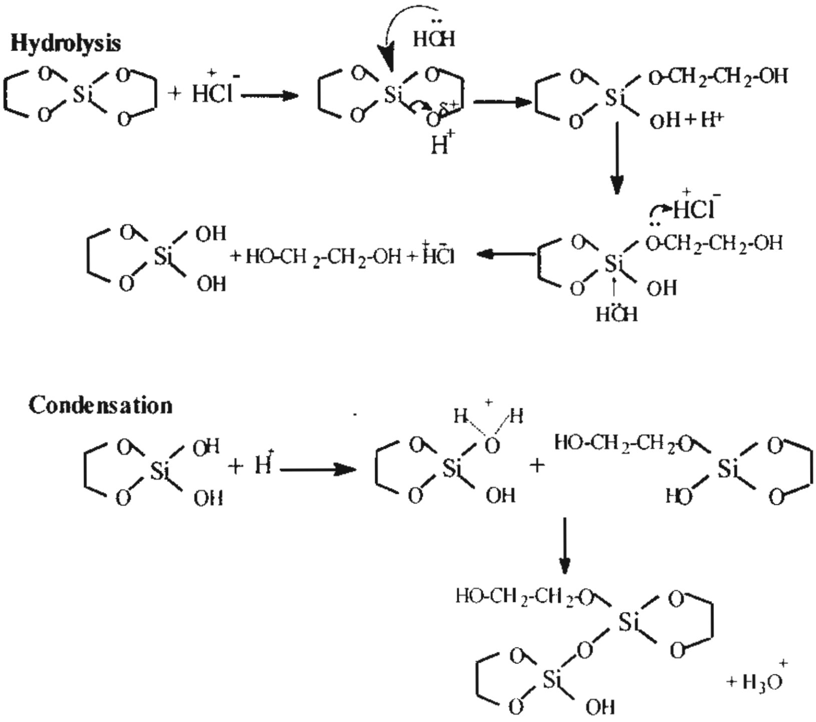
กระบวนการโซล-เจลของสารประเภทซิลิกอนแอลคอกไซด์ค่อนข้างง่าย เมื่อเทียบกับสารประเภทโลหะทรานซิชันแอลคอกไซด์ ซึ่งมีหลายระดับพลังงานในด้านของจำนวนโคออดิเนชัน(4) สารตั้งต้นซิลิกอนแอลคอกไซด์มักอยู่ในรูปของโมเลกุลอิสระ โดยมีโครงสร้างแบบทรง 4 หน้า ($Si(OR)_4$) สารตั้งต้นที่นิยมใช้กันมากในการเตรียมแก้วซิลิกา คือ สารเตตระเอธิลออโธซิลิเคต (TEOS)(5-6) โดยขนาดและรูปร่างของอนุภาคโซล รวมถึงความเร็วในการเกิดเจล สามารถควบคุมได้จากการเปลี่ยนแปลง pH(7-8) ปริมาณของน้ำในระบบ ซึ่งมีผลต่ออัตราเร็วของกระบวนการย่อยสลาย (hydrolysis) ปัจจัยเหล่านี้ จะส่งผลต่อการเกิดรูพรุนของสาร(9-12)

สารตั้งต้นแอลคอกไซด์ชนิดอื่นๆ ก็สามารถนำมาใช้เพื่อให้เกิดเจลที่มีสมบัติต่างๆ กัน(13-15) ออกไป ในปัจจุบัน จากการสังเคราะห์โลหะแอลคอกไซด์โดยกลุ่มวงศ์เกษมจิตต์ ซึ่งเน้นการสังเคราะห์สารประเภทโลหะแอลคอกไซด์ชนิดต่างๆ โดยใช้สารตั้งต้นราคาถูกและวิธีการสังเคราะห์ง่ายภายในขั้นตอนเดียว กระบวนการนี้เรียกว่ากระบวนการ "OOPS"(16-18) ซึ่งย่อมาจาก <u>O</u>xide <u>O</u>ne <u>P</u>ot <u>S</u>ynthesis ประโยชน์ของสารประเภทนี้ คือ สามารถเกิดการย่อยสลายได้ มีราคาถูก สังเคราะห์ง่าย และปลอดภัยต่อสิ่งแวดล้อม นอกจากนี้ กลุ่มวงศ์เกษมจิตต์ยังศึกษากระบวนการโซล-เจล ของสารประเภทไซลาแทรน(19) ผลการศึกษาพบว่า หลังกระบวนการเผาเพื่อขจัดเอาสารอินทรีย์ออก จะได้สารประเภทเซรามิกซ์ที่มีความสม่ำเสมอของโครงสร้างภายในสูง และมีพื้นที่ผิวสูงถึง 313-417 ตารางเมตรต่อกรัม จุดมุ่งหมายของบทความนี้ คือ เพื่อชี้ให้เห็นว่า ผลของตัวทำละลาย ความเป็นกรดหรือด่าง เวลาที่ใช้ในการเกิดเจล และอุณหภูมิ มีผลต่อกระบวนการโซล-เจลของสารประเภทสไปโรซิลิเคตอย่างไร(18)

