JOURNAL OF MATERIALS SCIENCE **21** (1986) 842–848

Synthesis of SiO_2 glass fibres from $Si(OC_2H_5)_4$–H_2O–C_2H_5OH–HCl solutions through sol–gel method

KANICHI KAMIYA, TOSHINOBU YOKO
Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan

Various factors affecting the spinnability of the $Si(OC_2H_5)_4$–H_2O–C_2H_5OH–HCl solutions have been investigated in order to find appropriate experimental conditions for making gel-derived SiO_2 glass fibres. The molar ratios of H_2O, C_2H_5OH and HCl to $Si(OC_2H_5)_4$ were changed in the range from 0.5 to 10.0, 0.5 to 7.0 and 0.001 to 0.1, respectively. The solutions were reacted at 30 and 80° C. It has been reconfirmed that the most important factor determining the spinnability of the solution in the course of the hydrolysis reaction is the molar ratio of water to $Si(OC_2H_5)_4$ in the solution. The rise of the reaction temperature led to the remarkable shortening of the time required for drawing fibres. The increase of the amount of HCl decreased the upper limit of the $H_2O/Si(OC_2H_5)_4$ molar ratio range where the spinnability is found as well as reaction temperature. The solutions with a $H_2O/Si(OC_2H_5)_4$ ratio larger than 2.0 gave often fibres having a circular cross-section, while other solutions gave fibres with a non-circular one. The tensile strength of the gel-derived SiO_2 glass fibres was also reported.

1. Introduction

The sol–gel method for making oxide glasses from metal alkoxides through their hydrolysis and polycondensation, and gelling has been developing as one of the new glass making techniques since 1971. This method has been applied to many oxide systems to obtain glasses at relatively low temperatures near glass transition temperatures by many investigators. Conventional and new glasses which could not be made easily by the conventional melting technique because of a too high melting temperature and tendency toward phase separation or rapid crystallization during cooling have been successfully made [1].

The present authors have shown that for hydrolysis and gelling of the $Si(OC_2H_5)_4$–H_2O–C_2H_5OH–HCl solutions to obtain SiO_2 glass fibres or the bulk SiO_2 glass, careful adjustment of the composition of the starting solution is quite important [2]. They have noticed that the amount of water added for hydrolysis has to be most carefully controlled depending on which form of SiO_2 glass, i.e., fibres, sheets or bulk is aimed. Namely, the solutions in which the molar ratio of water to $Si(OC_2H_5)_4$ is smaller than about 4.0 while the molar ratio of HCl added as a reaction catalyst is kept at 0.01 to 0.03, give viscous sols in the course of hydrolysis and polycondensation reactions. Fibrous gels can be drawn from such solutions and then converted to SiO_2 glass fibres by heating to 800 to 1000° C. On the other hand, the addition of a relatively large amount of water results in a bulk gel which can be converted to the bulk SiO_2 glass.

The formation of the primarily linear siloxane polymers, which is believed indispensable for fibre drawing, in the region of small water content and the formation of three-dimensional network siloxane polymers at a region of higher water content were confirmed on the basis of the relation between the molecular weight M_n and the intrinsic viscosity $[\eta]$ of growing polymers in the respective sols [3]. Moreover, it has been reported that the shape of the cross-section of fibres is circular, eliptical or more complex, depending on the reaction condition [4]. The water content also seemed the important factor controlling the shape of the cross-section of fibres.

However, so far, no systematic research on the effect of the $HCl/Si(OC_2H_5)_4$ molar ratio on the properties of the solution or sol has been conducted yet. In the present study, a further investigation of factors affecting the spinnability of the $Si(OC_2H_5)_4$–H_2O–C_2H_5OH–HCl solutions and the shape of the cross-section of the resultant fibres, especially the effect of the HCl content on those properties was conducted, in order to find the appropriate condition for drawing fibres with a controlled shape of cross-section from the solutions within a time as short as possible. The tensile strength of the SiO_2 glass fibres thus made is also reported.

2. Experimental details

2.1. Preparation of starting $Si(OC_2H_5)_4$–H_2O–C_2H_5OH–HCl solutions

Tetraethoxy-orthosilicate, $Si(OC_2H_5)_4$ (hereafter, abbreviated to TEOS), was supplied by Nippon Colcoat Co. (Tokyo) and Wako Chemicals Co. (Osaka). TEOS was diluted in a glass beaker with

0022–2461/86 $03.00 + .12

anhydrous or 95% pure C_2H_5OH (EtOH). Half of the alcohol was used for this and another half was used to dilute the water and acid. The mixed solution of EtOH–H_2O–HCl was added dropwise to the above TEOS–EtOH solution using a glass buret under vigorous stirring at room temperature (20 to 25° C). The rate of addition was slow so as to avoid the formation of flocculent or colloidal SiO_2 particles due to a too rapid hydrolysis reaction. Usually, it took 1.5 to 2.5 h to complete the preparation of the TEOS–H_2O–EtOH–HCl solution of a desired composition.

