

Effects of hydrolysis processing on the character of forsterite gel fibers. Part I: preparation, spinnability and molecular structure

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Abstract

A sol-gel process was developed to produce forsterite fibers. Effects of acetic acid, water, and ethanol on the spinnability and the rheological property of the precursor alkoxide solutions were investigated. It was observed that the time of gelation and the length of gel fiber are functions of the respective concentrations of acetic acid, water, and ethanol in a given solution composition. IR study indicated that acetate ligands retained in the dried gel fibers; the concentration of acetate ligands also significantly affected by the content of water and ethanol. It was observed that acetic acid could act as a ligand, a solvent, and an inhibitor for the hydrolysis-condensation reaction. The influences of water, acetic acid, and ethanol on the spinnability and rheology of the spinnable sols, and on the molecular structures of gel fibers have been investigated in the part I of this work. The crystallites and microstructural evolutions of the gel fibers will be reported in part II. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Fibres; Forsterite; Mg₂SiO₄; Rheology; Spinnability; Sol-gel processes

1. Introduction

The sol-gel processing of preparing glass and ceramic fibers has been studied extensively over the past two decades.^{1–3} This method is of interest because it enables glass and ceramic fibers to be prepared at lower processing temperature than via a melt process. Melt drawing of oxide fibers containing magnesia is a difficult and expensive process because of the high melting temperature caused by the addition of magnesia. In addition, the sol-gel process is also able to modify the molecular structures of the sol solution by varying the hydrolytic polycondensation conditions of the precursor alkoxides.⁴ The nature or type of the hydrolyzed molecules is known to depend on the concentration of alkoxides, the catalysts, the amount of water and the reaction temperature etc.^{4–6} Thus, controlling the kinetics of the hydrolysis-condensation reaction of the alkoxides made it possible to modify the polymeric structures that are suitable for preparing the fibers. Many glass and ceramic fibers have been prepared successfully by spinning of the viscous sols followed by heating.^{1–3}

Forsterite (Mg₂SiO₄) is known to be an insulator at high frequencies; its precursor powders and xerogels have been synthesized via the sol-gel method.^{7–9} However, the preparation of forsterite fiber has received little attention. In the present study, a sol-gel process was developed to prepare forsterite gel fibers; the investigation of factors affecting the spinnability and rheology of the spinnable sols, and the molecular structures of the gel fibers, especially the effect of water and ethanol on those properties was conducted. The effect due to acetic acid was also compared by infrared study, which confirmed that acetate anion behaves as a ligand and modifies the hydrolyzed species at a molecular level therefore enhancing the solution spinnability.

2. Experimental procedure

2.1. Preparation of spinnable sols and gel fibers

The alkoxide precursor of stoichiometric forsterite was synthesized from tetraethylorthosilicate, Si(OC₂H₅)₄ (TEOS; 98%, Aldrich), and magnesium methoxide, Mg(OCH₃)₂. TEOS was previously dissolved in anhydrous ethanol (99.8%, RDH) at an ethanol/ TEOS

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molar ratio of 3/1. Magnesium methoxide was synthesized from the reaction of magnesium turnings (100%, RDH) and methyl alcohol (99.9%, RDH).¹⁰ The precursor solution was prepared by dissolving 21.5 wt.% methanol solution of magnesium methoxide in the TEOS solution. The mixed alkoxide solution was stirred and refluxed at 0–5 °C for 1 h, and then a mixture of deionized water and glacial acetic acid (100%, RDH) was added dropwise for hydrolysis. After well stirring and refluxing for 4 h, the alkoxide solution was kept open and concentrated by evaporating the solvent at ambient temperature.

Spinnability of the sol was estimated from the capability of fiber formation by immersing a glass rod of about 1.8 mm in diameter into the sols and then pulling it up by hand. The gel fibers were drawn from the spinnable sols, and were dried at room temperature. In order to approach the effects of solution concentrations on the spinnability of solution and the property of the gel fiber, solution samples with different concentration of water, acetic acid and ethanol were prepared during hydrolysis. The concentration of water, acetic acid and ethanol were expressed in terms of molar ratio to TEOS, in which the molar ratio of water, CH₃COOH, and ethanol were in the range of 0.5–5.0, 0.05–1.2, and 3–20, respectively; for convenient statement, the molar ratio of water, CH₃COOH, and ethanol were also labeled as R, C, and E values, respectively.

2.2. Characterization

Gelation time was measured as the time at which the maximum viscosity of the sol is reached under a constant shear rate.¹ The viscosity of the solutions was measured at 25 °C using a Brookfield viscometer (Model DV-II+) equipped with a thermostat and with a UL adaptor. In order to investigate the difference in flow characteristics between the precursor sols, which were prepared under various solution concentrations, the shear rate was changed at intervals of 1 min and the viscosity value was read just before the change of the shear rate. Viscosity was measured with increasing and then decreasing shear rate, using the method similar to Kozuka and coworkers.¹¹ The molecular structure of the gel fiber was investigated by infrared spectrum with a Bomen-Michelson Fourier transform-infrared spectrometry model MB100. Infrared spectra of dried gel fibers and xerogel were recorded in the 450–4000 cm⁻¹ frequency range with 2 cm⁻¹ precisions using a constant powder sample imbedded in 200 mg KBr pellet; for IR samples, fibrous gels and xerogel were dried at 60 °C in air before grinding into fine powders for the measurements. The microstructures of the gel fibers, after drying at room temperature, were observed by scanning electron microscopy (SEM; JSM-T330 Jeol). Specific surface area was performed on the dried fibers without

crushing by a Brunauer–Emmett–Teller (BET) measurement, using a surface area analyzer (Micromeritics ASAP 2400).