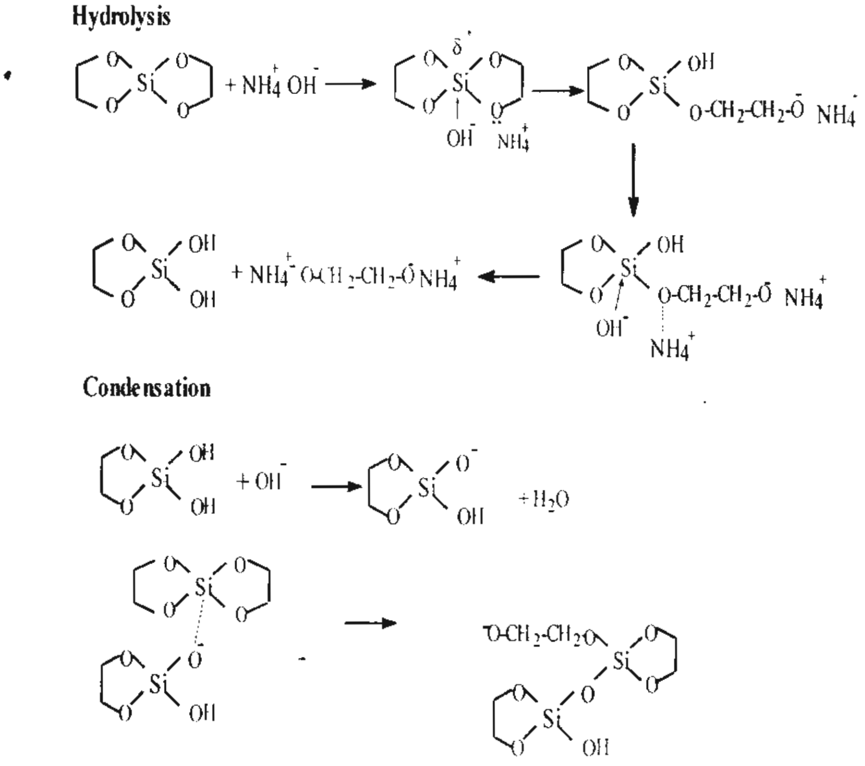
กลไกลทางเคมีของการเกิดเซรามิกซ์

เป็นที่รู้กันดีว่า สารเร่งปฏิกิริยาในกระบวนการทำให้สารตั้งต้นเปลี่ยนเป็นโซล และเจล มีผลสำคัญต่อโครงสร้างภายในของเจลที่สร้างขึ้นในระหว่างกระบวนการโซล-เจล(20) ดังแสดงในรูปที่ 1 และ 2 ซึ่งแสดงกลไกทางเคมีของการเกิดกระบวนการย่อยสลาย และการควบแน่น ของเตตระโคออดิเนตสไปโรซิลิเคตภายใต้สภาวะกรดและด่าง

กลไกของการเกิดปฏิกิริยานี้ สามารถติดตามได้โดยการใช้ดครื่อง FTIR ซึ่งเมื่อศึกษาจากรูปที่ 3(a) จะพบว่า สเปคตรัมของระบบที่ใช้สารละลายกรดเกลือที่มีเข้มข้น 0.001 โมลาร์ ความเข้ม (intensity) ของพีคที่ความยาวคลื่น 3405 2951 2883 และ 1086 ซม$^{-1}$ จะลดลงเมื่อเวลาเพิ่มขึ้น การลดลงของพีคที่ 3405 ซม$^{-1}$ เกิดจากการลดลงของปริมาณหมู่ Si-OH อันเป็นผลเนื่องมาจากการควบแน่นของหมู่ไซลานอล(21) ซึ่งเป็นสาเหตุเดียวกันกับการลดความเข้มของพีคที่ 1648 ซม$^{-1}$ของหมู่ไฮดรอกซิล (-OH)(22)