62.5 g of TEOS was used. The amount of water was varied from 0.5 to 10.0 in the molar ratio to TEOS (the H_2O/TEOS ratio). The molar ratio of EtOH to TEOS (the EtOH/TEOS ratio) ranged from 0.5 to 7.0. The molar ratio of HCl (the HCl/TEOS ratio) added as a reaction catalyst was varied in the range from 0.001 to 0.1. The volume of the resultant mixed solution was in the range from 80 to 200 cm^3. The 25 to 35 solutions with different compositions were prepared and used in the experiments.

2.2. Hydrolysis of the solutions

The alkoxide solutions thus prepared were kept open in the ambient atmosphere at 30 or 80° C to be subjected to the hydrolysis and polycondensation reactions. In the case of the reaction at 80° C, the mixed solution was heated in the polyethylene glycol bath with gentle stirring until the reaction was completed or the solution had solidified into a gelly mass.

2.3. Fibre drawing, gelation time and fibre cross-section

The spinnability of the solution was checked by immersing a glass rod of about 8 mm in diameter into the alkoxide solution and then pulling it up quickly by hand in the course of the hydrolysis and polycondensation reactions. The gelation time t_g was defined as a time when on declining the container no more fluidity of the sol was observed. The cross-section of the drawn fibres was observed under the optical microscope with a magnification of × 100.

2.4. Measurement of the tensile strength of the SiO_2 fibres

The drawn gel fibres were converted to SiO_2 glass fibres by heating to 500 or 800° C. A single fibre was mounted with the organic adhesive onto a thin rectangular paper of 15 mm × 30 mm in size having a square hole of 10 mm × 10 mm in size at its centre. The paper was fixed between the heads of a machine for measuring tensile strength, then the paper was cut off at the both sides of the hole. The fracture strength of the fibre was measured with a strain rate of 10 mm min^{-1} to obtain the tensile strength.

3. Results

3.1. The effect of the amount of HCl on the miscibility in the solutions

Fig. 1 shows the mutual solubility of each component contained in the TEOS–H_2O–EtOH–HCl solution at room temperature. When no HCl is added, the miscibility region is quite limited. The initial addition of HCl, that is, the addition of a small amount of 0.001 in the HCl/TEOS ratio, considerably enlarges the miscibility region. It is also seen in Fig. 1 that a HCl/TEOS ratio larger than 0.01 is not effective in further enlarging the miscibility region. The miscibility region remained almost unchanged at the higher temperature of 80° C.

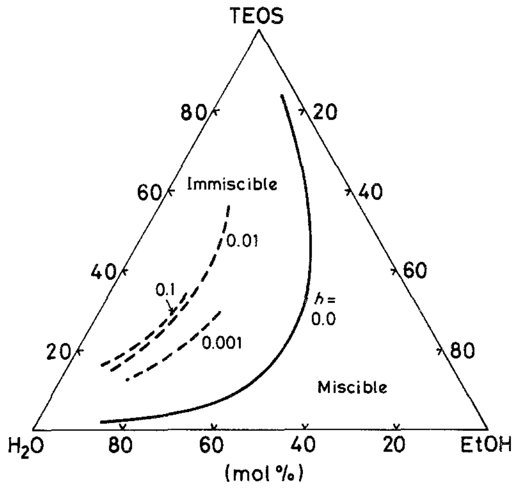

Figure 1 Variation of miscibility region in the TEOS–H_2O–EtOH–HCl solution with the HCl/TEOS molar ratio.

3.2. Spinnability of the solution

Fig. 2 shows the relation between fibre drawing behaviour and the composition of the TEOS–H_2O–EtOH – HCl solution with the HCl/TEOS ratio of 0.01 at 80° C. Four characteristic composition regions, i.e., Areas A, B, C and D, are observed in the figure. The solutions with compositions in Area A showed remarkable spinnability in the course of hydrolysis reaction. The solutions in Area B gelled into elastic bulk masses without exhibiting spinnability. As previously mentioned [5], in Area C solutions did not gel practically, remaining in a low viscosity state for a much longer time compared to other solutions, except for those in Area D where the components are not miscible. It was noticed that Region A in which a solution becomes spinnable is divided by two lines corresponding to H_2O/TEOS ratios of 1.5 to 1.7 and 5.0, respectively. Fibre drawing became difficult as the

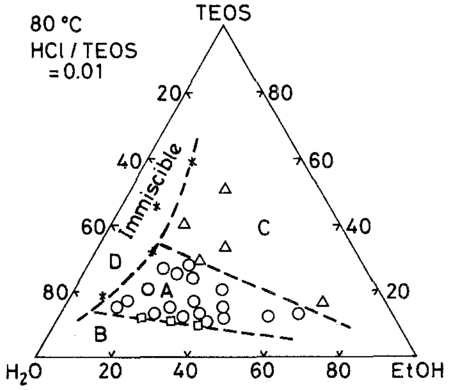

Figure 2 Fibre drawing behaviour of TEOS–H_2O–EtOH–HCl solutions with a HCl/TEOS molar ratio of 0.01 at 80° C. In Area A (○), solutions exhibit spinnability, in B (□), solutions gel without showing spinnability and in C (△), solutions are not practically gelling. Area D (*) is the immiscibility region.