3. Results and discussion

3.1. Spinnability-solution concentration relationships

Table 1 shows the characteristics of forsterite precursor sols prepared by hydrolyzing with various amount of solution concentrations, in which sols F1, F2, and F3 exhibit remarkable spinnability. All of the solutions, except solution G3, were cloudy just after being well-mixed, and gradually transferred into yellowish translucent or transparent, clear state during gelation, depending on the respective concentrations of water, acetic acid, and ethanol used for the hydrolysis. This result also indicated that hydrolysis could be further achieved by exposure of the sols to atmosphere. However, the spinnability of the sols was remarkably dependent on the amount of acetic acid; the spinnability disappeared when no acetic acid was involved in the hydrolyzed solution, irrespective of the amount of water or ethanol. For the solution hydrolyzed with water/TEOS molar ratio (i.e. *R* value) of 0.5, only the sol with acetic acid concentration (i.e. *C* value) above 0.5 molar ratio showed spinnability when employing an *E* value (i.e. ethanol concentration) of 3. That is, the adequate amount of acetic acid was required and critical for spinnability.

In addition to spinnability, the appearances of the sols and the resultant gels were also influenced by the amount of acetic acid. With small acetic acid concentration of *C*=0.05 and with low water content of *R*=0.5, the sol was cloudy without exhibiting spinnability and resulted in a translucent gel, as in the case of sol G1; whereas for sol G2, corresponding to *C*=0.3, although still no spinnability was observed, a transparent aspect was observed during gelation. This result revealed that the use of acetic acid could promote the formation of homogeneous sol. With higher water content of *R*≥5, the influence on the homogeneous state due to acetic acid was still presented, but no spinnability was observed even though a large amount of acetic acid was involved, as in the case of sol G4; whereas for sol G3, corresponding to the addition of much lower amount of acetic acid, a fast gelation due to excess water would lead to an inhomogeneous state and result in an opaque aspect. These results suggested that the use of acetic acid was available to increase the solubility of the precursor sol and to increase the gelation time, as listed in Table 1, therefore, the state of sol was improved; on the other hand, water content could also influence the time of gelation and the spinnability.

The influences of the amount of water and acetic acid on the gelation time are shown in Fig. 1, expressed as

Table 1
The spinnability and gelation time of the precursor solutions

Samples	(H ₂ O) ^a	(Ethanol) ^a	(CH ₃ COOH) ^a	Gelation time	Spinnability	Aspects ^b
F1	0.5	3	1.0	52.0	Good	Fiber, transparent
F2	2	3	1.0	32.0	Good	Fiber, transparent
F3	0.5	20	1.0	85.0	Good	Fiber, transparent
G1	0.5	3	0.5	12.4	No	Xerogel, translucent
G2	0.5	3	0.3	29.8	No	Xerogel, transparent
G3	5	3	0.05	≤0.05	No	Xerogel, opaque
G4	5	3	1.0	1.6	No	Xerogel, transparent

^a Molar ratio to TEOS.

^b After drying at 60 °C in air.

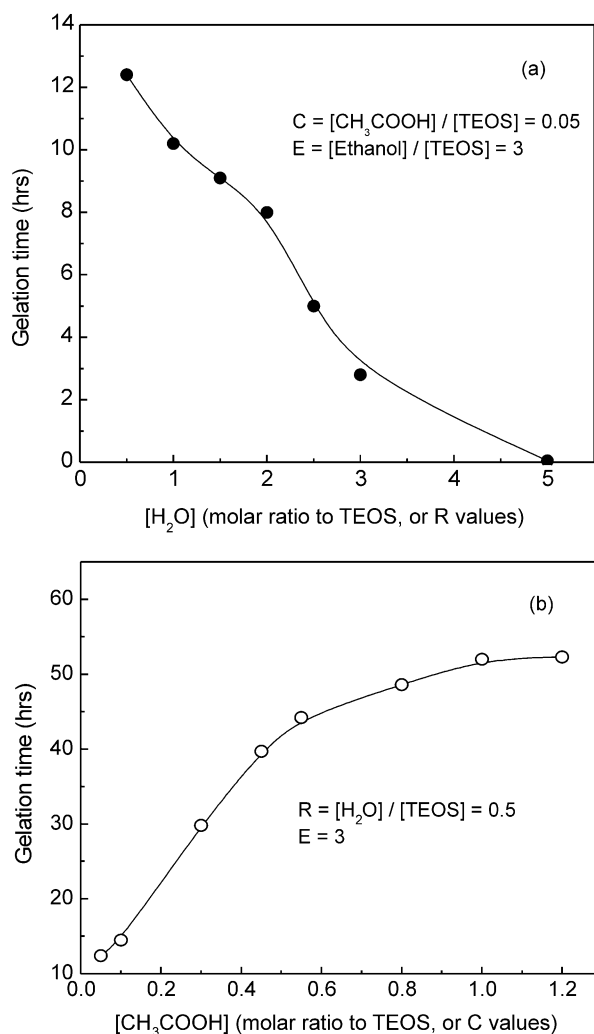


Fig. 1. Gelation time versus (a) water concentration, and (b) acetic acid concentration of the precursor sol solutions prepared with the indicated conditions.

the molar ratio of water and acetic acid to TEOS, respectively. For precursor sol prepared with $C=0.05$ and $E=3$, Fig. 1a shows that the gelation time decreases as the water content increases; a similar trend was also observed even though the sols became more dilute. No

