

SOL-GEL SILICA FIBER FORMING INVESTIGATIONS

FINAL PROJECT REPORT

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1. INTRODUCTION

The method of producing ceramic oxides through hydrolysis and polycondensation of metal alkoxides is referred to as the sol-gel process. The term 'sol', which is used to describe the metal alkoxide reaction solutions, is borrowed from colloidal sols where a sol is defined to be a dispersion of fine particles in a liquid.

The sol-gel method of making glasses by using metal alkoxides has certain advantages [1,2]; high purity ceramics can be produced, and different compositions of mixed ceramic oxides can be produced which can not be obtained by conventional melting techniques because of problems such as liquid immiscibility at the melting temperature and phase separation and crystallization during cooling. Relatively low temperatures are required to produce ceramic oxides by the sol-gel route. Conventional methods of fabrication of bulk and fibrous oxide ceramic products involve melting at very high temperatures. Sol-gel processing offers a new method of making such products without involving melting techniques. The disadvantages of the sol-gel process are the high cost of raw materials and the unlikelyhood that it will replace any existing 'heavy' industrial process [1].

This report describes the research efforts at Georgia Tech, funded by PPG Industries Inc. To identify promising routes for the formation of silica fibers by the sol-gel process. Among the initial requirements in converting precursor materials, such as tetraethylorthosilicate, to continuous silica fibers are:

1. Directing the course of hydrolysis and polycondensation of the tetrafunctional monomer to yield stable, essentially linear polymer

structures. The requirement of essentially linear, uncrosslinked structures is for obtaining solutions of the polymer with "spinnable" rheological characteristics. Stability of composition and structure of this fluid prior to fiber formation is necessary to ensure that the fibers extruded from these solutions at different times would have the same characteristics.

2. Directing the "stable" spinning fluid to undergo rapid sol-gel transition in the threadline of a fiber formation process to yield precursor fibers which can be cohesively consolidated/converted to silica fibers. It is necessary to meet the apparently contradictory requirement of a precursor fluid which would remain stable till fiber formation but undergo rapid gelation in the threadline.

3. Directing the precursor fibers to undergo consolidation and conversion to silica fibers without embrittlement. Obtaining a uniform structure in continuous silica fibers produced at different times after the initial fiber formation is an additional constraint because the large incompatibility in the rates of the precursor fiber formation (rapid) and consolidation (very slow) requires separation of these two steps. Georgia Tech's research efforts pertaining to sol-gel routes for silica fibers, with emphasis on meeting the requirements specified in (1) and (2) above, are presented in this report.

2. PREPARATION OF SPINNABLE SOLUTIONS

2.1 INITIAL RESEARCH

Hydrolysis of tetraethylorthosilicate (TEOS) has been well documented in the literature [2-6]. The initial water content of TEOS solutions, as well as type of catalyst, play an important role in relation to the nature of the species produced in solution. It has been reported in the literature that hydrolysis under alkaline conditions results in the formation of polymeric species having three dimensional network or even colloidal particles. The solutions thus prepared are not suitable for drawing fibers. Hydrolysis using large amounts of water (>4 equivalents) under acidic conditions also yields similar results, i.e., solutions prepared under these conditions are also not suitable for producing fibers. However, use of small amounts of water (< 4 equivalents), coupled with acid catalysts has been shown to yield solutions from which long fibers could be drawn by hand. These solutions are said to exhibit 'spinnability'. Spinnability of a solution has been defined in the literature as the ability to draw fibers from a viscous solution by immersing a glass rod into the solution and pulling a fiber out of it. Table I summarizes the literature data on the effect of hydrolysis conditions on the spinnability of solutions.

The focus of reported research has been on the hydrolysis of TEOS. However, there have been only a few reports [7,8] on the production of silica fibers by the sol-gel route using silicon alkoxides as the precursor materials. All the reports in the

Table I

Effects of Hydrolysis Conditions

[H ₂ O]/[TEOS]	Catalyst	Nature of Solution
1.0	HCl	Spinnable
2.0	HCl	Spinnable
4.0	HCl	Spinnable
5.0	HCl	Not Spinnable
10.0	HCl	Not Spinnable
20.0	HCl	Not Spinnable
1.0	NH ₄ OH	Not Spinnable
2.0	NH ₄ OH	Not Spinnable

technical literature so far on fiber formation studies refer to the production of silica fibers by hand drawing techniques only, although the trade literature [9] refers to the production of continuous silica fibers which are now available commercially from Japan.

The research work was started in the middle of June 1985. Initial experiments in this project involved the study of hydrolysis and polycondensation of TEOS to produce spinnable solutions. Effect of varying initial water concentrations at a fixed concentration of HCl as catalyst was studied. In accordance with the literature data given in Table I it was found in our studies that solutions prepared using up to 4 equivalents of water exhibited spinnability and that the use of higher initial concentrations of water yielded solutions that are not spinnable. The effect of varying water concentrations on spinnability is shown in Table II.

A typical experimental procedure for the preparation of spinnable solution by the sol-gel route is as follows: To a solution of 300 ml TEOS (1.34 mol) and 150 ml absolute ethanol, which was maintained at 80°C, was added dropwise 36.2 ml H₂O (2.01 mol) containing catalytic amounts of HCl (0.028 mol) ([H₂O]/[TEOS]=1.5). The dropwise addition of water was completed in about 20 minutes and the reaction mixture was maintained at 80°C for another two hours. The solution was then transferred into a beaker and placed in an oven maintained at a constant temperature in the range 50-70°C. Moist air was passed into the oven to create a humid atmosphere. After several hours of aging in a humid

Table II

Effect of $[H_2O]/[TEOS]$ on Spinnability

$[H_2O]/[TEOS]$	Spinnability
1.5	yes
2.0	yes
3.0	yes
6.0	no
12.0	no

Catalyst: $[HCl]/[TEOS] = 0.021$

atmosphere the viscosity of the solution increased due to evaporation of solvent ethanol and polycondensation of the hydrolyzed species in solution. Change of viscosity of solution was followed as a function of aging time. Figure 1 shows the change of viscosity with time for solutions prepared using 1.5, 3.0 and 12.0 equivalents water in the initial composition.

Solutions prepared using up to 4 equivalents of water become very viscous and fibers could be drawn by hand from these solutions before the gel point. But the solutions prepared by using 6 and 12 equivalents of water were not spinnable before gelation occurred and these solutions gelled at lower viscosities.

2.2 FORMATION OF ELASTIC SOLUTIONS:

Initial water concentration of 1.5 mole per mole of TEOS was found to be suitable to produce spinnable solutions. In our earlier experiments fibers drawn from these solutions dried almost instantaneously after drawing and could be wound and unwound. However, at a later stage of the project it was found that TEOS solutions containing 1.5 equivalents of water yielded fluids that are different in nature from those obtained with initial water content of 1.6 equivalents. The drying nature of the solutions was compared by spreading two drops of each spinnable solution on a watch glass and exposing to air at room temperature. It was found that solutions containing 1.6 and 1.7 equivalents of water dried after several minutes. But the solution containing 1.5 mole of H₂O per mole of TEOS remained sticky and did not dry even after several days. It was also noticed that fibers drawn from this solution,