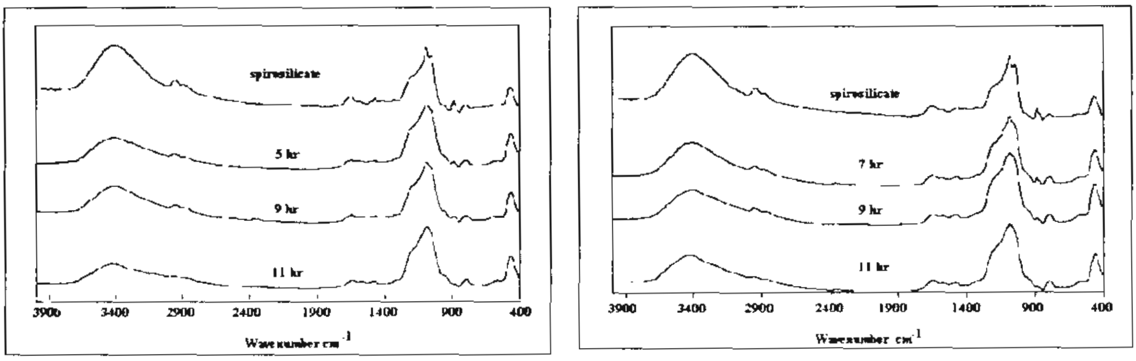
รูปที่ 1 แผนภาพแสดงการเกิดปฏิกิริยาการย่อยสลายและการควบแน่นในระบบที่มีสารละลายกรดเป็นตัวเร่งปฏิกิริยา



รูปที่ 2 แผนภาพแสดงการเกิดปฏิกิริยาย่อยสลายและการควบแน่นในระบบที่มีสารละลายแอมโมเนียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยา

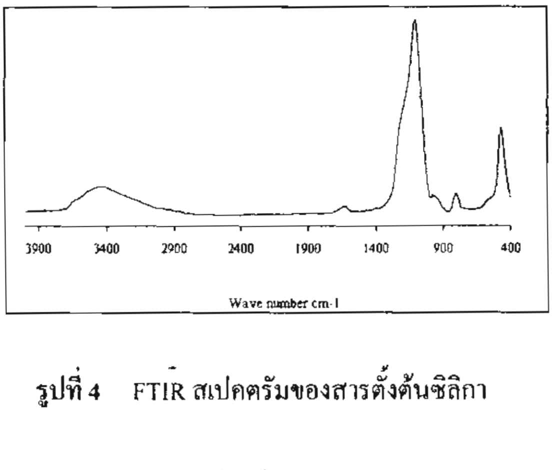
การเพิ่มความเข้มของพีคที่ตำแหน่ง 1086 ซม$^{-1}$ เกิดเนื่องจากการเพิ่มหมู่ Si-O-Si ที่ได้จากปฏิกิริยาการย่อยสลาย และการควบแน่น ผลที่ได้สามารถยืนยันได้จากการเปรียบเทียบการหายไปของพีคที่ 3405 2951 และ 2883 ซม$^{-1}$ ซึ่งเป็นการหายไปของโมเลกุลของสารอินทรีย์ที่ล้อมรอบ เป็นที่น่าสังเกตว่า เมื่อเวลาผ่านไป 9 ชั่วโมง ความเข้มของพีคที่ 3405 2951 2883 และ 1086 ซม$^{-1}$ เปลี่ยนไปในทิศทางย้อนกลับ ซึ่ง Brinker และผู้ร่วมงานก็พบเหตุการณ์เช่นเดียวกันนี้ คำอธิบายในเรื่องนี้ คือ หมู่ไฮดรอกซิลที่อยู่บนผิวหน้าเกิดการควบแน่นแล้วเกิดเป็นหมู่ไซลอกเซนขึ้น อนุภาคจะเกิดการรวมตัวกัน และเกิดการย้อนกลับของขั้นตอนการเกิดกระบวนการโซล-เจล(23-24) โครงสร้างของสไปโรซิลิเคตที่ได้หลังผ่านกระบวนการย่อยสลายเป็นเวลา 11 ชั่วโมง จะใกล้เคียงกับโครงสร้างของซิลิกาดังแสดงในรูปที่ 4