spinnability was observed in those sols, which was probably because the amount of acetic acid was insufficient. Fig. 1b shows that the gelation time was also a function of acetic acid concentration, but presents the opposite effect to water; the gelation time increased with increasing the concentration of acetic acid; moreover, some of the solutions exhibited spinnability as the acetic acid concentration was of $C \geq 0.5$. A similar result was also observed on the effect of ethanol concentration that, as was listed in Table 1, the gelation time increased as the ethanol content increased. Comparing sol F3 with sol F1, with an ethanol content up to 20 molar ratio, the sol was still suitable for spinning when the adequate amount of acetic acid and a small water content are involved. However, it was observed that a higher degree of dilution with ethanol above 30 molar ratio was not suitable for spinning. The higher ethanol content implies the lower concentration of oxide solid in the solution and thus increases the time of gelation. Generally, the gelation process of metal alkoxide solution involves both simultaneous reactions of hydrolysis and condensation.¹² The higher water content in general could promote the hydrolysis and condensation reaction of alkoxide solutions;^{4,5} moreover, a nuclear magnetic resonance (NMR) study has been shown that silica network structure was more highly cross-linked when the molar ratio of water to alkoxide was higher.¹³ Some water along with a sufficient amount of acetic acid were required to promote spinnability, but too much water diluted the sol and caused a branched network rather than a linear structure. It was observed that sol G4 resulted in bulk gels without exhibiting spinnability. This result might be attributed to the fact that the higher water content markedly enhanced viscosity and thus promoted the formation of a three-dimensional network, which led to a cross-linked colloidal polymer.^{1–4,14}

The use of acetic acid in the preparation not only enhanced the spinnability but also increased the solubility of the precursor solution and resulted in a transparent sol during gelation. Moreover, the gelation time increased with increasing the amount of acetic acid,

thereby the stability of the sols was improved; the sols became spinnable with the addition of the appropriate amount of acetic acid. Acetic acid apparently played an important role in the spinnability of the sols. The chain-like or linear-type polymers were well known to be required for drawing fibers, while the formation of three-dimensional network structures would be favorable for the bulk or monolithic gel.^{1,2,14} It is then reasonable to consider that the presence of a high amount of acetic acid in the precursor sols could promote the formation of linear polymeric structures and inhibit the formation of three-dimensional network polymers during gelation. An appropriate amount of acetic acid was deemed to be a necessary condition for obtaining spinnable sols. However, both water and ethanol content could also influence the time of gelation and spinnability, as listed in Table 1. For the spinnable sols F1, F2, and F3, the gelation time decreased with increasing water content but increased with increasing ethanol content. The time of gelation and the spinnability were apparently dependent strongly on the respective concentrations of water, acetic acid, and ethanol, but acetic acid does predominate the spinnability. Of course, in a given experiment these three parameters were not independent. For the sol solutions with acetic acid concentration or C value rang 0.5–1.2, spinnability was observed in the composition region of $R=0.5$ –2.5 and $E=3$ –20 of water and ethanol, respectively.

For spinnable sols, the content of water and ethanol also significantly affected the length of drawn fiber. The present study thus aimed at the investigation of factors affecting the property of the spinnable sols, e.g. rheological behavior and fiber length, and the molecular structures of the gel fibers, especially the effect of water and ethanol on those properties. The effect due to acetic acid was also compared and confirmed by IR study; however, those properties of the xerogels will be reported systematically and in detail elsewhere.

3.2. Rheological behaviors of the spinnable sols

The time-dependent and shear rate-dependent viscosities of several sol-gel systems have been used to improve the spinnability or to study the structural evolution of a gel.^{5,11,15–17} It is well established that the viscosity-time and viscosity-shear rate dependences were directly related to the solution structure of a sol. Fig. 2 shows the viscosity dependence as a function of aging time for spinnable sols, F1, F2 and F3. A similar behavior for all three samples can be seen; the viscosity of all the sols remained almost constant in the initial stage of the hydrolysis-condensation reaction and increased gradually in the latter stage, finally the viscosity increased so rapidly that in a very short time gelation occurred. The time-dependent viscosity showed typical behavior for alkoxide-derived sols.^{1,5} All of the

sols were kept open to ambient atmosphere during the aging process in the present study, thus the increase in viscosity could be attributed to the evaporation and hydrolysis-condensation reaction of the sols.^{1,2} These three sols became remarkably spinnable when the viscosities reached about ten poise to several hundred poise; this result was consistent with the previously studied in the preparation of gel-derived fibers.^{1–3,11} However, fiber drawing became difficult as the viscosity rose above 10^3 poise and subsequently gelled into elastic bulk monoliths with a remarkably increase in viscosity.

For sol F1, the viscosity exceeded 10 poise after an aging time of about 49.3 h and it became spinnable, while the time required for the sols to reach the spinnable state was reduced to about 29.8 h and increased to about 82.6 h for sol F2 and sol F3 respectively. In addition to gelation time, the time required for the sol to reach the spinnable state was also dependent on the respective solution concentrations. The time period that the sol remained spinnable was longer in sol F1 than those in sols F2 and F3. This result indicated that the variation of viscosity could be controlled by the content of water and ethanol when a constant amount of acetic acid was used. It was also observed that these spinnable sols could be stable without a significant change in viscosity and the spinnable state could persist for a longer time when stored in a sealed container at room temperature.

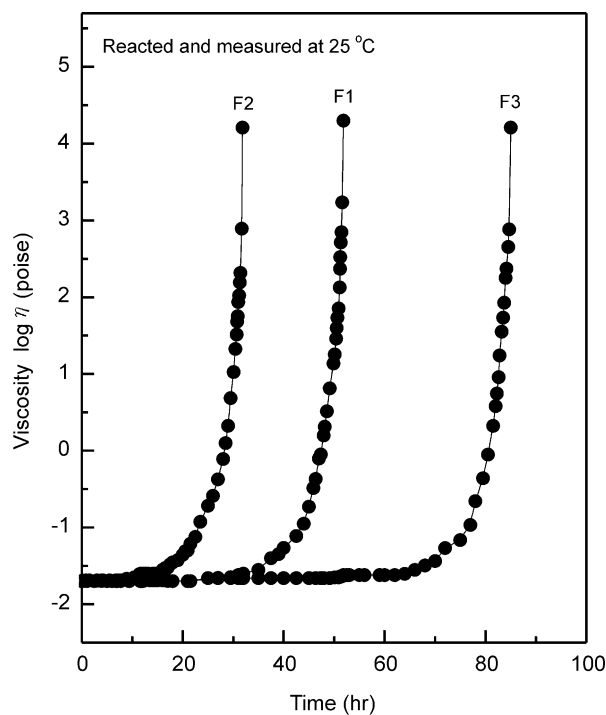


Fig. 2. Plots of viscosity versus aging time for the three different forsterite precursor sols F1, F2, and F3, samples are identical to those in Table 1.