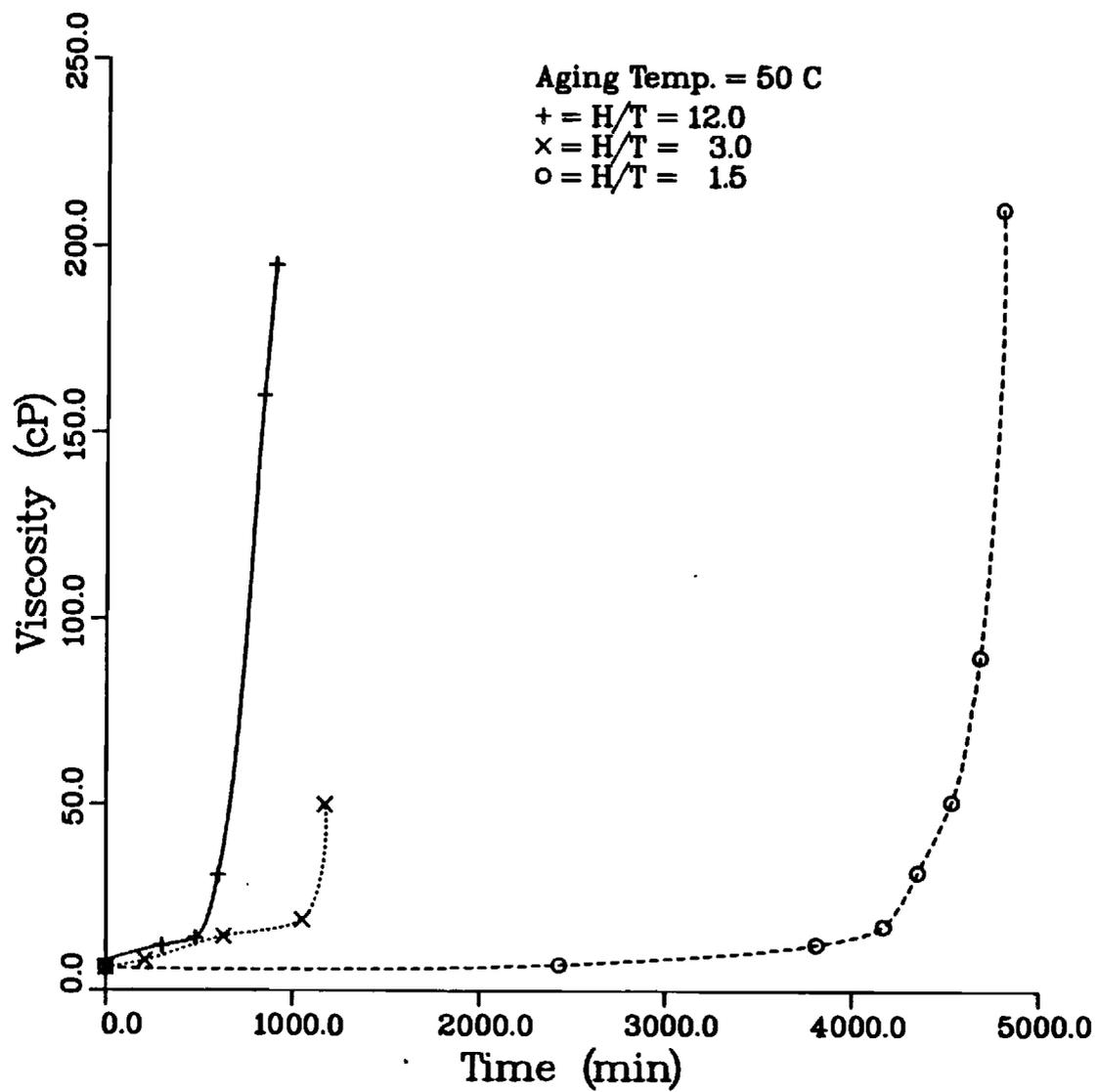


Figure 1. Effect of Water concn. on TEOS sols

($[\text{H}_2\text{O}]/[\text{TEOS}]=1.5$) remained sticky for several hours after drawing and could be elongated further. When the thread line is extended until it breaks, the drawn fiber shrinks to the tip of the glass rod used for drawing. This kind of elastic behaviour was not exhibited by the solutions prepared by using 1.6 equivalents of water. In contrast, the fibers drawn from these solutions dried almost instantaneously after drawing. It appeared that the elastic behaviour of the spinnable fluids depended upon the initial water content used for hydrolysis. In order to confirm this, the following experiments were conducted using a narrow range of varying amounts of initial water contents. Also TEOS obtained from two different sources i.e. Fisher Scientific Co., and Aldrich Chemical Co., was used in parallel experiments to compare results.

A solution of 100 mL TEOS (0.45mol) and 50 mL absolute ethanol was prepared in an 8oz glass bottle and varying amounts of water containing a fixed amount of HCl (0.0095mol) were added. Initial water content was varied from 1.3 - 1.7 mol per mole of TEOS. The addition of water containing HCl was completed in about 3 minutes and the solution was stirred for another minute. All the reaction bottles were then tightly closed with screw caps and placed in an oven kept at 70°C for 90 minutes to allow hydrolysis and polycondensation. The screw caps were then removed from the bottles and the solutions were exposed to humid atmosphere at 70°C to increase the viscosity. The viscosity data collected after aging are given in Table III.

The drying nature of the above solutions was tested by spreading two drops of each solution on a watch glass and exposing

Table III

Effect of [H₂O] on Viscosity - Comparison of TEOS
obtained from Two Sources

Batch No.	TEOS Source	[H ₂ O]/[TEOS]	1.30	1.40	1.45	1.50	1.55	1.60	1.70	Aging Time (hr)
I	Fisher	Viscosity (Poise)	0.6	1.3	-	7.2	-	20	gel	43
	"	"	0.9	3.0	-	80	-	-	-	66
II	Fisher	"	-	-	15	50	170	300	-	48
	Aldrich	"	-	-	22	65	305	195	-	48

to air at room temperature. Solutions containing 1.6 and 1.7 equivalents of H_2O dried after several minutes whereas solutions containing 1.30 - 1.55 equivalents of H_2O remained sticky and did not dry even after several days. Also fibers drawn from the solutions containing 1.30 - 1.55 moles of H_2O per mole of TEOS did not dry even after several minutes of exposure to air and when the thread line broke with prolonged elongation, the drawn fiber shrank to the tip of the glass rod used for drawing. However, fibers drawn from solutions containing 1.6 and 1.7 equivalents dried immediately after drying. In the second batch of experiments, the results obtained using TEOS purchased from Fisher Scientific Co., and Aldrich Chemical Co., were compared. The viscosities of the solutions made from Aldrich sample of TEOS were higher for water contents of up to 1.55 equivalents as shown in Table III. However, another comparative study using both Fisher and Aldrich samples of TEOS, did not show similar trends for viscosities of solutions containing 1.5 and 1.55 equivalents of water. After 48 hours of aging the viscosities obtained for solutions containing 1.5 equivalents of water are 32 poise for Aldrich sample and 124 poise for Fisher sample. After 27 hours of aging the viscosity of solution containing 1.55 equivalents of Aldrich sample of TEOS increased to 25 poise and that of solution containing Fisher sample of TEOS increased to 74 poise. From the above set of experiments it was confirmed that initial water content up to 1.55 mole per mole of TEOS used for hydrolysis results in the formation of elastic solutions.

Table IV

Effect of Aging Conditions on Change of Viscosity

S. No.	Aging Method	Aging Time (hrs)	Viscosity (poise)	Spinnability
I	Direct aging in open system in Humidiator	49	100	Yes
II	Direct aging in open system in dry atm.	70	250	Yes
III	Concentrated and aged in open system in humid atm.	26	109	Yes
IV	Concentrated and aged in closed system	46	24	Yes

3 PREPARATION OF SPINNABLE FLUID AND EFFECT OF REACTION

CONDITIONS

After having established that a critical initial water concentration of >1.6 mole per mole of TEOS is necessary in order to obtain a spinnable fluid and ensure rapid drying of drawn fibers, we studied the following variations in the method of preparation of spinnable fluids using 1.6 equivalents of water. The reason for undertaking this study was to identify and establish reaction conditions under which spinnable fluids could be produced in a relatively shorter reaction times in a reproducible manner. The initial experimental procedure was as follows: A solution of 500 mL TEOS (2.24 mol) and 250 mL absolute ethanol was heated to reflux in a 1 liter flask. To this solution was added dropwise a mixture of 47.1 mL of 1M HCl and 17.5 ml H_2O . Addition was completed in about 20 minutes and the reaction mixture was refluxed for 3 hours more. The reaction mixtures thus prepared in separate experiments carried out under identical conditions were aged as follows:

Reaction mixture was exposed to humid atmosphere at $70^{\circ}C$ created by passing moist air into oven.

) Reaction mixture was kept at $70^{\circ}C$ in the relatively dry atmosphere of oven and moist air was not passed into the oven.

I) Reaction mixture was concentrated on rotary evaporator to about 225 mL and the concentrated solution was exposed to humid atmosphere at $70^{\circ}C$.

Reaction mixture was concentrated to about 190 ml on a rotary evaporator and maintained at $70^{\circ}C$ in a closed system.

Viscosities of the solutions were determined at room temperature. The collected data are reported in Table IV. Solutions prepared by all the above methods exhibited good spinnability and the fibers drawn from these solutions dried almost instantaneously. Concentration of the reaction mixture to a smaller volume prior to the aging process reduced considerably the aging time required to obtain spinnable viscosity.

The above experiments indicated that spinnable solutions prepared by using an initial water content of 1.6 equivalents did not exhibit the elastic behavior. However, in some of the later experiments, it was found that spinnable fluids prepared by using 1.6 equivalents of water did not dry after exposure to air and the drawn fibers were elastic. It was also noticed that by passing moist air through these elastic solutions, the behaviour of the solutions can be altered. After passing moist air through the elastic solution obtained using 1.6 equivalent of H₂O, fibers could be drawn from the resulting pasty material. These fibers were not elastic but dried immediately.

2.4 EFFECT OF AGING ATMOSPHERE ON THE FORMATION OF ELASTIC SOLUTIONS:

In a separate experiment, hydrolysis and polycondensation of TEOS was carried out using 1.50 equivalents of water at room temperature. The solution was exposed to air at room temperature in an open bottle. After several hours of aging at room temperature a spinnable solution was obtained. Fibers drawn from this solution were not elastic but dried immediately after

drawing. This behaviour was in contrast to the earlier observations (Table III) where elastic solutions were formed after aging at 70°C in an oven flushed with moist air.

The experiments conducted to study the formation of elastic spinnable solutions indicate that aging conditions such as relative humidity of the aging atmosphere and probably the aging temperature are also important factors in addition to a critical initial water concentration. The effect of water content on the nature of sols is given in Table V. In order to eliminate the possibility of forming elastic spinnable solutions, we employed 1.7 equivalents of water in all subsequent experiments and the solutions were aged in a humid atmosphere at 70°C.