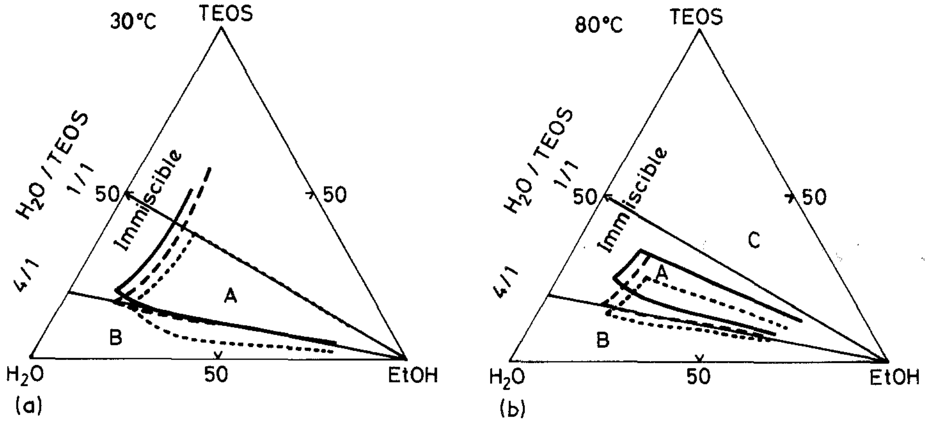

Figure 3 Change of the border between spinnability (A) and non-spinnability (B not spinnable or C not gelling) with the HCl/TEOS ratio (a) at 30° C, and (b) at 80° C. HCl/TEOS; (· · · ·) 0.001, (– – –) 0.01, (——) 0.1.

composition of the solution approached the border between Areas A and B.

Figs. 3a and b show the composition region in which a solution exhibits spinnability in the course of hydrolysis for different HCl/TEOS ratios. Area A, the spinnability region is limited by lines showing constant H_2O/TEOS ratios, irrespective of the HCl content and the reaction temperature. Only exceptions can be shown by solutions with the HCl/TEOS ratio of 0.001 at low EtOH content. There is Area C where the solution does not gel practically for all the HCl/TEOS ratios at 80° C and for the HCl/TEOS ratio of 0.001 at 30° C. The occurrence of Area C reduces the region of compositions where the spinnability appears.

It is seen from Figs. 3a and b, that the water contents or H_2O/TEOS ratios corresponding to the borders between Areas A and B, and A and C are decreased as the HCl/TEOS ratio is increased. The H_2O/TEOS ratio limiting the spinnability is smaller at 80° C than at 30° C for respective HCl contents. In other words, increasing the reaction temperature from 30 to 80° C gives rise to a decrease in the area of compositions where the spinnability appears.

3.3. Gelation time of $Si(OC_2H_5)_4$–H_2O–C_2H_5OH–HCl solutions

The gelation times t_g for 80° C of the solutions with the HCl/TEOS ratio of 0.01 is shown in Fig. 4a. The thick solid lines in the figure representing the contours of t_g have been drawn on the basis of the t_g values of 35 solutions. The t_g of those solutions for 30° C is shown in Fig. 4b. Figs. 5a and b show the t_g values of the solutions with the HCl/TEOS ratio of 0.1 for 80 and 30° C, respectively. In Figs. 6a and b, t_g of the solutions with different HCl/TEOS ratios for 80 and 30° C are plotted against the H_2O/TEOS ratio with the EtOH/TEOS ratio being kept at 2.0, and against the EtOH/TEOS ratio with a constant H_2O/TEOS ratio of 2.0, respectively.

It is seen, at first, that the gelation time t_g of the solution changes with variables such as the composition of the solution and the reaction temperature. Among those variables, the effect of the reaction temperature on t_g is the most remarkable. The rise in the reaction temperature from 30 to 80° C resulted in 50 to 100 times shorter t_g than that at 30° C. However, the change of the gelation time with the solution composition is rather complex.