Figs. 3–5 show the comparisons of the change of viscosity with shear rate based on various aging time for these three spinnable sols F1, F2 and F3, respectively. The viscosity of sol F1 was independent of the shear

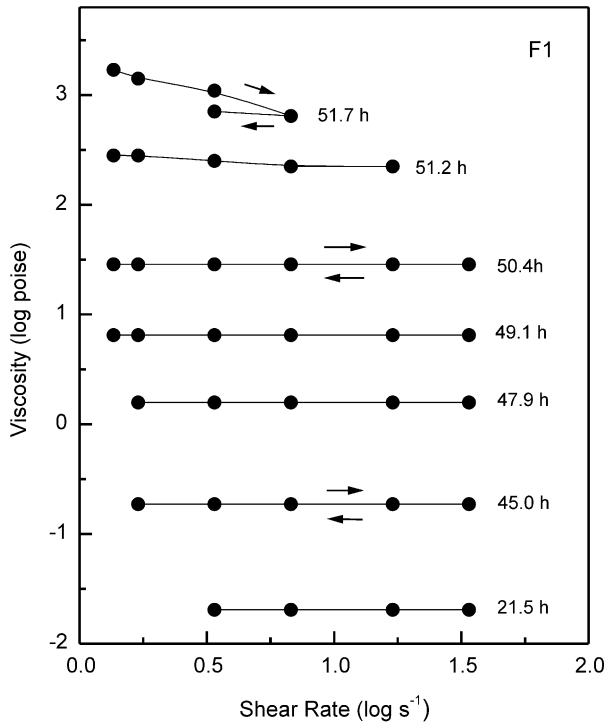


Fig. 3. Dependence of viscosity on shear rate of sol F1 obtained from various reaction times at 25 °C.

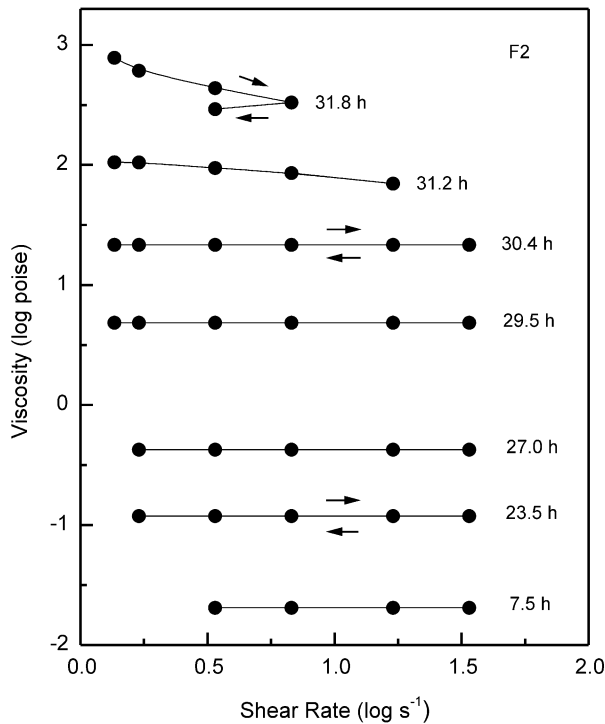


Fig. 4. Dependence of viscosity on shear rate of sol F2 obtained from various reaction times at 25 °C.

rate (i.e. Newtonian flow behavior) to a high viscosity range and then slightly decreased with the shear rate after 51.2 h of aging (i.e. slightly shear-thinning behavior), as shown in Fig. 3. With further aging ($t = 51.7$ h), a thixotropic flow characteristic could be observed and followed the occurrence of gelation. A similar trend was also observed in sols F2 and F3, but they remained Newtonian or near Newtonian flow behaviors to lower viscosities in contrast to sol F1, as shown in Figs. 4 and 5. As noted previously, the viscosity suitable for spinning was between the orders of 10–100 poise for the three sols and, thus, rheological measurements suggested that the sols exhibited spinning when they were viscous and Newtonian or near Newtonian until near the time of gelation. The sols became unspinnable when thixotropic flow behaviors were observed. The Newtonian or near Newtonian flow behavior of sols which could be drawn to fibers has also been measured in the cases of silica sols^{1–3,11} and zirconium acetate-alkoxide solution.¹⁷ Sacks and Sheu found that the best spinnability was when silica sols showed highly shear thinning behavior without exhibiting thixotropy.¹⁶ Although the shear rate was not high enough in the present study, some qualitative and quantitative measurements of the rheological property could still be obtained. The rheological measurements indicated that the viscous sols were essentially Newtonian or near Newtonian flow in the spinnable viscosity ranges, as the sols aged in open containers.

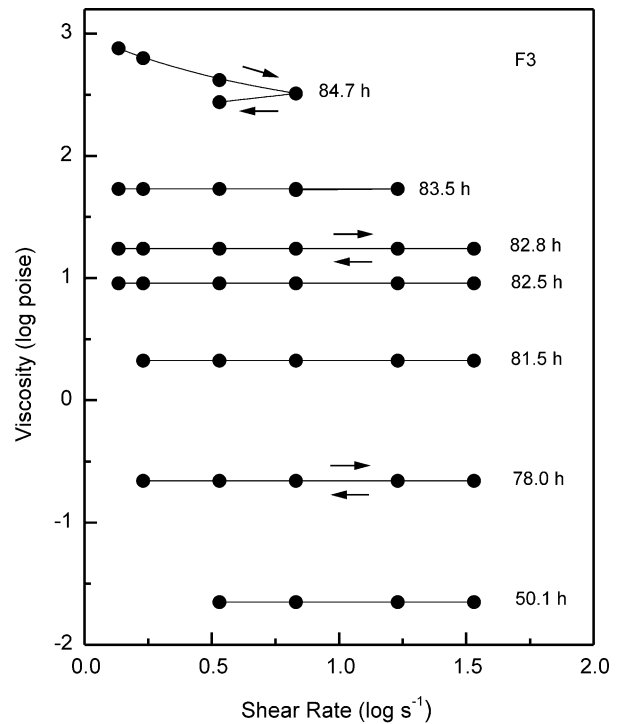


Fig. 5. Dependence of viscosity on shear rate of sol F3 obtained from various reaction times at 25 °C.