Table V

EFFECT OF [H₂O]/[TEOS] ON THE NATURE OF SOLS

[H ₂ O]/[TEOS]	NATURE OF SOL*
1.30	Spinnable; sols do not dry; Elastic fibers
1.40	Spinnable; sols do not dry; Elastic fibers
1.45	Spinnable; sols do not dry; Elastic fibers
1.50**	Spinnable; sols do not dry; Elastic fibers
1.55	Spinnable; sols do not dry; Elastic fibers
1.60***	Spinnable; sols do not dry; Elastic fibers
1.70	Spinnable; fibers dried quickly

* Sols aged at 70°C in humid atmosphere

** When aged at RT, fibers drawn from spinnable solutions dried quickly

*** Sometimes sols are not elastic but fibers did not dry

3. DEVELOPMENT OF SPINNING TECHNIQUES

The technical literature on the formation of silica precursor gel fibers by sol-gel routes have dealt invariably with the production of discontinuous fibers by hand drawing techniques. For an industrial process to be feasible continuous spinning techniques have to be developed. The three spinning techniques which have been established for the production of silica precursor fibers through our research are shown schematically in Figure 2, 3 and 4.

3.1 DRY SPINNING:

In the initial experiments a glass rod was dipped into a viscous spinnable solution and slowly pulled out of it while gently blowing air on the thread line being drawn to produce the precursor gel fiber. Fibers ranging in length up to 100 cm were produced by hand drawing. The fact that the hand drawn fibers dried almost instantaneously indicated the possibility of a dry spinning process. Continuous threadline formation was achieved by extruding a spinnable solution through a syringe needle. A spinning unit was made from a 20 cm long and 3 cm diameter stainless steel pipe. Provisions were made to attach a nitrogen hose to one end and a syringe needle adapter to the other end. A spinnable solution having about 100 poise viscosity was taken in this unit and extruded through a 3 mm long syringe needle (#24 gauge) by applying about 20 psi N₂ pressure. The spinning unit was vertically mounted at about 9-10 feet above the ground and the solution was extruded through the needle. When the solution formed a continuous thread

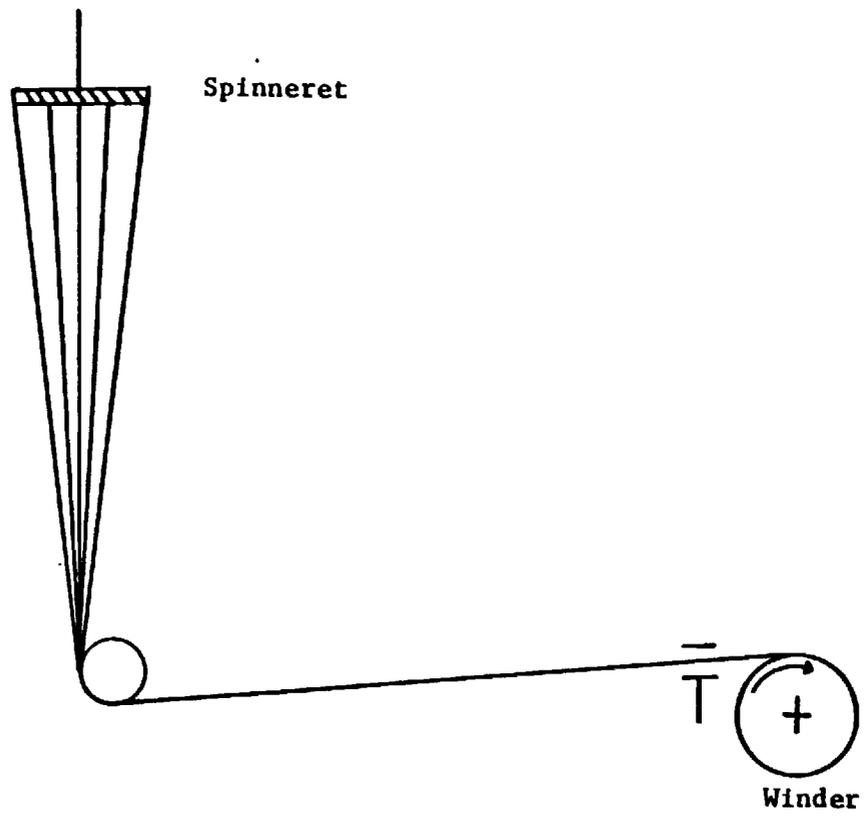


Figure 2. DRY SPINNING

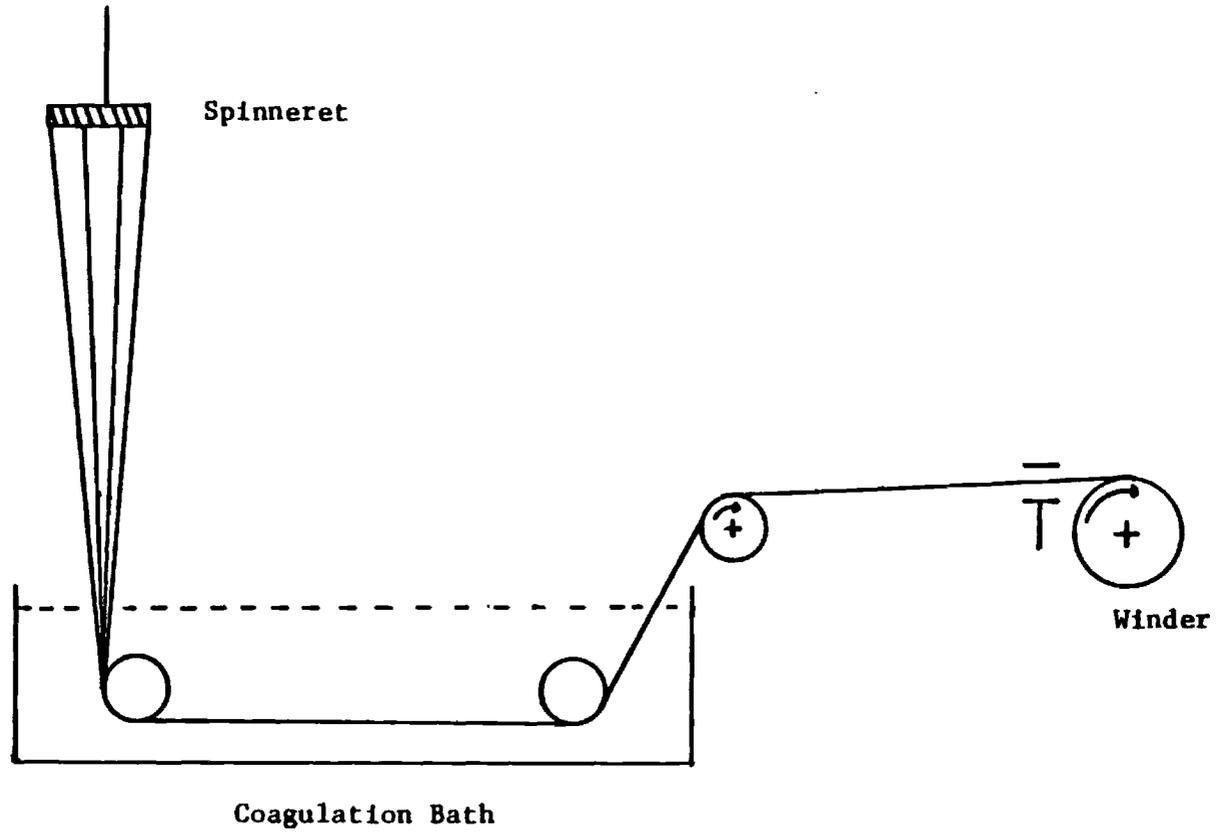


Figure 3. DRY-JET WET SPINNING

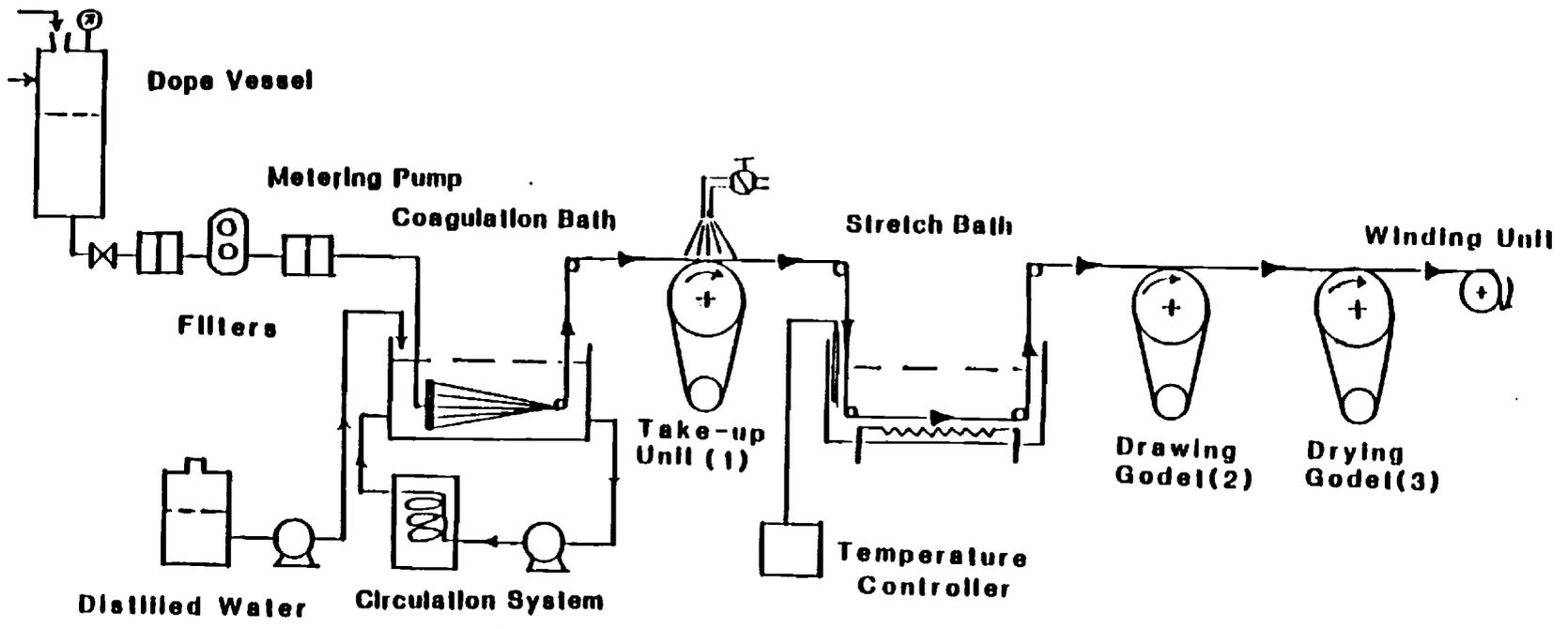


Figure 4. WET-SPINNING

line, nitrogen supply was cut off abruptly to arrest the flow of solution through the needle.