3.4. Cross-section of drawn fibres

The drawn fibres have cross-sections of different shapes such as circle, ellipsoid, dumb-bell and more complex ones, as illustrated in Fig. 7. Fig. 8 shows the result of observation on the cross-section of fibres drawn from the solution with the HCl/TEOS ratio of 0.1 reacted at 80° C. The closed circle in the figure indicates that more than about two thirds of fibres drawn from the corresponding solution have a

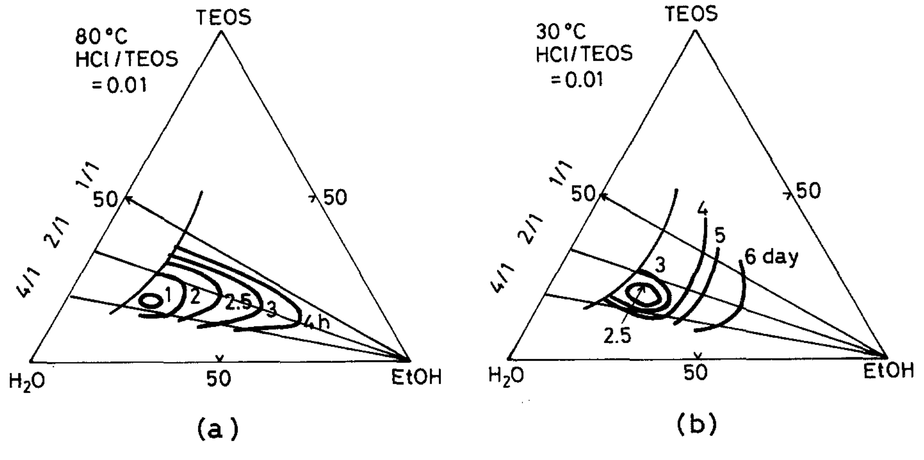

Figure 4 Change of gelation time t_g of the TEOS–H_2O–EtOH–HCl solutions with the HCl/TEOS ratio of 0.01 with the solution composition (a) at 80° C, and (b) at 30° C.

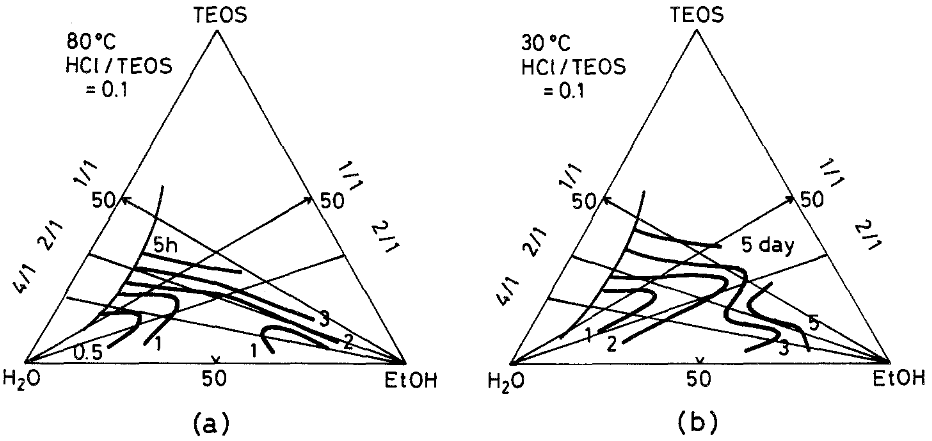

Figure 5 Change of gelation time t_g of the TEOS–H_2O–EtOH–HCl solutions with the HCl/TEOS ratio of 0.1 with the solution composition (a) at 80° C and (b) at 30° C.

circular cross-section. Figs. 9a and b show the composition ranges, in which the probability of obtaining fibres with a circular cross-section is large, for the solutions of different HCl/TEOS ratios reacted at 30 and 80° C, respectively. No solutions with the HCl/TEOS ratio of 0.001 kept at 30° C, and those with the HCl/TEOS ratio of 0.05 reacted at 80° C gave fibres with a circular cross-section. Although fibres with a circular cross-section are obtained in different composition ranges for different HCl/TEOS ratios and reaction temperatures, it can be remarked that the composition in which the fibre has a circular cross-section is limited to the range where the H_2O/TEOS ratio is larger than 2.0.

3.5. Tensile strength of drawn fibres

The fibres were drawn from the solutions with the H_2O/TEOS ratio of 2.0, the EtOH/TEOS ratio of 1.0 and the HCl/TEOS ratio of 0.03 reacted at room temperature (about 25° C) and heated to 500 and 800° C for measurements of tensile strength. Most of the fibres had non-circular cross-sections but some (about one fourth) of the fibres had a circular cross-section. Results are shown in Figs. 10a and b, where tensile strength is plotted against the cross-sectional area. For comparison, the previously reported tensile strengths of the fused silica fibre [6] is given in the figure. It is seen that the tensile strength of the present fibre changes as a function of the cross-sectional area, as well known. The present fibres show the strengths as high as the gel-derived fibres obtained by LaCourse [7], but the strengths are still lower than those of the fused silica fibres even at small cross-sectional areas. No significant difference in the tensile strength between fibres with the circular cross-sections and non-circular ones has been noticed.