The inclusion of chain-like or linear-type polymers was known to be required for the solution to exhibit spinnability.^{1,2,14} The viscous sols showed spinnability in the present study suggesting that some kinds of linearly polymeric species should be formed in the spinnable sols. Moreover, the polymeric species in those spinnable sols could be considered to grow linearly until near the gelation time.^{1,3} This was reflected on the observation of Newtonian flow at a high viscosity range of the sols. However, spinnability at a higher viscosity range observed in sol F1, indicated that, despite a higher concentration in this sol, a higher degree of linearly polymeric structures remained and a less networked structure developed in contrast to the two other sols. This interpretation was consistent with the observation that much longer gel fibers could be drawn from sol F1. Gel fibers with the diameter of 20–200 μm could be drawn from the three viscous sols. The diameter of gel fibers was also influenced by the respective solution concentrations, but influenced mainly by the speed of withdrawal of the glass rod from the viscous sols. However, the length of gel fibers was highly dependent on the respective solution concentrations.

Fig. 6 shows the length of gel fibers are functions of the amount of acetic acid, water and ethanol, respectively, as compared to their optimum viscosities. The length of gel fibers increased with increasing the amount of acetic acid, and decreased as the content of water and ethanol increased for a given solution composition. As already mentioned, in a given experiment these three parameters were not independent, but acetic acid does predominate the spinnability. As can be seen in Fig. 6a, gel fiber is difficult to draw from the sols when the concentration of acetic acid was lower than 0.5 molar ratio to TEOS. A sufficient amount of acetic acid, therefore, was critical for the spinnability. It is considered that the fiber length could also provide another evaluation of the ability to draw the fiber (i.e. spinnability) from the sol, and the molecular structure of the sol. Namely, the longer length of gel fiber implies the higher degree of spinnability of the sol; furthermore, the higher degree of the spinnability of the precursor sol in this study might be reflected on the formation of polymeric species with more chain-like or linear-type structures and /or with less branched or cross-linked structures in the spinnable sols. Accordingly, the length of gel fibers increased with increasing the amount of acetic acid in a given solution composition, suggesting that the addition of sufficient amount of acetic acid seemed to favor the formation of linear-type structures and inhibit the formation of network structures in the sols because the spinnability improved markedly. In contrast, a higher water content was favorable to form more branched polymers and /or lower degree of linear-type structures, consequently a much shorter gel fiber was drawn. It thus might be considered that, when a sufficient amount of acetic acid

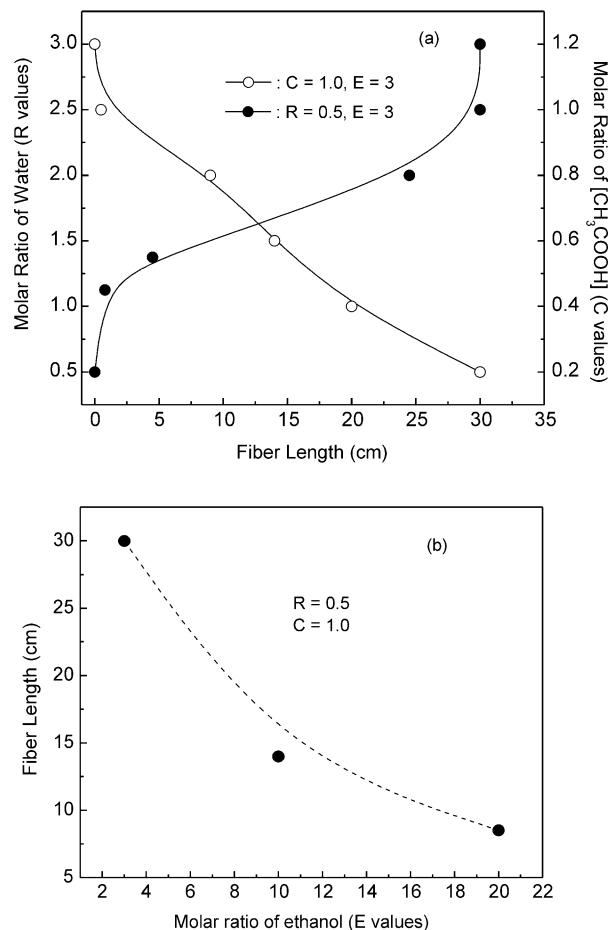


Fig. 6. Effects of the respective concentrations of (a) water and acetic acid, and of (b) ethanol on the length of the drawn gel fibers, precursor sols are prepared with the indicated conditions.

was added, sols with a lower content of water and ethanol were favorable to form less branched polymers and thus the gel fibers had longer length.

In addition, increasing the amount of acetic acid suppressed the hydrolysis and condensation reactions of the precursor alkoxide solutions. The inhibition effect of acetic acid in the hydrolysis-condensation reaction was reflected on the longer gelation time, as shown in Table 1 and Fig. 1b. Conversely, increasing water content enhanced the hydrolysis-condensation reaction, which was reflected in the decrease in the gelation time, and might promote the formation of more branched or cross-linked structures, consequently increasing the difficulty in drawing the fibers; as was listed in Table 1, the addition of a relatively large amount of water resulted in a bulk gel. Thus, presumably the shortening of the drawn fibers upon increasing the water content could be attributed to the formation of a greater extent of branched or cross-linked structures. On the other hand, the shortening effect on the fiber length due to ethanol content might be explained in terms of fewer linear-type

structures and lower oxide solid content in the sols, in light of the dilution effect.