The fiber thus formed between the syringe needle and ground was allowed to dry at room temperature for a minute or two and wound on a bobbin.

Fibers up to about 300 cm long were collected by this method.

3.1.1 Dry Spinning at Low Temperatures

It was also found that using solutions having lower viscosities at room temperature in the range 20-30 poise, continuous fiber formation could be achieved by extruding these solutions at low temperatures. The change of viscosity with temperature is shown in Table VI for a solution having 67 poise viscosity at room temperature and made by using 1.5 equivalents of water. Fibers made by dry spinning at ambient or low temperatures were bright and shiny.

3.2 WET SPINNING:

Conventional wet spinning routes for the formation of fibers involves extrusion of a polymer solution into a coagulation bath containing a fixed composition of a solvent and a non-solvent mixture. Polymer coagulates in filament dry form from the polymer solution under controlled coagulation conditions. Extrusion of spinnable precursor solutions from the present study into hexane or ether as non-solvents did not result in the formation of cohesive filaments. Water was chosen as the medium for wet spinning to ensure further hydrolysis of alkoxide groups leading to gelation

Table VI

Change of Viscosity with Temperature

Temperature (°C)	Viscosity (poise)
22	67
18	79
14	100
7	150
-4	>1000

through cross linking as well as coagulation of the polymeric species in solution.

The possibility of a wet spinning process was inferred from the following experiment: A spinnable solution having about 100 poise viscosity was extruded into a 35 cm long column of water kept at about 50°C by keeping the syringe needle immersed in the bath. The downward flow of solution formed a threadline inside the water bath. The fiber thus formed was bright and shiny initially but became opaque with prolonged immersion in water. Fibers up to about 30 cm in length were collected by this method. It was also found that fibers could be drawn by at least 4-5 times their original length by gently pulling them out of water immediately after extrusion.

3.3 DEVELOPMENT OF CONTINUOUS DRY SPINNING

As described earlier, continuous threadline formation was achieved by extruding solutions having about 100 poise viscosity through a needle. The flow rate of solution in this experiment was too rapid at this viscosity to ensure complete drying in order to wind the fibers continuously. When this extruded fiber was wound continuously it stuck to the bobbin and could not be unwound. The following methods were tried to dry the fibers as they were extruded from the syringe needle.

a) Hot Tube Drying

A tubular heater was built using a 4' L x 4" D glass tube. The temperature profile given in Table VII was created in the

TABLE VII

Temperature Profile of Tabular Heater

Distance from top end (inches)	0	6	12	18	24	30	36	42	48
Temp (°C)	60	85	101	125	160	200	240	253	184

vertically mounted tubular heater. The top end of the spinning unit was covered with a 1 inch thick wooden disk having 3/4" diameter hole in the center. The spinning unit was mounted on top of the heater with the syringe needle placed inside the hole on the wooden disk. A solution having 115 poise viscosity was extruded through the needle and the fiber that emerged from the hot tube was still sticky and not suitable for winding. The following problems were associated with the hot tube drying technique:

- i) Threading of the extruded fiber through the heater was difficult. Upward currents of hot air made the fiber fly around and stick to the walls of heater. This problem was encountered when the spinning unit was mounted a few inches above the top end of heater.
- ii) When the spinning unit was placed on the wooden disk which was used to cover the top end to prevent the upward current of hot air, temperature of spinning solution increased and hence the decrease in viscosity resulted in increase of flow rate. This was again not suitable for rapid drying of the threadline.

b) Steam Tube Drying:

Steam was passed through the top end of the 4 foot long tubular heater which was maintained at 100°C. Steam atmosphere provides high humidity for further hydrolysis leading to gelation as well as a high temperature for rapid evaporation of solvent ethanol to ensure drying. A spinning fluid having a viscosity of about 400 poise was taken in the spinning unit and extruded through

the syringe needle. Initially the solution emerging through the needle formed a bulb and spraying of ethanol on the bulb allowed it to fall down through the hot steam tube, pulling along with it a fine fiber. The flow of solution was then continuous for a few minutes. Fiber collected through the bottom of the steam tube was not sticky. The flow rate of solution increased due to decrease in viscosity as it was warmed up in the spinning unit. The fiber emerging subsequently was wet and sticky. Hence under the conditions described above a continuous dry spinning could not be carried out beyond the initial period. Steam tube drying remains, nevertheless, a potentially successful method for producing fibers continuously.

3.3.1 Dry Spinning at Room Temperature:

Use of solutions with viscosity in the range 100-115 poise required higher than desirable flow rates in order to form a continuous threadline. However, it was noticed that continuous fiber formation could be achieved at lower flow rates by using solutions of higher viscosity, in the range 250-400 poise. The lower flow rate provides a longer residence time for the fiber before it is taken up on a winding bobbin.

Also it was noticed that by using a spinneret with a much smaller hole than that in a syringe needle, very fine filaments could be produced and this helped in drying and continuous winding of the fibers.

3.3.2 Multifilament Dry-Spinning of Precursor Gel Fibers:

The possibility of multifilament dry spinning process was demonstrated by the following experiment using a spinneret having 3 closely spaced holes. A spinnable solution was prepared using 1.6 equivalents of water for hydrolysis and polycondensation of TEOS. The viscosity of the spinning dope was 270 poise at room temperature and the solution did not exhibit the elastic behavior. The experimental set up is shown in Figure 3. The spinning fluid was extruded through a 3 hole spinneret under 35-40 psi N₂ pressure. Wiping the spinneret surface with alcohol helped the formation of filaments. Filaments were guided onto the winding bobbin as shown in Figure 2 and continuous spinning was carried out. Filaments were wound at up to 16 ft/min take up speed. The individual filaments did not fuse together. This successful experiment shows clearly that multifilament dry spinning with spinneretes having closely spaced holes is possible. A major problem associated with the multifilament dry spinning process is initiating the filament formation from each hole on the spinneret. It is necessary to identify a suitable finish for the spinneret face to prevent sticking of the solution.

3.4 WET AND DRY-JET WET SPINNING PROCESSES:

Preliminary experiments indicated that cohesive filament formation could be obtained by extruding a spinnable fluid into a water bath maintained at 50°C. An L-shaped spinning unit was built from stainless steel pipe and provisions were made to attach a nitrogen pressure hose on the long tube end and a syringe needle

adapter on the short tube end of the unit. A spinnable solution was prepared by using 1.5 equivalents of water and polymerization was allowed until the viscosity of the solution was 80 poise. Fibers drawn from this solution by hand dried rapidly and the solution did not exhibit elastic behavior. This solution was placed in the spinning unit and the syringe needle end was immersed in the coagulation bath containing water at 50°C. The solution was extruded under 20 psi of N₂ pressure. Initially the solution emerging from the needle formed a bulb. Filament formation was initiated by pulling this bulb through the bath. The filament could not be guided through the water bath and also flow of solution in the form of filament was discontinuous due to the intermittent formation of bulbs at the needle. At this point it was thought that a dry-jet wet spinning process in which solution is extruded into an air gap above the surface of coagulation bath might be suitable for producing fibers. An advantage of the dry-jet wet spinning process in this case is that the gravitational force helps in preventing reformation of the bulb at the needle after the filament formation is initiated. Thus, in the following experiment, a solution having 80 poise viscosity was extruded through the needle onto the surface of the coagulation bath containing water at 50°C. Continuous threadline formation was obtained but the solution extruded onto the surface of the bath formed a film by spreading. Flow rate of the solution having 80 poise viscosity to obtain continuous thread line was probably too rapid to ensure at least partial drying of filament in the air before it reached the water bath. As a result of this the extruded

filament did not have enough cohesive strength to retain its shape and formed a film on the water surface. The coagulation bath was then made alkaline by adding NH_4OH to obtain 9-10 pH. Under these conditions gelation of the extruded fluid filament should be fairly rapid to provide cohesive strength to the filament. It was noticed that the extruded solution did not spread on the surface of the coagulation bath containing NH_4OH and the filament could be guided through the bath. The filament emerging from the coagulation bath was, however, wet and sticky. This meant that the filament required a longer residence time in the coagulation bath to form a solid filament. With solutions having higher viscosity, in the range of 250-300 poise, continuous threadline formation could be achieved at lower flow rates. Thus by reducing the flow rate of solution, the residence time of the filament in the bath could be increased to insure gelation.