4. Discussion

Factors affecting the spinnability, gelation time or time required for the $Si(OC_2H_5)_4$–H_2O–C_2H_5OH–HCl

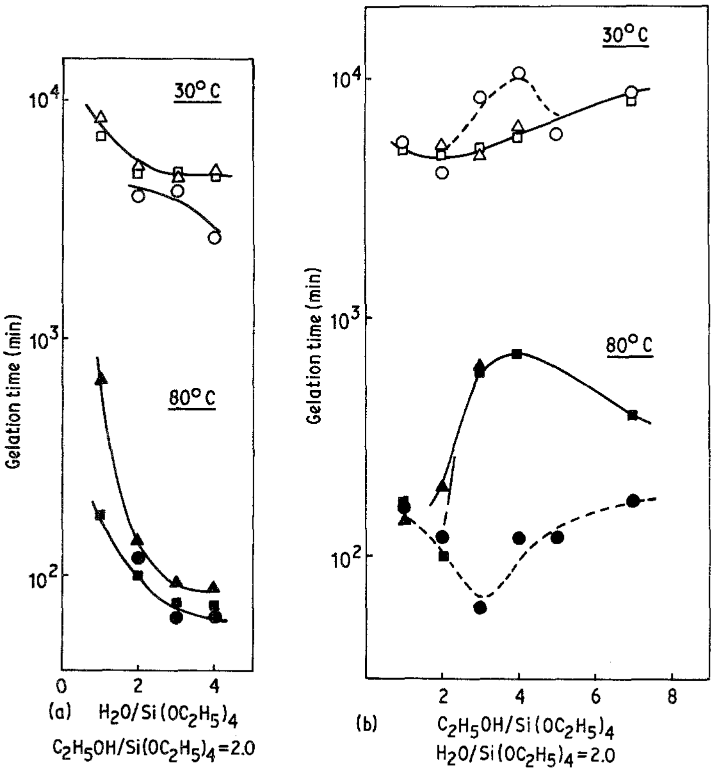

Figure 6 (a) Gelation time t_g of the TEOS solutions of the EtOH/TEOS ratio of 2.0 as a function of the H_2O/TEOS ratio for different HCl/TEOS ratios. (b) Gelation time t_g of the TEOS solutions of the H_2O/TEOS ratio of 2.0 as a function of the EtOH/TEOS ratio for different HCl/TEOS ratios. (○, △, □) 30° C, (●, ▲, ■) 80° C.

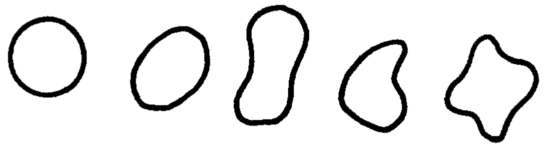

Figure 7 Schematic shapes of the cross-section of gel-derived SiO_2 glass fibres.

solutions to attain the spinnability and the shape of the cross-section of the fibres have been investigated. Results are summarized as follows.

1. The spinnability occurred in the solutions in the course of hydrolysis and polycondensation reactions over a certain composition region at both reaction temperatures of 30 and 80° C for all the HCl/TEOS ratios used. Moreover, it was concluded that whether the solution shows spinnability or not is determined mainly by the H_2O/TEOS ratio. However, an increase of the HCl/TEOS ratio and reaction temperature caused the shift of the spinnability-non spinnability border toward smaller H_2O/TEOS ratios.
2. The time required for the solutions to gel was remarkably reduced by increasing the reaction temperature. At 80° C, the fibres could be drawn from solutions within a few hours, while it took several days to draw fibres at 30° C. The gelation behaviour was rather complex in the present study and its systematic change with the solution composition was not observed.
3. Fibres with different cross-sections were produced. A circular cross-section was possessed by fibres drawn from the solutions in some restricted composition ranges in which the H_2O/TEOS ratio is larger than 2.0.
4. No significant difference in tensile strength between fibres with circular cross-sections and non-circular ones was observed.

Those results connected with the experimental conditions will be discussed below.