The optimum spinnability was found in the solution with acetic acid in the molar ratio of 1.0 to TEOS and with the minimum amount of water and ethanol required to give a homogeneous sol, as in the case of sol F1. Higher acid ratios were not explored in the subsequent study, because the enhancement of spinnability was no longer prominent; instead, the length of fiber became shorter as the large excess acetic acid was added; moreover, the amount of organic residues increased, which would complicate the subsequent burnout.

3.3. IR spectrum

The infrared spectra of the three dried gel fibers derived from spinnable sols F1, F2 and F3, and a xerogel G1 are illustrated in Fig. 7, samples are derived from the different precursor sols that were identical to those in Table 1. The spectra clearly displayed that acetate ligands were retained in the three dried gel fibers, whereas the xerogel lacked the characteristic peaks of acetate ligands. For specimen F1 as shown in Fig. 7a, according to the literature,^{18–20} the frequency separation with $\Delta\nu=153\text{ cm}^{-1}$, between the stretching asymmetric $\nu_{\text{asym}}(\text{COO})$ vibration at 1595 cm^{-1} and the stretching symmetric $\nu_{\text{sym}}(\text{COO})$ vibration at 1442 cm^{-1} , suggests that acetate anions acted as bidentate ligands^{18–20} or bridging bidentate ligands

because the frequency separation of bridging acetate usually lay between 120 and 160 cm^{-1} ,^{18,20} and a smaller doublet with $\Delta\nu=94\text{ cm}^{-1}$, between the $\nu_{\text{asym}}(\text{COO})$ at 1536 cm^{-1} and the $\nu_{\text{sym}}(\text{COO})$ at 1442 cm^{-1} , corresponding to the chelating bidentate ligands^{19–20} because the frequency separation of chelating acetate was usually smaller than that of bridging acetate.

In contrast, a decrease in the intensity of the bands around 1500 cm^{-1} can be seen in the fibers that derived from the sols with higher water content and/or more dilute, as shown in Fig. 7b and c. For specimen F2, Fig. 7b displays the frequency separation ($\Delta\nu=138\text{ cm}^{-1}$) between the $\nu_{\text{asym}}(\text{COO})$ at 1576 cm^{-1} and the $\nu_{\text{sym}}(\text{COO})$ at 1438 cm^{-1} that is also consistent with bidentate acetate ligands,^{18–20} but its larger value suggests bridging acetates rather than chelating acetates.^{19,20} The spectra of specimen F3 shown in Fig. 7c also displayed a similar feature to that of specimen F1; the frequency separation ($\Delta\nu=155\text{ cm}^{-1}$) between the $\nu_{\text{asym}}(\text{COO})$ at 1595 cm^{-1} and the $\nu_{\text{sym}}(\text{COO})$ at 1440 cm^{-1} was consistent with bridging acetates; a shoulder around 1540 cm^{-1} due to $\nu_{\text{asym}}(\text{COO})$ also suggested the presence of bidentate acetate ligands or chelating acetate groups in light of a smaller frequency separation of $\Delta\nu=100\text{ cm}^{-1}$.¹⁸ These values of $\Delta\nu$ were consistent with those previously studied on the bidentate acetate ligands.^{18–20}

For both dried gel fiber specimens F1 and F3, peaks at around 1690 – 1688 cm^{-1} and 1348 cm^{-1} corresponded to free acetic acid or probably due to the unidentate acetate.^{19,20} According to the literature,¹⁹ the spectra of unidentate acetate group showed a large increase in the $\nu_{\text{asym}}(\text{COO})$, and a similar decreased in the $\nu_{\text{sym}}(\text{COO})$, these frequencies corresponding approximately to $\nu(\text{C=O})$ and $\nu(\text{C-O})$. For specimen F2, the peak at around 1348 cm^{-1} was also assigned to the symmetric stretching vibration of COO mode as a result of free acetic acid.^{18,19} The peak at 1637 cm^{-1} of specimens F1 and F3 was assigned to adsorption of water,²¹ which was also observed in the xerogel G1 as shown in Fig. 7d at around 1650 cm^{-1} . In contrast, xerogel specimen G1 displayed a weaker intensity of the $\nu_{\text{asym}}(\text{COO})$ at around 1588 and 1535 cm^{-1} , but lacked the characteristic peaks of acetate ligands. This might be due to an insufficient amount of acetic acid. Those peaks at 1483 and 1427 cm^{-1} as shown in Fig. 7d were assignable to C–H vibration in alkyl groups,^{21,22} implying that OR groups remained in the structures in light of an incomplete hydrolysis.

A survey of the literature showed that the position of the characteristic bands of bonded acetate groups also depended on the nature of the metal atom. Many correlations between infrared spectra and structural data of metallic acetates could be found in the literature,^{18–20} but the structures of Mg, Si-acetate complexes prepared in this work have not yet been reported. However, in this paper the characteristic peaks of the frequency