เมื่อใช้ความเข้มข้นของสารละลายกรดเกลือเพิ่มขึ้นเป็น 0.002 โมลาร์ ผลที่ได้จะใกล้เคียงกัน (รูปที่ 3b) อย่างไรก็ตาม การลดลงของพีคที่ 3405 2951 2883 และ 1086 ซม$^{-1}$ จะเร็วกว่าเมื่อเทียบกับระบบที่มีความเข้มข้นของเกลือต่ำกว่า



(a) (b)

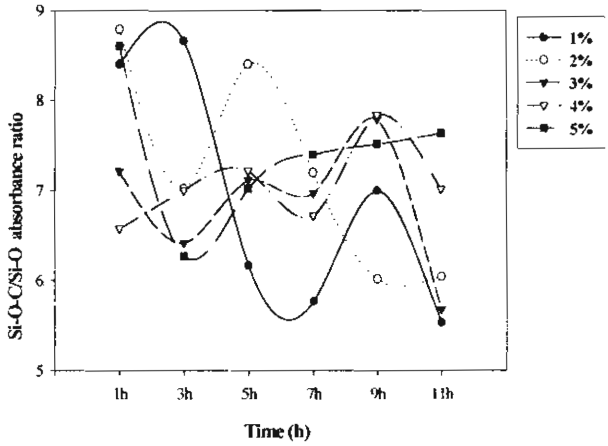
รูปที่ 3 FTIR สเปคตรัมแสดงปฏิกิริยาไฮโดรไลซิสที่อุณหภูมิห้องของสไปโรซิลิเคตโดยสารละลายกรดไฮโดรคลอริกเข้มข้น (a) 0.001 โมลาร์ และ (b) 0.002 โมลาร์



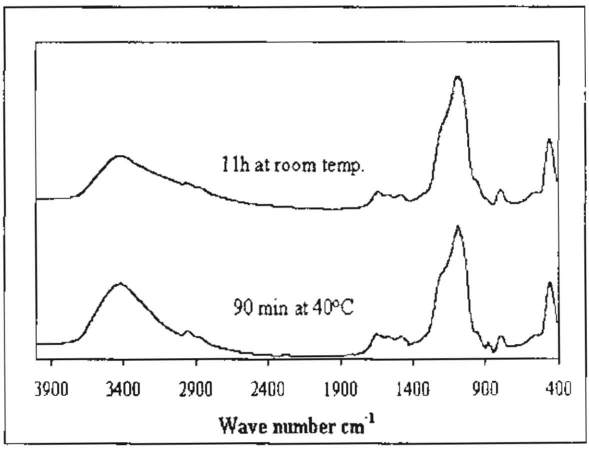
รูปที่ 4 FTIR สเปคตรัมของสารตั้งต้นซิลิกา

ผลการทดลองโดยรวมแสดงอยู่ในรูปที่ 5 ซึ่งจะแสดงความสัมพันธ์ระหว่างสัดส่วนของ Si-O-C/Si-O-Si (พีคตำแหน่งที่ 1086 และ 463 ซม$^{-1}$) โดยแสดงกราฟเทียบกับเวลาที่ใช้ในการย่อยสลายที่ความเข้มข้นของกรดต่างๆ กัน

จากรูปจะเห็นได้ว่า สภาวะที่ดีที่สุดในการเกิดการย่อยสลาย คือ ความเข้มข้นของกรดเท่ากับ 0.001 โมลาร์ เช่นเดียวกับรายงานของ Lippert ที่ทำการศึกษาโดยใช้ TEOS เมื่อปี 1988(25) ดังนั้น ระบบนี้จึงเป็นระบบที่ถูกเลือกขึ้นมา เพื่อศึกษาเพิ่มเติมถึงผลของอุณหภูมิ ดังแสดงในรูปที่ 6 เมื่อดูจากรูปพบว่า ที่อุณหภูมิ 40 องศาเซลเซียส อัตราการเกิดการย่อยสลายจะเร็วกว่าที่อุณหภูมิห้องมาก ที่ 40 องศาเซลเซียส การเปลี่ยนจากสไปโรซิลิเคตไปเป็นซิลิกาจะใช้เวลาน้อยกว่า 1 ชั่วโมง ในขณะที่อุณหภูมิห้อง ต้องใช้เวลามากกว่า 10 ชั่วโมง