4.1. Relation between the spinnability of the solution and the experimental condition

As to the hydrolysis and polycondensation reactions of TEOS, it is easily assumed that other variables than the molar ratios of the constituents in solutions relative to the amount of the alkoxide has to be taken into account. In the present work, the amount of TEOS was kept constant and the molar ratios of H_2O, EtOH and HCl to TEOS were systematically changed. The volume of the starting solution, accordingly, the concentration of TEOS expressed by wt % of SiO_2 and the concentration of hydrogen ion expressed as the pH value of the solution are different from composition to composition of the solution. The latter two variables may also affect the hydrolysis and polycondensation reactions. In order to give an aid for the understanding of the results obtained in the present work, change of the TEOS concentration represented as wt % of SiO_2 with the solution composition is shown in Fig. 11, and that of pH value of the solutions with the HCl/TEOS ratio of 0.1 in Fig. 12. The trend of pH change with composition should be similar in the solutions with the HCl/TEOS ratios of 0.001, 0.005 and 0.01, although absolute pH values are different from those given in Fig. 12. By comparing Fig. 3a with Figs. 11 and 12, it can be stated that the border lines for spinnability of the solution correspond neither with a SiO_2 concentration contour nor with a pH contour, but they correspond with lines indicating constant H_2O/TEOS ratios. This should also be valid for a reaction temperature of 80° C. Namely, it is reconfirmed that the most important factor controlling the spinnability of the TEOS solution is the molar ratio of water to the alkoxide, although the ultimate H_2O/TEOS ratio limiting the spinnability varies with the HCl/TEOS ratio and reaction temperature.

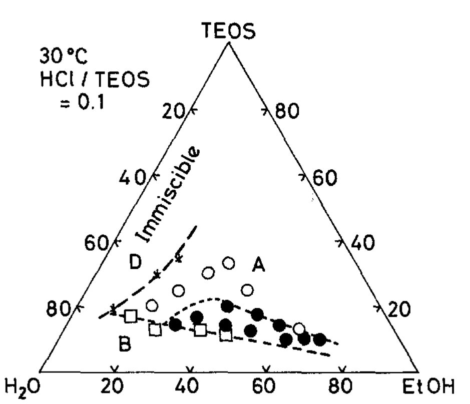

Figure 8 Relation of shape of the cross-section of drawn fibres with composition of the TEOS solution: (●) more than two thirds of drawn fibres have a circular cross-section, (○) fibres with non-circular cross-sections.

It has been believed that the inclusion of primarily linear polymers is required for the solution to exhibit spinnability. Previously, the formation of linear siloxane polymers in solutions with small H_2O/TEOS ratios was assumed and this was revealed in a way described below. The relation between the molecular weight $\overline{Mn}$ and the intrinsic viscosity $[\eta]$ of the siloxane polymers indicated that linear polymers were formed in the solutions with H_2O/TEOS ratios of 1.0 and 2.0, and polymers having some degree of branching or cross-linking were formed in the solutions with the H_2O/TEOS ratio larger than 5.0 [3]. The increase of the degree of branching or cross-linking in the siloxane polymers formed in the course of hydrolysis and polycondensation reactions of TEOS may correspond to the increasing difficulty in drawing fibres with increasing the H_2O/TEOS ratio.

The increase in the reaction temperature gives rise to an increased reaction rate, which, is reflected on the decrease in the gelation time, and may promote the formation of the cross-linking, resulting in the shift of the border for spinnability toward low H_2O/TEOS ratios. The shift of the boundary with the HCl/TEOS ratio in the same manner as that with reaction temperature is considered to be associated with the increasing formation of the cross-linking.

4.2. Gelation time of the $Si(OC_2H_5)_4$ solution

In the term "gelation", the hydrolysis of TEOS to form silicic acid, the polycondensation or growth of polymers with Si–O–Si linkages and aggregation or

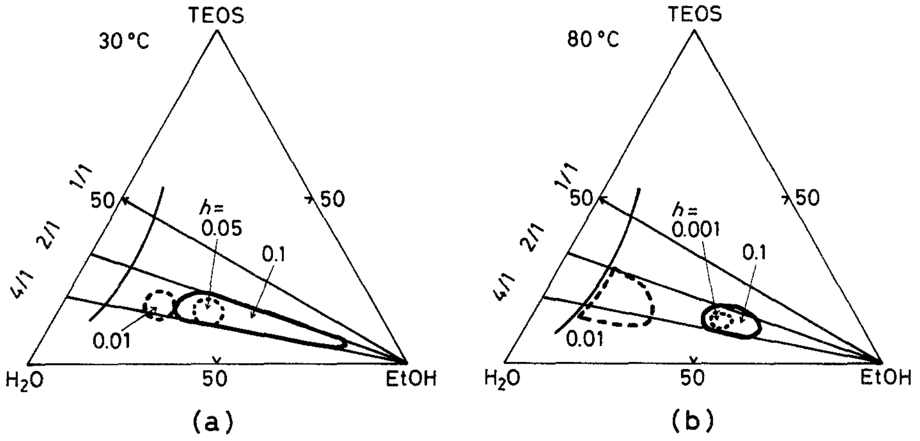

Figure 9 Composition regions of the solutions giving fibres more than two thirds of which have a circular cross-section (a) at 30° C, and (b) at 80° C.