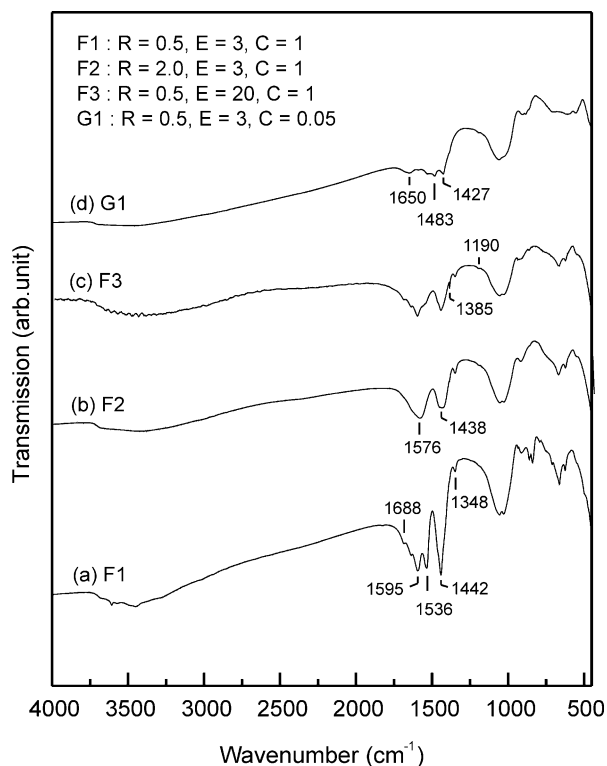


Fig. 7. Infrared spectra of the dried gel fibers (a): F1, (b): F2, (c): F3, and (d) xerogel G1, samples obtained from different precursor solutions as listed in Table 1; the preparation conditions are indicated.

separation or the doublets were consistent with the previously studied acetate ligands.^{18–20} Accordingly, the spectra of gel fiber samples obviously suggested that the three gel fibers contained bidentate acetates. Although it was difficult to distinguish between the two independent metal ions (Mg and Si), and which ones would be bonded to bridging or chelating acetates, the characteristic peaks did show that acetates bonded to the metal ions. In contrast to xerogel sample G1, the intensity of the doublets in the three gel fiber samples clearly increased with the large amount of acetic acid, as illustrated in Fig. 7. This result inferred that OR groups were replaced by acetate ligands and thus the molecular structures of their sols were modified, giving therefore a large opportunity for the formation of spinnable or linear-type polymer structures. Moreover, the modified structures could be retained even after being dried. However, the gel fiber samples displayed the disappearance of the peaks at 1483 and 1427 cm^{-1} due to residual OR groups, as shown in Fig. 7. This also suggested that OR groups were replaced by acetate ligands to some extent, increasing evidence supporting the role of acetate anions in the ligands effect.

Sakka and Kamiya have shown that silica gel fibers could be drawn from acid-catalyzed TEOS solution when the amount of added water is small.¹ However, in this study no spinnability was observed even though little water was involved, once the amount of acetic acid was insufficient. Moreover, the use of acetic acid in the hydrolysis-condensation reaction of the present study apparently involved a mechanism substantially different from the conventional acid-catalyzed hydrolytic condensation of metal alkoxides.^{6,18} Acetic acid affected not only the rate of gelation, but also the molecular structures of polymeric species in the hydrolyzed solution. Increasing the amount of acetic acid in the sol preparation corresponded to an increase in the intensity or concentration of acetate ligands in the polymeric species backbone. The spinnability of the sol was increased with increasing the amount of acetic acid up to the optimum concentration of acetic acid in a given solution composition. It then could be considered that the spinnability was related to the concentration of acetate ligands. That is, the relative precursor sol comprising reasonable acetate ligands could show excellent spinnability. Xerogel G1 showed the lack of acetate ligands thus its precursor solution became an elastic gel without showing any spinnability during gelation. This meant that a sufficient degree or concentration of acetate ligands was required in order to enhance the formation of linear-type molecular structures rather than three-dimensional networks in the viscous sols.

Namely, it was inferred that the concentration of linear-type structures in the sols was related to the concentration of acetate ligands. The higher concentration of acetate ligands in the polymeric species implied a

higher degree of the spinnable structures in the sol. This suggested that the higher degree of the replacement of alkoxy groups by acetate anions would enhance the polymeric species with a greater extent of linear-type structures. Moreover, the polymeric species in the three spinnable sols could be deemed to grow linearly up to high viscosity range. This was consistent with the observation of Newtonian flow behaviors at a high viscosity range of the three spinnable sols. In addition, it might be expected that a higher degree of linearly polymeric structures remained and a less networked structure developed in sol F1 than in the two other sols F2 and F3, because a lower intensity of acetate ligands were observed in the latter two. This was consistent with the observation of sol F1 exhibiting spinnability at a higher viscosity range and that longer gel fibers could be drawn from this sol. However, the replacement of alkoxy groups by acetate anion was limited, because excess acetic acid gave rise to more residual organics.

The replacement of alkoxy groups by acetate anions occurred during the hydrolysis-condensation process, which would lead to the formation of soluble molecular species and bidentate acetate ligands. This was consistent with the observation that the use of acetic acid could increase the solubility of the polymeric species in the hydrolyzed solution and give rise to a homogeneous sol without the occurrence fast gelation. The bidentate acetate ligand groups slowed down both hydrolysis and condensation reactions increasing therefore the time of gelation, as shown in Table 1 and Fig. 1b. In addition to the ligand effect, acetic acid could also act as a solvent and an inhibitor for the hydrolysis-condensation reaction. However, the replacement effect was also strongly dependent on the content of water and ethanol.

For sol F1, the optimum amount of acetic acid does enhance the spinnability, but further addition of water such as in the case of sol F2, would hydrolyze the acetate ligand groups in the chain, leading to a reduction in the type and the concentration of acetate ligands, as was shown in Fig. 7b. The reduction in both intensity and type of the characteristic peaks of acetate ligands could be considered mainly due to the breaking of the acetate ligands because a higher water content was involved; higher water content was mainly to promote the hydrolysis-condensation process, thus could also promote the hydrolysis of the acetate ligand groups therefore reduced the type and the degree of acetate ligands. Presumably, this result would lead to the polymeric species with a greater extent of branched or crossed-linked structures, thus shortening the length of drawn fiber and the time of gelation, as illustrated in Table 1 and Figs. 1a and 6a. On the other hand, the higher ethanol content could increase the gelation time and decrease the intensity of acetate ligands, as was illustrated in Table 1 and Fig. 7c.