In the following experiment, the same solution which was used in the experiment described above was aged in a closed system at 50°C for 2 hours to increase the viscosity to 260 poise. This solution did not exhibit elastic behavior. Dry-jet wet spinning was carried out by extruding this solution through a needle which was placed 4 inches above the coagulation bath. The coagulation bath contained NH_4OH (pH 9-10) and was maintained at 50°C . The filament extruded through the needle was guided through the coagulation bath and wound continuously on a godet. Continuous spinning was carried out at speeds up to 70 ft/min. During the spinning process, the fiber did not stick to the guides or to the winding godet. But the continuously spun monofilament fused

together on the package. After complete drying, the fiber was also dull and opaque in appearance and very brittle.

3.4.1. Use of Coagulation Catalysts

3.4.1.1 Use of an Acid Catalyst:

Dilute HCl at 1M concentration was used as a coagulating medium for wet spinning. The syringe needle was immersed into a long column of dil. HCl and a spinnable solution was extruded. Downward flow of the solution in the HCl bath formed a threadline. Even after keeping it for several minutes inside the HCl bath, the filament remained sticky and wet. The appearance of this filament was different from the one obtained by using an alkaline catalyst for coagulation. Filament extruded in the HCl bath remained bright and shiny even after being kept for several minutes in the bath. Acid catalysed gelation was, however, slow and the filament requires unreasonably long residence times in the coagulation bath.

3.4.1.2. Use of NaOH as Catalyst for Gelation

Aqueous sodium hydroxide (1% w/w) was used as a coagulating medium for wet spinning. Filaments extruded inside this alkaline coagulation bath became opaque immediately after extrusion and did not dry as rapidly as they did in the water bath. These filaments were also very brittle.

3.4.1.3. Use of Organic Amines as Catalysts for Gelation

Solutions of organic amines such as Emery 6760 U, Emery 6717

and Cation Softener-X are not alkaline ($\text{pH} < 7$) but the amino groups might catalyze the gelation reaction because of the nucleophilic nature. The structure of Emery 6760 U is shown in Figure 5. It has been mentioned in the literature [10] that long chain amines such as Primene JMT are used as catalysts for gelation in sol-gel process. About 1% (w/w) concentration solutions each of Emery 6760 U, Emery 6717 and Cation Softener-X were prepared in water at room temperature. Cation Softener-X solution was turbid at room temperature. Emery 6717 solution was clear at room temperature. Increasing the temperature of this solution to above 35°C caused turbidity and the solution was milky white at 45°C . But Emery 6760 U solution remained clear at higher temperatures. It is easier to work if the solution in coagulating bath is clear. For this reason Cation Softener-X and Emery 6717 U were not explored as catalysts for gelation in wet spinning processes. Filaments extruded into the Emery 6760 U solution at 50°C gelled quickly and non-sticky fibers were obtained.

3.4.2. Continuous Dry-jet Wet Spinning Using Emery 6760 U as Catalyst:

A coagulation bath was prepared by dissolving 10 gm of Emery 6760 U catalyst in 4 liters of water and the solution was kept at 47°C . A spinnable solution was prepared by using 1.6 equivalents of water for hydrolysis and polycondensation of TEOS. The viscosity of the spinning dope was 260 poise and the solution did not exhibit elastic behavior. The spinnable fluid was extruded through a one hole spinneret which was kept 2 inches above the

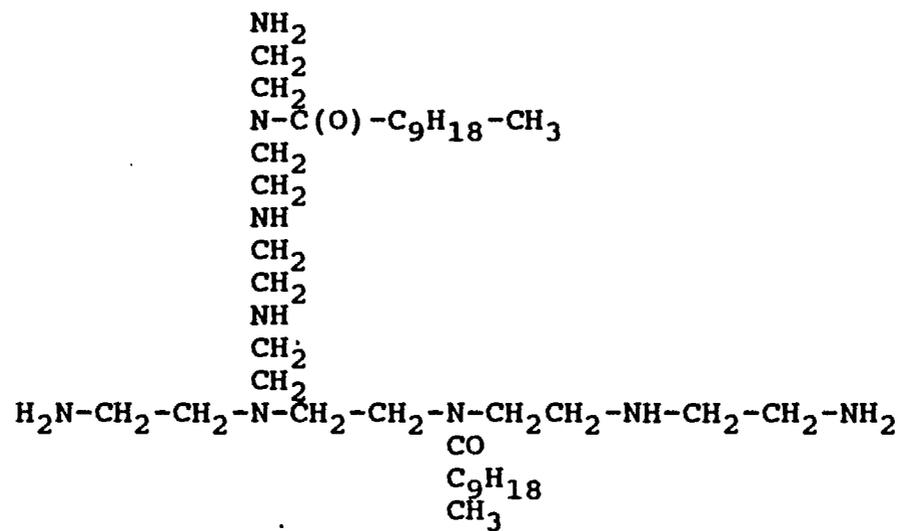


Figure 5. STRUCTURE OF EMERY 6760 U

coagulation bath (Fig. 3). The filament was guided through the coagulation bath containing Emery 6760 U solution and wound continuously at a rate of about 23 ft/min. It did not stick to the godet and could be unwound. The fiber remained bright and shiny after complete drying and was similar in appearance to a dry spun fiber. This was in contrast to the opaque and dull fiber produced from dry-jet wet spinning using NH_4OH as the catalyst.. Also filaments spun in a bath of Emery 6760 U were not as brittle as the ones obtained using NH_4OH as catalyst for gelation.

3.4.3. Multifilament Dry-jet Wet Spinning:

A spinnable solution having 260 poise viscosity which was prepared by using 1.6 equivalents of water was used. The composition of the coagulation bath was 10 gm of Emery 6760 U catalyst in 4 liters of water and the solution was maintained at 47°C . The viscous spinning dope was extruded through a 3 hole spinneret under nitrogen pressure. The spinning unit was mounted above the coagulation bath such that the distance between the spinneret and the bath was 2 inches (Fig. 3). Filament formation was initiated by wiping the spinneret surface with alcohol or Emery 6760 U solution. Flow of solution in filament form was continuous. The extruded filaments were guided through the coagulation bath. Continuous spinning of precursor fiber was carried out at about 20 ft/min take up speed. The filaments spun together in this experiment did not fuse together. Also the filaments could be unwound easily from the spool. Thus a multifilament dry-jet wet spinning of silica precursor gel fiber in

Emery 6760 U coagulation bath using a spinneret having closely spaced holes was established. Similar to the dry spinning process, the problem associated with the dry-jet wet spinning operation is in initiating the filament formation through each hole in the spinneret.

3.4.4 Multifilament Wet Spinning

Preliminary experiments indicated that when a spinnable fluid was extruded in a water bath cohesive filaments were formed. Dry-jet wet spinning process using Emery 6760 U as the gelation catalyst in coagulation bath indicated that 3 filaments spun together did not stick to each other and the fiber could be unwound easily from the spool on which it was wound. Based on the successful results obtained from these experiments, we attempted a wet spinning process using a multihole spinneret.

A spinnable solution was prepared by the sol-gel process using 1.6 moles of water per mole of TEOS. Viscosity of the solution was 385 poise and the solution did not exhibit elastic behavior. Also fibers drawn from this solution by dipping a glass rod dried almost immediately after drawing. The spinning bath was prepared by dissolving 25 gm of Emery 6760 U in 8 liters of water and the bath was maintained at room temperature (21°C). About 125 ml of spinning dope was transferred into a spinning unit and extruded under 25 psi N₂ pressure through an 80 hole spinneret having 0.15 mm diameter holes. After the solution emerged from the spinneret holes, the spinneret was immersed into the spinning bath. The solution which had partially gelled and stuck to the spinneret face

was removed with a spatula and this allowed the solution to flow in filament form. The extruded filaments were then gently pulled along the spinning bath and then guided onto godet 1 (Figure 4) at 5 ft/min. The filaments were washed under a water shower placed on godet 1 and then passed through a drawing bath containing water at 75°C. After guiding the fiber through the hot water drawing bath, it was wound on godet 2. But continuous winding was not possible on godet 2 because fibers frequently broke in the drawing bath which was kept at 75°C irrespective of the drawing speed of godet 2. Then, the temperature of water in drawing bath was reduced to 65°C and fibers were again guided through the bath. At this temperature the fibers did not break and were wound continuously on godet 2. The winding speed of godet 2 could be increased to above 30 ft/min before breakage of filaments occurred. The filament bundle was pulled continuously around godet 2 at 30 ft/min take up speed and collected on a winder rotating at the same speed. The initial winding speed at godet 1 was 5 ft/min and this means that the fiber was drawn by about 6 times its original length. Drying of fiber before it was collected on the winder was attempted by wrapping the filaments on a hot godet 3. This was not successful because the dried fiber was very brittle and could not be wound. For this reason wet fiber was collected on bobbins. However, after the fiber was allowed to dry at room temperature, it became very brittle and the bundle of fiber on the bobbin broke apart. The fiber obtained by continuous wet spinning followed by drawing in the warm water bath was dull and opaque, in contrast to the dry-jet wet spun fiber which was bright and shiny. Also, the yarn spun

into the Emery 6760 U bath and drawn in the water bath was not resistant to solvents. When this yarn came into contact with ethanol or acetone the filament structure collapsed and a paste has formed. In contrast to this, the dry spun or dry jet wet spun fibers retained their shape even in boiling ethanol. The wet spun and drawn fiber yarn was soaked overnight separately in 0.1 N HCl and 2% (v/v) NH_4OH at room temperature. After this treatment, the fibers were air dried at room temperature and soaked in ethanol and acetone. These fibers retained their shape but they were still brittle and the strength of the fibers did not seem to improve after the acid or alkali treatment.