cross-linking of the polymers are involved. The gelation behaviour of the solution is a sequential and/or parallel progress of those elementary reactions. In general, the reaction temperature, and the concentrations of TEOS and water affect the hydrolysis and polycondensation in a direct manner [8]. However, the concentration of hydrogen ions or pH values of the solution affect the gelation alternatively. It is well known that the gelation time of the silicic acid solution shows a maximum at pH of 1.0 to 2.0 [9]. As already mentioned, the present work was aimed at finding out the appropriate experimental conditions for drawing SiO_2 fibres from the TEOS solution and then the concentrations of TEOS and H^+ (pH value) is not kept constant but varied with the solution composition as shown in Figs. 11 nd 12. Therefore, the gelation behaviour of the present solutions is too complex to discuss quantitatively on the basis of the kinetics or reaction mechanisms reported so far. Further investigations are needed in order to explain this.

4.3. Relationship between the cross-section of fibres and the experimental condition

As to the cross-section of fibres drawn from the solution with the HCl/TEOS ratio of 0.01 reacted at 80° C, the authors suggested that the small volume change of the gel fibres occurring during the solidification process leads to the circular cross-section [4]. Since the solution is kept open to air during the hydrolysis and gelling processes in the present study, some part of the starting solution, especially EtOH and H_2O are lost by vaporization, causing the decrease of the solution volume. This shows that the smaller decrease in volume of the solution is encountered at the shorter gelation time as reported previously. The fibres are usually drawn (if possible) at relative times t/t_g of 0.8 to 0.9 (where t_g is the gelation time). The fibres drawn from the solutions which gel quickly, therefore, show a small volume shrinkage during solidification relative to those from solutions gelling slowly. This explanation may also be valid to the solutions with the HCl/TEOS ratios of 0.001 and 0.1, since the fibres having circular cross-sections are obtained from the solutions which have compositions in the area for spinnability and have the shortest gelling times. If only the rapid gelling is required for the formation of the circular cross-section one could not obtain fibres with a circular cross-section at 30° C at all, because gelling of all the solutions is quite slow. The fact that fibres can have a circular cross-section on reacting at 30° C suggests that not shorter gelling time but smaller volume change on gelling is an essential requirement for fibres with a circular cross-section.

The type of the polymers formed in the course of reaction may be another factor affecting the volume

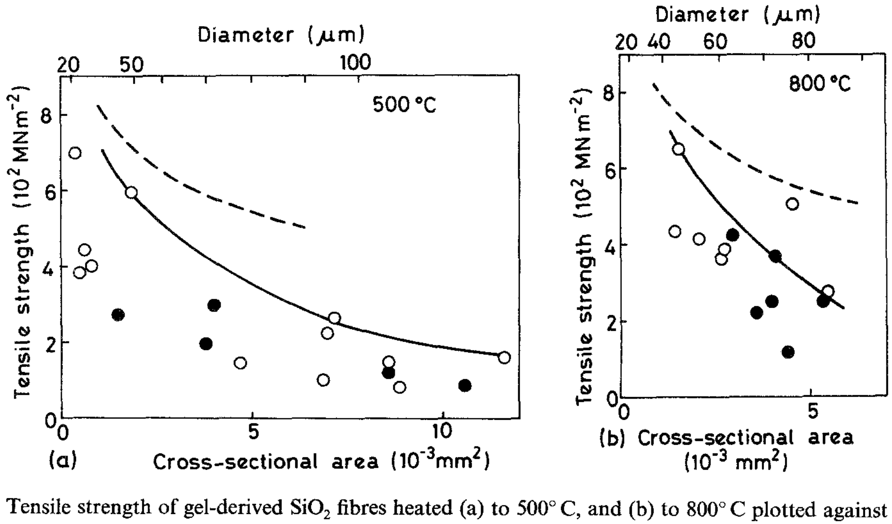

Figure 10 Tensile strength of gel-derived SiO_2 fibres heated (a) to 500° C, and (b) to 800° C plotted against cross-sectional area. (●) Fibres with a circular cross-section, (○) fibres with non-circular cross-sections and (– – – –) fused silica glass fibres.

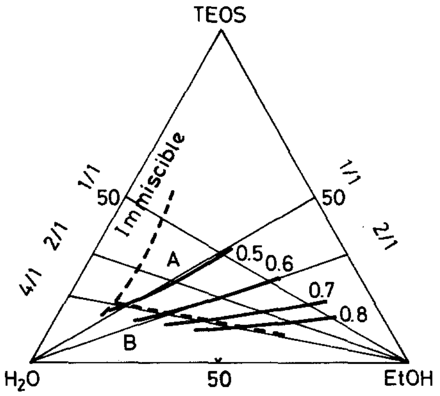

Figure 11 Concentration of TEOS represented by wt % of SiO_2 of the solutions used in the experiment.

change of the solution on gelling. The occurrence of the circular cross-section for the solutions with the H_2O/TEOS ratios larger than 2.0 may support the above assumption. The hypothetical volume change of the solution on gelling is shown in Fig. 13 for the solutions containing linear polymers and cross-linked polymers. It is apparent that the volume shrinkage of the latter solution is smaller than the former because of a larger steric hindrance against the latter solution to shrink. Here, further investigation on the type of siloxane polymers produced in the TEOS–H_2O–EtOH–HCl solutions under different experimental conditions may be needed to confirm the above scheme.