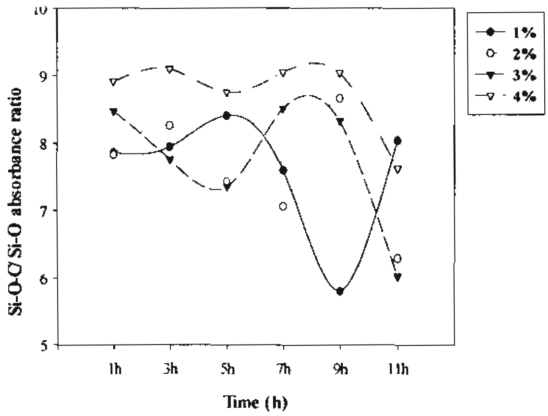


รูปที่ 5 ผลของเวลาต่อปฏิกิริยาการย่อยสลายของสไปโรซิลิเคตโดยใช้กรดเกลือที่มีความเข้มข้น 0.001-0.005 โมลาร์ ที่อุณหภูมิห้อง



รูปที่ 6 FTIR สเปคตรัมซึ่งแสดงผลของอุณหภูมิต่อปฏิกิริยาการย่อยสลาย

เมื่อเปลี่ยนตัวเร่งปฏิกิริยาจากกรดเป็นด่าง โดยใช้สารละลายแอมโมเนียมไฮดรอกไซด์เข้มข้น 0.001 โมลาร์ แทนดังแสดงผลในรูปที่ 7 ผลที่ได้จะแตกต่างจากระบบที่ใช้กรดคือ โครงสร้างของ Si-O-C และ Si-O-Si เปลี่ยนแปลงเพียงเล็กน้อยในช่วง 1-8 ชั่วโมง แต่เมื่อเวลาผ่านไป 9 ชั่วโมงการลดลงของสัดส่วนทั้งสองจึงปรากฏให้เห็น อย่างไรก็ตามหลังผ่านไป 11 ชั่วโมงสัดส่วนดังกล่าวก็เพิ่มขึ้นอีกครั้ง



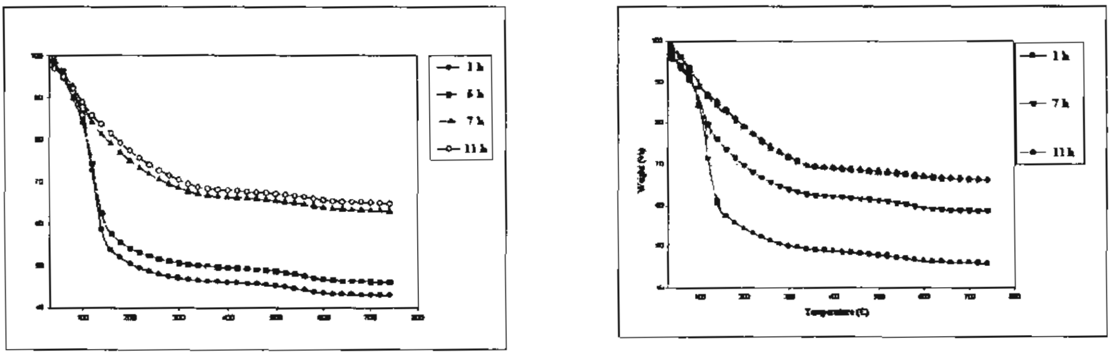
รูปที่ 7 ผลของเวลาต่อปฏิกิริยาการย่อยสลายของสไปโรซิลิเคตโดยใช้สารละลายแอมโมเนียมไฮดรอกไซด์ที่มีความเข้มข้น 0.001-0.005 โมลาร์ ที่อุณหภูมิห้อง

โดยสรุปแล้ว อัตราเร็วของกระบวนการโซล-เจลของสารสไปโรซิลิเคตจะช้าที่สุดที่ความเข้มข้นของกรดเกลือเท่ากับ 0.001 และ 0.002 โมลาร์ ซึ่งที่ความเข้มข้นนี้ วัด พี-เอช ได้ประมาณ 2 และที่พี-เอช นี้ เป็นจุดที่ประจุรวมของระบบเป็นศูนย์ [isoelectric point](26) ดังแสดงในตารางที่ 1 ผลการศึกษานี้สอดคล้องกับการศึกษาของ Brinker และผู้ร่วมงาน(24) ที่แสดงสภาวะที่ดีที่สุดในการเกิดเจลของ TEOS ที่ พี-เอช ประมาณ 2