3.4.5. The Effect of the Presence of NaOH in Drawing bath:

As indicated above, the wet spun and drawn fibers were very brittle and continuous winding was not possible if the fibers were dried prior to winding. In the earlier continuous wet spinning experiment the fibers were drawn in a warm water bath. It was felt that addition of a catalyst to the drawing bath to increase the rate of hydrolysis and degree of gelation during the spinning process could improve the cohesive strength of the fibers. The rate of polycondensation is relatively rapid in alkaline medium. 0.1% NaOH solution was used in the drawing bath which was maintained at 60°C . A spinnable solution was prepared by hydrolysis and polycondensation of TEOS using 1.6 equivalents of water. The viscosity of solution was 385 poise and the fibers drawn by hand dried immediately. This solution was placed in the spinning unit and extruded through a 80-hole spinneret having 0.15

mm diameter holes. The composition of the coagulation bath was identical to the one employed in the previously described wet spinning experiment, i.e. 25 gm of Emery 6760 U in 8 liters of water and the temperature of bath was 21° C. The extruded filaments were guided through the spinning bath and wound around godet 1 at a rate of 15 ft/min. The fibers were then passed through the drawing bath containing 0.1% NaOH solution at 60°C. The filaments broke in the drawing bath and could not even be guided through the bath. The concentration of NaOH in the drawing bath was decreased to 0.05% and the temperature was maintained at 60°C; under these conditions the filaments were guided through the bath and drawn by about 1.6 - 2 times their original length. Higher draw ratios were not possible in dilute NaOH (0.05%) in contrast to the draw ratio of 6 obtained by using only warm water. This was probably due to higher degree of crosslinking of chains leading to gelation in the presence of NaOH. The fibers were opaque but shiny.

3.4.6. Use of a Solution having >1000 poise Viscosity for Wet Spinning:

A solution was prepared using 1.6 moles of water per mole of TEOS for hydrolysis and polycondensation. Viscosity of the solution was allowed to increase to >1000 poise. At this high viscosity, the solution was still homogeneous and did not contain any gel-like material. This solution was very much spinnable and hand drawn fibers dried immediately. This solution was diluted with absolute alcohol and the viscosity decreased to 190 poise.

Further aging of the diluted solution increased the viscosity to about 390 poise. This value is comparable to the viscosity of the solution used for wet spinning in the previously described experiments. Thus a solution having about 390 poise was extruded in an Emery 6760 U spinning bath through an 80 hole spinnerett. The spinning bath composition was the same as described earlier. The filaments were wound on godet 1 at 5 ft/min take up speed and then passed through a water bath kept at 60°C. Filaments could be drawn by only about 2 times their original length. Although the viscosity of the spinning dope was comparable to that of the solution used earlier in continuous wet spinning experiments, the initial viscosity of the solution used in the present experiment was >1000 poise. This higher viscosity was probably due to partial crosslinking of polymeric chains and hence filaments could not be drawn beyond a draw ratio of 2. The fibers were bright and shiny.

3.5 PREPARATION OF GEL FIBERS CONTAINING AN ORGANIC POLYMER:

Silica precursor gel fibers produced by the sol-gel process of TEOS using dry, dry-jet wet and wet spinning techniques as described earlier were brittle. By incorporating a linear chain organic polymer into the fibers, the cohesive strength of the fibers could be improved. Also the fibers could become more flexible. Spinnable solutions containing 2% polyethyleneoxide (PEO) having 100,000 molecular weight were prepared by the following method using 1.7 equivalents of water.

3.5.1 Preparation of Spinnable solution containing 2% PEO:

A solution of 300 mL TEOS and 100 mL absolute ethanol was heated to 60°C in a 1 liter beaker and a solution containing 50 mL ethanol, 28.4 mL of 1M HCl, 12.9 mL H₂O and 5.6 gm of PEO was added dropwise in about 15 minutes. The solution was aged in a humid atmosphere at 70°C for about 50-55 hrs and the viscosity of solution increased to 270 poise. This solution was hazy but spinnable. Below 24°C, precipitation of PEO from solution occurred. Fibers drawn from this solution appeared to dry slowly at room temperature.

3.5.2 Dry Spinning of Gel Fibers Containing 2% PEO:

A spinnable fluid containing 2% PEO was extruded through a 2 hole spinneret under nitrogen pressure, initially at room temperature. The filaments collected on a paper did not dry rapidly and remained sticky even after several minutes of air drying at room temperature. Hence dry spinning was carried out at a higher temperature (120°C) to ensure complete drying of the extruded fibers.

The spinning unit was clamped about 4½ feet above ground level and the polymer fluid at room temperature was extruded through a 2 hole spinneret. The filaments were threaded through a 1 foot long hot tube which was maintained at 120°C. The distance between the spinneret and hot tube was about 1 foot. Dried fibers were guided to the winder as shown schematically in Figure 5. Continuous spinning was carried out at speeds of up to 32 ft/min. The filaments did not stick to each other and could be unwound from the

package. Fibers containing PEO were fairly flexible. Presence of PEO in the spinning dope improved the spinnability of solution and initiating fiber formation was relatively easier when compared to solutions without PEO.

3.5.3 Dry-jet Wet Spinning

A coagulation bath containing about 0.6% of Emery 6760 U catalyst was prepared. Filaments were extruded through a 2 hole spinneret and passed through the coagulation bath and wound at take up speeds of up to 22 ft/min. But the filaments were sticky and fused together. The stickyness of fiber was probably caused by the presence of 2% PEO which is soluble in water.

3.6 EFFECT OF DRYING CONTROL CHEMICAL ADDITIVES IN SOL-GEL PROCESS:

It was noticed in our experiments that precursor gel fibers prepared by the sol-gel route of TEOS appeared to have become more brittle after storing at room temperature for several days. In one experiment (Section 3.4.4) the fibers, made by the wet spinning process and further drawn by 6 times their original length in a hot water bath and kept at room temperature, gradually became very brittle. After a few months of storage at room temperature, the fiber on the bobbin broke into fine particles and looked like fluffy cotton. It has been reported in the literature [7] that aging of hand drawn gel fibers at room temperature for a week resulted in a decrease of strength of the consolidated silica fibers. Rapid drying of gels causes cracking because of the large

capillary forces generated in the tiny (3-10 nm) pores [11]. Two general approaches have been proposed to circumvent the problem of drying. Hypercritical drying of gels at the critical temperature of solvent eliminates the liquid-vapor interface and thus prevents the development of capillary stresses [12,13]. Another method is the use of a drying control chemical additive (DCCA) which permits relatively rapid drying but the mechanism is not clear [14]. It has been proposed that DCCA makes the stress spatially uniform by narrowing the distribution of pore sizes [15]. Also it has been reported that DCCA control the vapor pressure of the solvent to reduce the rate of evaporation of solvent from the surface of gel to be compatible with the rate of diffusion of solvent within the gel. Solvents such as formamide, dimethyl formamide, acetonitrile and dioxane have been used as DCCA's in the literature [14,16]. We have used tetrahydrofuran, (THF) which is a polar-aprotic solvent and has the ability to form strong hydrogen bonds with the system as a DCCA in our studies. Spinnable fluids, containing THF were prepared by the sol-gel process of TEOS.

3.6.1 Preparation of Spinnable Solution Containing THF:

Since water and TEOS are miscible with tetrahydrofuran, it was used as a solvent for the sol-gel processing of TEOS. In this experiment 300 mL of TEOS was mixed with 150 mL of THF (THF/TEOS = 0.5 v/v) To this was added dropwise 28.4 mL of 1M HCl and 12.9 mL H₂ at room temperature. After a few drops of water and HCl were added it was found that the solution was not clear. 50 mL of ethanol was added to the reaction mixture in order to get a clear

solution and improve the miscibility of water.

In another experiment, to a solution of 300 mL TEOS and 230 mL of THF maintained at 40°C was added dropwise 28.4 mL of 1M HCl and 12.9 mL H₂O. Even at this higher volume ratio of solvent (THF) to TEOS, addition of a few milliliters of water and HCl resulted in the formation of a precipitate. Hence it was established that THF could not be used as a solvent by itself for sol-gel processing of TEOS. Ethanol is necessary at least at a volume ratio of TEOS/EtOH = 6 in sol-gel solutions in order to get good miscibility of water. Thus, in a following experiment, 300 mL of TEOS was mixed with 150 mL THF and 50 mL absolute ethanol and to this was added 1.7 equivalents of water containing 0.021 equivalent of HCl as catalyst. Addition was completed in about 15 minutes and the solution was aged in a humid atmosphere at 70°C for about 55 hrs. Viscosity of the solution increased to 230 poise. The solution did not exhibit elastic behavior and the hand drawn fibers dried quickly.