4.4. Tensile strength of sol–gel derived SiO_2 glass fibres

The increase of the tensile strength of the gel-derived SiO_2 glass fibres with decreasing diameter or cross-sectional area should be ascribed to the decrease in the number of the surface cracks or flaws as found in conventional glass fibres made by the melting method. On heating the gel fibres to 500 or 800° C, their tensile strength increased to a great extent. However, the ultimate tensile strength of the heated fibres at a diameter of 20 to 30 μm was still lower than that of fused silica glass fibres. In making the gel-derived glass fibres, the volatile matters such as water, alcohols and other organic groups remaining in the gel fibres are removed by heating, at the same time the gel structure becomes dense and stiff. Accordingly, the difficulty in removing the volatile matters from the gel should be increased as the heating temperature is raised. The forced escape of these volatile matters out of the solidifying gel or glass at high temperature may leave some defects such as cracks and flaws on the surface. Those defects may lower the tensile strength. If the gel-derived SiO_2 fibres heated to 800° C were etched by an aqueous HF solution to remove the defective surface layer, the increase in their tensile strength could be seen as in the case of the conventional glass fibres.

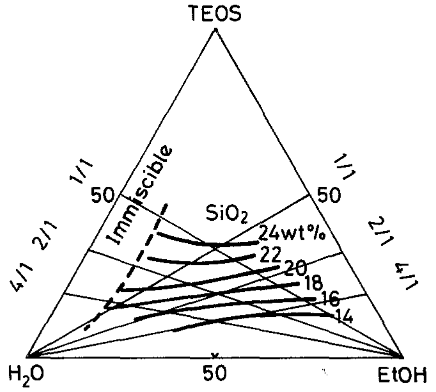

Figure 12 pH-values of the TEOS–H_2O–EtOH–HCl solutions with the HCl/TEOS ratio of 0.1.

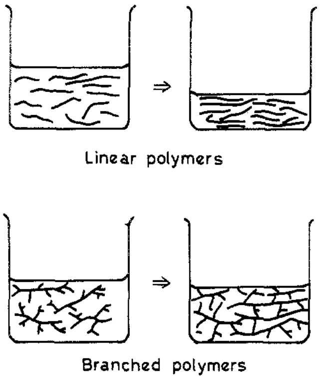

Figure 13 Schematic volume change on gelling of the solutions containing linear siloxane polymers and cross-linked siloxane polymers.

As mentioned in the previous section, no significant difference was seen in the tensile strength between glass fibres with circular cross-section and non-circular ones. It can be said, therefore, that there should be no problem if the gel-derived fibres are used in reinforcing other materials such as organic plastics and concrete, and as fire-resistant materials.

Acknowledgement

The authors wish to thank Professor Sumio Sakka of Kyoto University for valuable discussions and helpful examination of the manuscript. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. Thanks are also due to T. Kato, H. Asao and T. Nishiyama who assisted in the experiments.

References

1. S. SAKKA, in "Treatise on Materials Science and Technology" Vol. 22, edited by M. Tomozawa and R. Doremus (Academic Press, New York, 1982) pp. 129–67.
2. S. SAKKA and K. KAMIYA, *J. Non-Cryst. Solids* **42** (1980) 403.
3. K. KAMIYA, T. YOKO and S. SAKKA, *Yogyo-Kyokai-Shi* **92** (1984) 242.
4. S. SAKKA and K. KAMIYA, "Materials Science Research" Vol. 17, edited by R.F. Davis, H. Palmour and R. L. Porter (Plenum, New York and London, 1984) pp. 83–94.
5. S. SAKKA, K. KAMIYA and T. KATO, *Yogyo-Kyokai-Shi* **90** (1982) 555.
6. F. O. ANDEREGG, *Industr. Eng. Chem.* **31** (1939) 290.
7. W. C. LACOURSE, "Materials Research Society Symposium Proceedings" Vol. 32, edited by C. J. Brinker, D. E. Clark and D. R. Ulrich (Elsevier Science, North Holland, 1984) pp. 53–8.
8. R. AELION, A. LOEBEL and F. EIRICH, *J. Amer. Chem. Soc.* **72**, (1950) 5705.
9. R. ILER, "The Chemistry of Silica" (John Wiley, New York, 1979) pp. 172–304.

Received 19 March
and accepted 1 April 1985