ตารางที่ 1 ค่า พี-เอชของตัวเร่งปฏิกิริยาในแต่ละความเข้มข้น

ความเข้มข้นของกรดเกลือ (1โมลาร์) (%)	**ค่า พี-เอช**	**ความเข้มข้นของสารละลายแอมโมเนียมไฮดรอกไซด์ (1 โมลาร์) (%)**	**ค่า พี-เอช**
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

การวิเคราะห์ทางเทอร์โมกราวิเมตริก (TGA) แสดงในรูปที่ 8 ยืนยันผล FTIR ที่แสดงอยู่ในรูปที่ 3 และ 5 ของสารที่ผ่านปฏิกิริยาการย่อยสลายด้วยกรดเกลือที่ความเข้มข้น 0.001 และ 0.002 โมลาร์ โดยเปอร์เซ็นต์เซรามิกซ์ที่ได้สอดคล้องกับผลของการลดลงของหมู่ Si-O-C และการเพิ่มขึ้นของหมู่ Si-O-Si นั่นคือ เปอร์เซ็นต์เซรามิกซ์เพิ่มขึ้นเกิดจากการลดลงของหมู่ Si-O-C และการเพิ่มขึ้นของหมู่ Si-O-Si เช่นเดียวกัน ที่เวลา 9 ชั่วโมง ผลของFTIR แสดงการเพิ่มขึ้นของหมู่ Si-O-C เมื่อใช้กรดเข้มข้น 0.001 โมลาร์ ส่งผลให้เปอร์เซ็นต์เซรามิกซ์ลดลงเช่นกัน



(a)

(b)

รูปที่ 8 เทอร์โมแกรมแสดงเปอร์เซ็นต์เซรามิกซ์เทียบกับเวลาที่ใช้ในการย่อยสลายด้วยกรดเกลือที่ความเข้มข้น (a) 0.001 โมลาร์ (b) 0.002 โมลาร์

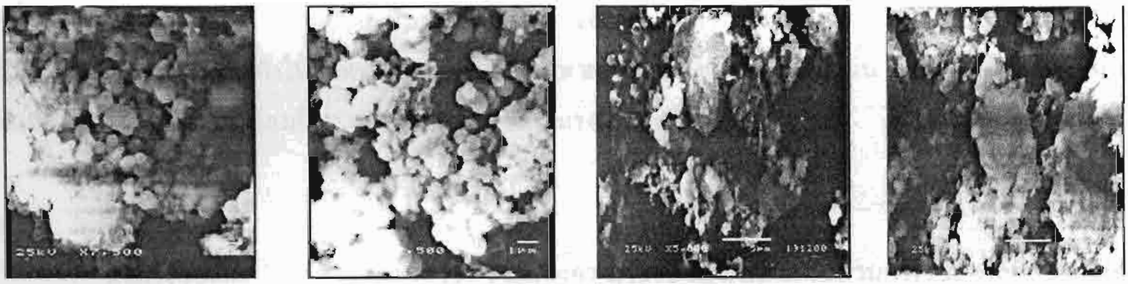
ผลอันน่าแปลกใจนี้ เกิดเนื่องมาจากปฏิกิริยาสามารถเกิดในทิศทางตรงข้าม หรือย้อนกลับ ซึ่งเรียกว่าปฏิกิริยารีเอสเทอร์ริฟิเคชัน (reesterification) ซึ่งเกิดจากโมเลกุลของแอลกอฮอร์ของแอลคอกไวด์เข้าแทนที่หมู่ไฮดรอกซิลในการผลิตหมู่แอลคอกไซด์ล้อมรอบซิลิกอน(24)

การศึกษาพื้นที่ผิวของซิลิกอนไดออกไซด์เมื่อผ่านกระบวนการเผาสารผลิตภัณฑ์ที่ได้จากปฏิกิริยาการย่อยสลาย และการควบแน่นของสารสไปโรซิลิเคตที่อุณหภูมิ 750 องศาเซลเซียสเป็นเวลา 7 ชั่วโมง โดยวิธี BET ได้สรุปไว้ในตารางที่ 2 ซึ่งสอดคล้องกับผลของ FTIR และ TGA นั่นคือ เมื่อปริมาณของหมู่ไฮดรอกซิลและหมู่ Si-O-C ลดลง จะเพิ่มเปอร์เซ็นต์เซรามิกซ์ และพื้นที่ผิว