3.6.2 Dry Spinning of Solution Containing THF:

A spinnable solution containing THF, prepared as described above was extruded under 40 psi N₂ pressure through a two hole spinneret. It was noticed that initiating filament formation was relatively easier with this solution when compared to those prepared by using only EtOH as solvent. Filaments were extruded at room temperature and wound continuously at 45 ft/min take up speed. Also it was possible to increase the take up speed up to about 100 ft/min without changing the N₂ pressure to increase the

flow rate of solution. This was not possible earlier with the solutions that did not contain THF. This indicates that the spinnability of the solution was improved by using THF as a co-solvent for sol-gel process. Also it was noticed that the solution containing THF and having 230 poise viscosity remained spinnable even after about 20 hrs of storing at room temperature, although the viscosity increased. Thus the stability of spinnable solution at high viscosity was improved by the presence of THF. In contrast to this, spinnable solutions prepared by using only ethanol as solvent tend to gel rapidly at high viscosities.

3.7 SPINNING EXPERIMENTS WITH ELASTIC AND/OR DIFFICULT-TO-DRY SOLUTIONS

3.7.1 Spinning of Elastic Solutions:

Solutions prepared by using up to 1.5 equivalents of water for hydrolysis and polycondensation of TEOS and aged at 70°C in a humid atmosphere exhibited elastic behavior. These solutions, as described earlier in this report, were spinnable at high viscosity. But the hand drawn fibers remained sticky even after several minutes of air drying. All attempts at dry spinning were not successful even at higher temperatures. Wet spinning was attempted, using NH_4OH as catalyst for gelation in the coagulation bath. Fiber formation could not be initiated when the syringe needle was immersed in the coagulation bath and hence continuous wet spinning was also not possible. When this solution was extruded through a needle onto the surface of the coagulation bath containing NH_4OH as catalyst, a film was formed. Even at high

concentrations of NH_4OH (200 mL conc. NH_4OH in 5 liters of H_2O) dry-jet wet spinning or wet spinning was not successful.

In some of the experiments, when 1.6 equivalents of water was used for sol-gel processing of TEOS followed by aging at 70°C in a humid atmosphere, the resulting spinnable solutions did not exhibit elastic behavior. The hand drawn fibers did not shrink when the threadline broke. However, these fibers did not dry even after several minutes of exposure to air at room temperature. Also, when a drop of the solution was spread on a watch glass and exposed to air, it remained sticky even after several hours. Continuous spinning was attempted with such solutions which were prepared by using 1.6 equivalents of water.

3.7.2 Continuous Spinning of Solutions that do not dry:

3.7.2.1. Preparation of Solution:

To a solution of 300 mL TEOS (Petrarch Systems, Inc) and 150 mL absolute ethanol was added 28.4 mL 1M HCl and 10.5 mL of H_2O ($[\text{H}_2\text{O}]/[\text{TEOS}] = 1.6$) in about 5 minutes at room temperature. The solution was aged in a humid atmosphere at 70°C for 49 hours and the viscosity increased to 40 poise. Fibers drawn from this solution by hand were not elastic but did not dry quickly. The solution was further aged to increase the viscosity to 250 poise. This solution was used in the following spinning experiment.

3.7.2.2. Dry Spinning:

Fibers extruded at room temperature through a 2 hole spinneret

remained sticky and continuous spinning was not possible. Dry spinning was also attempted at 120°C using a 1 foot long hot tube. But the fibers still remained wet and sticky and continuous spinning was not possible

3.7.2.3. Dry-jet Wet Spinning Using Emery 6760 U as Catalyst:

A coagulation bath was prepared containing 0.6% of Emery 6760 U. The temperature of the bath was maintained at 23°C. Fibers were extruded through a 2 hole spinneret which was kept 2 inches above the bath. The fiber was guided through the bath and wound on a godet at 15 ft/min take up speed. The filaments were sticky and fused together.

The temperature of the coagulation bath was increased to 50°C to facilitate the gelation process. When the distance between spinneret and bath was 2 inches, the extruded fibers stuck to the guide and could not be guided through the bath. Then the spinneret was moved to 8 inches above the bath. At this distance the fibers extruded into the bath did not stick to the guide and could be guided through the bath. The fibers were wound at speeds of up to 24 ft/min. The filaments wound on the godet in this manner also fused together. At this point the pH of the solution in coagulation was checked using a hydrion paper. The pH value was 6-7.

3.7.2.4 Effect of the presence of NH₄OH in Coagulation bath Containing Emery 6760 U:

The pH of coagulation was increased to 8 by adding conc. NH₄OH

solution. Under alkaline conditions, the polycondensation of silanol groups occurs rapidly and thus the rate of gelation will be increased.

The temperature of the bath containing Emery 6760 U and NH_4OH was maintained at 30°C . The spinneret was clamped 2 inches above the bath and fiber extruded into the bath. The fiber did not stick to the guide and was passed through the bath. The fiber wound on godet was not sticky but filaments still fused together. The temperature of bath was raised to 50°C to increase the rate of gelation to obtain nonsticky fibers. The coagulated fiber was wound continuously on the godet. After drying at room temperature, fiber could be unwound easily. This fiber was bright and shiny.

3.7.3 Dry-jet Wet Spinning Using a Solution having >1000 poise Viscosity:

The spinnable solution used in the previous experiment was aged at room temperature to increase the viscosity to >1000 poise. Fibers drawn from this solution did not dry quickly at room temperature although the fluid filament was not elastic. Dry-spinning was attempted using this solution but the fibers wound on the godet were sticky and they had also fused together. Hence dry-jet wet spinning was carried out using this solution as follows:

3.7.3.1 Use of Emery 6760 U and NH_4OH as Catalysts for Gelation:

Dry-jet wet spinning was carried out using a coagulation bath containing Emery 6760 U and NH_4OH . The pH of the bath was 8.0 and the temperature was kept at 23°C . At this temperature continuous

spinning was possible but the fiber was still sticky and could not be unwound. However, when the coagulation temperature was increased to 47°C, continuous dry-jet wet spinning could be carried out. A maximum take up speed (at 120 psi N₂ pressure) of about 30 ft/min was obtained. The fiber could be unwound from the bundle but it was dull and opaque in appearance.

3.7.3.2 Use of Emery 6760 U as Catalyst for Gelation:

A coagulation bath was prepared containing 23 gm of Emery 6760 U in 4 liters of water. Dry-jet wet spinning at 23°C bath temperature was not successful because the fiber stuck to the winding godet. Then the temperature of the bath was increased to 48°C and continuous dry-jet wet spinning was carried out. Take up speeds >35 ft/min at 120 psi N₂ pressure were obtained. This implies that smaller diameter fiber was produced when only Emery 6760 U was used as the catalyst. When NH₄OH was present in the bath, the maximum take up speed which could be obtained was only 30 ft/min. This was probably due to a higher degree of cross linking of polymeric chains leading to rapid gelation when NH₄OH was also present in the coagulation bath. The fibers produced using only Emery 6760 U as a catalyst in the bath was not opaque but was not as shiny as the dry spun fiber.

3.8 CONVERSION OF GEL FIBERS TO SILICA FIBERS:

Precursor gel fibers produced by continuous spinning routes discussed earlier were heated to high temperatures in air to produce silica fibers. A small bundle of fibers was laid in a

solution. Under alkaline conditions, the polycondensation of silanol groups occurs rapidly and thus the rate of gelation will be increased.

The temperature of the bath containing Emery 6760 U and NH_4OH was maintained at 30°C . The spinneret was clamped 2 inches above the bath and fiber extruded into the bath. The fiber did not stick to the guide and was passed through the bath. The fiber wound on godet was not sticky but filaments still fused together. The temperature of bath was raised to 50°C to increase the rate of gelation to obtain nonsticky fibers. The coagulated fiber was wound continuously on the godet. After drying at room temperature, fiber could be unwound easily. This fiber was bright and shiny.

3.7.3 Dry-jet Wet Spinning Using a Solution having >1000 poise Viscosity:

The spinnable solution used in the previous experiment was aged at room temperature to increase the viscosity to >1000 poise. Fibers drawn from this solution did not dry quickly at room temperature although the fluid filament was not elastic. Dry-spinning was attempted using this solution but the fibers wound on the godet were sticky and they had also fused together. Hence dry-jet wet spinning was carried out using this solution as follows:

3.7.3.1 Use of Emery 6760 U and NH_4OH as Catalysts for Gelation:

Dry-jet wet spinning was carried out using a coagulation bath containing Emery 6760 U and NH_4OH . The pH of the bath was 8.0 and the temperature was kept at 23°C . At this temperature continuous

spinning was possible but the fiber was still sticky and could not be unwound. However, when the coagulation temperature was increased to 47°C, continuous dry-jet wet spinning could be carried out. A maximum take up speed (at 120 psi N₂ pressure) of about 30 ft/min was obtained. The fiber could be unwound from the bundle but it was dull and opaque in appearance.