ตารางที่ 2 ผลการศึกษาพื้นที่ผิวโดยวิธี BET ของสารสไปโรซิลิเคตหลังผ่านกระบวนการย่อยสลาย และการควบแน่น ที่เวลาต่างๆ ด้วยกรดเกลือ และสารละลายแอมโมเนียมไฮดรอกไซด์ ที่ความเข้มข้น 0.001 โมลาร์ และนำไปเผาที่อุณหภูมิ 750 องศาเซลเซียสเป็นเวลา 7 ชั่วโมงเทียบกับสารตั้งต้น ซิลิกาที่เกิดจากการหลอม

เวลา (ชั่วโมง)	**พื้นที่ผิว (ตารางเมตร ต่อกรัม)**	
	0.001 โมลาร์ กรดเกลือ	**0.001 โมลาร์ แอมโมเนียมไฮดรอกไซด์**
3	307	296
5	354	278
7	369	307
9	339	347
11	596	280
fused ซิลิกา	167	167

การศึกษาสัญฐานของเจลที่ผ่านปฏิกิริยาการย่อยสลายด้วยกรดและด่างทำโดยการใช้เครื่องสแกนนิ่งอิเลคตรอนไมโครสโคป (SEM) ดังแสดงในภาพที่ 9 (a) และ (b) จะเห็นได้ว่า สัญฐานของเจลทั้งสองชนิดไม่เหมือนกัน อันเนื่องมาจากระบบที่ต่างกันของตัวเร่ง



(a) (b) (c) (d)

รูปที่ 9 ภาพ SEM ของ (a) และ (b) หลังกระบวนกาย่อยสลาย และการควบแน่น ด้วยกรดเกลือ และด่างแอมโมเนียมไฮดรอกไซด์ ตามลำดับ และ (c) และ (d) หลังผ่านกระบวนการเผาของสารที่ได้จาก (a) และ (b)

ภายใต้ระบบที่มีกรดเป็นตัวเร่ง โมโนเมอร์ที่ถูกย่อยสลายจะจัดเรียงตัวโดยผ่านการทำปฏิกิริยากับโปรตอน (H^+) จากนั้นปฏิกิริยาการควบแน่นจะเกิดตามมา แต่เมื่ออยู่ในระบบที่มีเบสเป็นตัวเร่งปฏิกิริยา อนุภาคของโซลจะพยายามผลักซึ่งกันและกัน เนื่องจากประจุลบของ SiO^- ที่เกิดขึ้นบนพื้นผิวดังแสดงในปฏิกิริยาต่อไปนี้

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

ปฏิกิริยาแต่ละชนิดที่เกิดขึ้นล้วนมีผลเฉพาะต่ออัตราการเกิดปฏิกิริยาควบแน่น และการเกิดรูพรุนของเจลที่แห้ง ดังนั้น จึงได้มีการศึกษาผลของตัวเร่งปฏิกิริยาต่ออัตราการเกิดปฏิกิริยาและสมบัติของเจล

ดังที่กล่าวมาแล้วว่า สภาวะที่ใช้กรดเป็นตัวเร่งปฏิกิริยาจะเกิดปฏิกิริยาช้าที่สุดที่ความเข้มข้นของกรดเกลือ 0.001 โมลาร์ และมี พี-เอช อยู่ในช่วงประมาณ 2-2.5 ซึ่งจะมีค่าใกล้เคียงกับค่าที่มีประจุรวมเท่ากับศูนย์ อันจะไม่ก่อให้เกิดการผลักกันของอนุภาค(26) เมื่อเพิ่มความเข้มข้นของกรดที่ใช้เป็นตัวเร่งปฏิกิริยา อัตราการเกิดปฏิกิริยาจะเพิ่มขึ้น ทำให้เวลาที่ใช้ในการเกิดเจลลดลง ในขณะที่ในระบบที่ใช้ด่างเป็นตัวเร่งปฏิกิริยา เกิดผ่านกระบวนการนิวคลีโอฟิลิก (nucleophillic reaction)(21) และปฏิกิริยาการควบแน่นผ่านหมู่ $Si\text{-}O^-$ ทำให้ปฏิกิริยานี้เกิดขึ้นได้เร็ว และเกิดขึ้นก่อนปฏิกิริยาการย่อยสลายจะสิ้นสุดลง ยิ่งไปกว่านั้น สำหรับตัวเร่งปฏิกิริยาที่เป็นด่าง การเกิดการผลักกันของอนุภาคโซลทำให้อนุภาคมีเวลามากพอที่จะเกิดการจัดเรียงตัวใหม่ อนุภาคขนาดใหญ่มีแนวโน้มที่จะจัดเรียงตัวขึ้นก่อน ซึ่งจะแตกต่างจากกรณีที่ใช้กรดเป็นตัวเร่งปฏิกิริยาที่ปฏิกิริยาจะเกิดผ่านกระบวนการเติม (addition reaction) อันทำให้มีแนวโน้มก่อให้เกิดอนุภาคขนาดเล็ก(27) ปรากฏการณ์นี้สามารถยืนยันจากผลของ SEM ในรูปที่ 9 (b) ซึ่งแสดงขนาดของรูพรุนที่ใหญ่กว่าในโครงสร้างโซล เมื่อเทียบกับ รูป 9 (a)

เป็นที่ทราบโดยทั่วไปว่า เจลจะประกอบด้วย 2 สถานะ คือ สถานะที่เป็นของแข็งซึ่งเชื่อมโยงกันเป็นร่างแห และสถานะที่เป็นรูพรุนที่มีของเหลวบรรจุอยู่ภายใน(4) เมื่อผ่านกระบวนการให้ความร้อน ของเหลวที่บรรจุอยู่ภายในจะระเหยออก และเจลจะเกิดการหดตัวภายใต้อิทธิพลของแรงแคปปิลารี (capillary force) ดังแสดงในรูปที่ 9 (a) โดยเจลที่เกิดจากกรดเป็นตัวเร่งจะมีรูพรุนขนาดเล็ก และถ้ามีน้ำปริมาณมากบรรจุอยู่ในรูพรุนเหล่านั้น เมื่อให้ความ

ร้อนเจลจะเกิดการหดตัวมากดังจะแสดงในรูป 9(c) ในทางตรงข้าม เมื่อใช้ด่างเป็นตัวเร่ง จะให้รูพรุนขนาดใหญ่กว่า และมีประมาณน้ำบรรจุอยู่น้อยกว่า ดังนั้นจะเกิดการหดตัวน้อยกว่า

ความหนาแน่นของสารผลิตภัณฑ์จากเจลที่ถูกย่อยสลายด้วยกรดเกลือที่มีความเข้มข้น 0.001 โมลาร์ มีค่าเท่ากับ 0.54 กรัมต่อลูกบาศก์เซนติเมตร ซึ่งมีค่าน้อยกว่าซิลิกาที่เกิดจากการหลอม (2.42 กรัมต่อลูกบาศก์เซนติเมตร) มาก สามารถอธิบายผลที่ได้จากความเป็นจริงที่ว่า การขจัดหมู่แอลคอกซี และไฮดรอกซิล โดยปฏิกิริยาควบแน่นเมื่อให้ความร้อนแก่เจล จะทำให้น้ำหนักของสารบางส่วนหายไป และน้ำหนักที่หายไปนั้น จะทำให้เกิดสารผลิตภัณฑ์ใหม่ที่โครงสร้างแบบเชื่อมโยงเป็นร่างแห และมีความแข็งแรงมากขึ้น(28)

สรุป

สไปโรซิลิเคตเป็นโลหะแอลคอกไซด์ซึ่งแสดงความว่องไวต่อการเกิดกระบวนการโซล-เจลที่อุณหภูมิห้องหรือที่อุณหภูมิสูงเพียงเล็กน้อย และที่ พี-เอช ประมาณ 2 อันเป็นจุดที่ใกล้เคียงกับ พี-เอช ที่ทำให้ประจุรวมของซิลิกาเป็นศูนย์ สารผลิตภัณฑ์ที่ได้จะให้เปอร์เซ็นต์เซรามิกซ์และพื้นที่ผิวสูง ซึ่งเป็นสมบัติที่ต้องการในกระบวนการผลิตเซรามิกซ์ นอกจากนี้ ผลจากกระบวนการโซล-เจล ที่สำคัญอีกประการ คือ ได้สารผลิตภัณฑ์ที่มีความหนาแน่นต่ำ ตัวแปรที่สำคัญอื่นๆ ที่มีผลต่อโครงสร้างของสไปโรซิลิเคต คือ อุณหภูมิและเวลาที่ใช้ในการพักเจล

การศึกษานี้ สามารถอ่านรายละเอียดได้จากวารสารนานาชาติต่อไปนี้

Srisuda Thitinun, Nopporn Thanabodeekij, Alex. M. Jamieson and Sujitra Wongkasemjit*, "Sol-gel processing of spirosilicates", ***J. Eur. Cer. Soc.***, In press

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