3.7.3.2 Use of Emery 6760 U as Catalyst for Gelation:

A coagulation bath was prepared containing 23 gm of Emery 6760 U in 4 liters of water. Dry-jet wet spinning at 23°C bath temperature was not successful because the fiber stuck to the winding godet. Then the temperature of the bath was increased to 48°C and continuous dry-jet wet spinning was carried out. Take up speeds >35 ft/min at 120 psi N₂ pressure were obtained. This implies that smaller diameter fiber was produced when only Emery 6760 U was used as the catalyst. When NH₄OH was present in the bath, the maximum take up speed which could be obtained was only 30 ft/min. This was probably due to a higher degree of cross linking of polymeric chains leading to rapid gelation when NH₄OH was also present in the coagulation bath. The fibers produced using only Emery 6760 U as a catalyst in the bath was not opaque but was not as shiny as the dry spun fiber.

3.8 CONVERSION OF GEL FIBERS TO SILICA FIBERS:

Precursor gel fibers produced by continuous spinning routes discussed earlier were heated to high temperatures in air to produce silica fibers. A small bundle of fibers was laid in a

stainless steel boat and placed in a tubular heater. The heating rate was manually controlled by changing the heating load of furnace. Conversion of gel fibers to silica fibers was not exhaustively studied. But the preliminary experiments indicated the following:

- 1) Fibers stored for extended periods at room temperature in air became very brittle after heat treatment.
- 2) Fibers stored at room temperature in a humid atmosphere immediately after spinning could be fired to higher temperatures without causing the brittleness. DCCA's such as THF would be useful in storage of the precursor fibers.
- 3) It is very important to control the rate of heating at below 2°C/min up to about 400°C. But the heating rate may be increased up to 5°C/min in the range 400°C to 800°C.
- 4) Heating of gel fibers in air produced glassy fiber.
- 5) When fibers were heated in N₂ atmosphere, the color of fibers turned black. This was probably due to deposition of carbon within the fibers.
- 6) Fibers produced by dry-jet wet spinning of solutions that were not elastic but did not dry (Section 3.7.3), when subjected to heat treatment stuck to the boat and the filaments fused together.

3.9 USE OF ETHYLSILICATE - 40 AS PRECURSOR FOR SOL-GEL PROCESS:

Use of ethylsilicate - 40 (ES-40) in sol-gel processing would be more cost effective than using TEOS as precursor. ES-40, supplied by Union Carbide was employed. The product information

given by Union Carbide indicates that ES-40 contains 20% TEOS, 78% higher polysiloxanes and 2% ethanol.

It has been reported in the literature that fibers have been hand drawn from solutions prepared by hydrolysis of ES-40 using 8-16% water ($[\text{H}_2\text{O}]/[\text{SiO}_2] = 0.67 - 1.35$) in the presence of dibutyltin diacetate as the catalyst [17]. Initial experiments in our laboratory using 0.8 and 1.3 equivalents of water and 0.02 - 0.2 equivalents of dibutyltin diacetate catalyst resulted in formation of gels. Spinnable solutions could not be obtained by the procedures mentioned in the literature [17]. Hence we studied the effect of water content on the nature of solutions obtained with ES-40 as the starting material. In our experiments, we employed HCl as the catalyst for hydrolysis and polycondensation of ES-40 solutions. Water concentration was varied in the range of 0.3 - 0.8 equivalents based on the silica content of ES-40. Experimental procedure was similar to that developed for sol-gel process of TEOS. In a typical experiment 25 mL of ES-40 was mixed with 12.5 mL EtOH. To this was added 0.9 mL of 1M HCl and 0.02 mL - 1.55 mL of water at room temperature and the solutions were aged at room temperature or at 70°C in a humid atmosphere.

When aging was carried out at 70°C, the solutions either exhibited elastic behavior or the fibers drawn by hand did not dry. Similar results were obtained for solutions prepared by using 0.3 and 0.4 equivalents of water and aged at room temperature. However, use of 0.5 - 0.8 equivalents of water followed by aging at room temperature yielded spinnable solutions which were suitable for continuous spinning. The results obtained from these experiments with ES-40 are given in Table VIII.

Table VIII

Effect of Water Content on the Nature of ES-40 Sol

[H ₂ O]/[SiO ₂]	Aging at RT	Aging at 70°C
0.3	Sols are spinnable Elastic Fibers	-
0.4	Sols do not dry Fibers are not elastic	-
0.5	Fibers dried quickly at RT	Elastic fibers
0.6	"	Sols do not dry Fibers are not elastic
0.7	"	"
0.8	"	"

RT - Room Temperature (≈20°C)

4. CONCLUSIONS AND RECOMMENDATIONS TO PPG:

4.1 SUMMARY OF IMPORTANT RESULTS:

The research at Georgia Tech on Sol-Gel fiber formation technology for the production of silica fibers yielded the following important results:

i) Established a method suitable for industrial application to produce spinnable formulations, with the required extent of stability, by the sol-gel process of TEOS.

ii) Identified a possible method to improve the stability as well as the spinnability of sols by using THF as a cosolvent in the preparation of sol.

iii) Established reaction conditions that lead to the formation of elastic solutions of exceptional stability which may be useful to produce silica coatings.

iv) Developed multifilament dry-spinning to produce precursor fibers.

v) Developed multifilament dry-jet wet spinning to produce silica precursor fibers.

vi) Developed multifilament wet-spinning to produce silica precursor fibers.

vii) Established the possibility of using ethylsilicate-40 as a precursor material in sol-gel processing which could prove to be cost effective in large-scale industrial production.

viii) Developed conditions to produce spinnable formulations by the sol-gel processing of ethylsilicate-40.

4.2 PREPARATION OF SPINNABLE SOLUTION:

It was established through our research at Georgia Tech that the critical parameters in preparing spinnable solutions are the initial water concentration employed for hydrolysis and the relative humidity of the aging atmosphere. Use of water concentrations below 1.7 equivalents produced either elastic spinnable solutions (i.e. fibers drawn from these solutions are elastic and do not dry), or spinnable solutions that are not suitable for dry spinning. Although dry-jet wet spinning could be carried out with solutions that do not dry, the fibers produced from these solutions fused together when subjected to heat treatment. For these reasons, at least 1.7 equivalents of water must be used to produce spinnable solutions that are suitable for continuous spinning.

For the preparation of a spinnable fluid, an appropriately scaled procedure based on the following formulation is recommended: "A solution of 50 mL TEOS (2.24 mol) and 250 mL absolute ethanol was heated to reflux in a 1 liter flask and to this was added dropwise 47.1 mL 1M HCl and 17.5 mL H₂O. Addition was completed in

about 20 min. and the reaction mixture was refluxed for 3 hrs. The reaction mixture was then concentrated on a rotary evaporator at 40°C to about 190 mL and then aged in a closed system at 70°C to obtain spinnable viscosity >250 poise. The solution thus prepared was not elastic and the drawn fibers dried almost instantaneously and hence was suitable for continuous spinning by any of the three fiber formations routes".

Our experiments using THF as a cosolvent with ethanol in the sol-gel processing of TEOS, indicated that the presence of THF in spinnable solutions improved both the stability of solution at high viscosities as well as the spinnability of the solution. Also THF could function as a drying control chemical additive because of its hydrogen bond forming ability with the silica gel system. Thus it may be useful in controlling the rate of drying of fibers during the storage prior to consolidation which is necessary to prevent their embrittlement. We recommend further studies of the effects of THF and other organic additives such as formamide, DMF, etc. as cosolvents for sol-gel process as well as DCCA's for silica systems.

4.3 ETHYLSILICATE-40 AS PRECURSOR:

We have established that ethylsilicate-40 is a potential low cost precursor material for sol-gel silica fiber technology. Our experiments showed that use of lower water concentrations in the range of 0.5-0.8 moles of H₂O per mole of SiO₂ for the hydrolysis of ethylsilicate-40, followed by aging at room temperature, yielded spinnable solutions which are suitable for continuous spinning.

Conditions under which elastic solutions could be formed were also established. We suggest that the use of ethylsilicate-40 as a precursor for making silica fibers by the sol-gel process should be explored further because it would offer a significantly lower cost option for the starting material.

4.4 PRODUCTION OF SILICA PRECURSOR FIBERS:

Research at Georgia Tech led to the development of three continuous spinning processes which are suitable for industrial application for the production of silica precursor fibers. The three spinning processes are i) Dry spinning, ii) Dry-jet wet spinning and iii) Wet spinning.

Multi-filament bundles of silica precursor fibers could be produced by all the above spinning processes. An advantage of the dry-spinning or the dry-jet spinning processes is that the fibers can be deformed to a significant extent immediately after extrusion before the polymer chains become cross linked, thus allowing higher rates of spinning when compared with wet spinning. The problem associated with the dry spinning and dry-jet wet spinning processes is in initiating the filament formation through each hole in the spinneret. However, this could be easily resolved by applying a suitable finish to the spinneret face to prevent spreading of the solution. In wet and dry-jet wet spinning, use of the organic amino compound, Emery-6760 U, provided non-sticky filaments and multi-filament spinning processes became feasible. Also it has been established that wet spun fibers could be drawn on-line during spinning by about 5-6 times their original length. This drawing

process would induce orientation of polymer chains along the fiber axis and help improve the mechanical properties of consolidated silica fibers.

The following are some of the critical factors necessary to conduct a continuous spinning process.

- i) Viscosity of spinning dope should be in the range 250-400 poise.
- ii) Homogeneity of the spinning dope should be checked. No traces of gel-like material should be present in the dope.
- iii) For wet spinning process Emery 6760 U catalyst (0.3 - 1% w/w) is recommended.

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