The lower intensity in the characteristic peaks of acetate ligands demonstrated from a comparison of Fig. 7a with 7c could be considered as a result of the excessive amount of ethanol. When a large amount of ethanol diluted the precursor solution, the relative concentration of metal alkoxide became lower; which in turn reduced the replacement of alkoxy groups by acetate anions, and consequently a lower degree or extent of acetate ligands was observed. Some peaks related to the remaining OR groups could be observed in Fig. 7c; a shoulder at 1190 cm^{-1} was attributable to the residual alkoxy groups²³ and an acute band at 1385 cm^{-1} was assigned to the C–H deformation vibration of the alkyl groups.^{21–23} This result also indicated that OR groups were replaced by acetate ligands less in the case of dilution. Higher ethanol content thus led to a polymeric species with a lower degree or extent of acetate ligands. It might be conjectured that higher ethanol content would lead to a polymeric species with a lower degree of linear-type structures or a greater extent of branched structures, thus decreasing the length of drawn fiber, as shown in Fig. 6b.

Infrared spectra clearly revealed that the acetate anion behaved as a ligand and changed the polymeric species at a molecular level. Such a ligand effect has also been performed by Livage, Doeuff and co-workers^{18,24} in order to avoid precipitation and to prepare TiO_2 monolithic gel. In their experiments, acetic acid was used to stabilize titanium alkoxide before hydrolysis, showing that acetate groups acted as bidentate ligands and were retained through hydrolysis and condensation. The ligand effect was also observed by many studies on the chemical modification of alkoxides with organic agents before hydrolysis.^{17,18,24–26} The organic agents, e.g. acetylacetone, acetic acid etc., were ordinarily reacted with alkoxide to form a new molecular precursor which could modify the hydrolysis-condensation reaction. The formation of acetate ligands in the polymer was also observed by Yoko and coworkers²⁵ on the preparation of BaTiO_3 fibers; in their experiments, acetic acid was used to modify the alkoxides before hydrolysis. Similar results were observed in this work, suggesting that the formation of bidentate acetate ligands could occur whether acetic acid was added before or after the hydrolysis of alkoxide solution. Moreover, a spinnable solution for drawing fiber can be obtained by adjusting the concentration of acetic acid, water and ethanol.

In addition, characteristic bands shown in Fig. 7 related to the Si-O^- anionic network structures were observed around $1055\text{--}490\text{ cm}^{-1}$; in which bands around $1055\text{--}1020\text{ cm}^{-1}$ were attributed to asymmetric Si–O–Si stretching modes;^{21,27} bands around 910 cm^{-1} were assigned to the stretching vibrations of nonbridging Si–OH;²¹ the band at 860 cm^{-1} was also assigned to stretching vibrations of Si–OH bonds;²⁸ bands in the

range of $840\text{--}650\text{ cm}^{-1}$ corresponded to Si–O–Si symmetric stretching vibrations,^{21,27} in which the band at 790 cm^{-1} was also associated to vibration modes of ring structure of SiO_4 tetrahedra;^{21,29} the band around 496 cm^{-1} was assigned to a Si–O–Si bending mode.²⁷ For all the samples, the frequencies of the bands around 1055 and 1025 cm^{-1} , attributed to LO and TO modes of Si–O–Si asymmetric stretching vibrations, respectively,²⁷ were lower than those of alkoxide-derived pure silica gel. The asymmetric stretching vibration of Si–O–Si bond shifted to lower frequencies, which was indicative of the occurrence of different structural units in these fibrous gels and xerogels. It is possible that the magnesium ion has been incorporated into the tetrahedral silicate framework for the three gel fibers and the xerogel samples. If this were the case, then it is plausible to consider that metaloxane structures of Si–O–Mg linkages could occur in the dried gel fibers and the xerogel. The band around 550 cm^{-1} has been assigned to vibration involving the MgO_4 tetrahedral in the silicate networks;²⁷ this result also suggested that Si–O–Mg linkages might occur in these samples. The shift to lower frequencies of the position of the ν_{asym} Si–O with increasing counter-cation substitution for silicon has been observed in the cases of high-quartz structures and magnesium silicates.^{27,30} Peaks around 660 and 625 cm^{-1} were associated with the deformation vibrations of OCO and the out-of-plane bending vibration modes of CH or COO ,²⁵ respectively. The broad absorption bands around $3000\text{--}3700\text{ cm}^{-1}$ as shown in Fig. 7, were attributed to the superposition of stretching vibration of adsorbed water and hydrogen bonded to different hydroxyl groups. The bands around 3450 and $1637\text{--}1650\text{ cm}^{-1}$ were assigned to absorption due to water,^{21,22,30} which might also come from the hygroscopic KBr. The bands centered on $3550\text{--}3680\text{ cm}^{-1}$ were ascribed to stretching vibration of SiO–H^{21,22} and/or Mg–OH.³¹ It then might be conjectured that the polymeric species in the dried gel fibers were composed of a mixture of metaloxane polymer, metal hydroxides, and metal acetate complex or metal cations which were bonded by acetate anions. For these samples, the absorption bands due to water, hydroxyl groups, Si–O[−] bonds, and acetate ligands showed a progressive decrease in the intensity upon heating.

Fig. 8 shows scanning electron micrographs of the processed gel fibers. As shown, all of the gel fibers had smooth and dense appearances without large pores formation after drying at room temperature; the dried gel fiber F3 exhibited a lower uniformity of the surface in contrast to gel fibers F1 and F2. All of the as-drawn gel fibers were flexible and tough but became somewhat brittle and fragile after aging at ambient temperature, indicating that a further polycondensation might occur. The cross-sections of these dried gel fibers were circular, ellipsoidal or dumbbell in shape with diameters ranging from 20 to $200\text{ }\mu\text{m}$. In addition to the length and surface

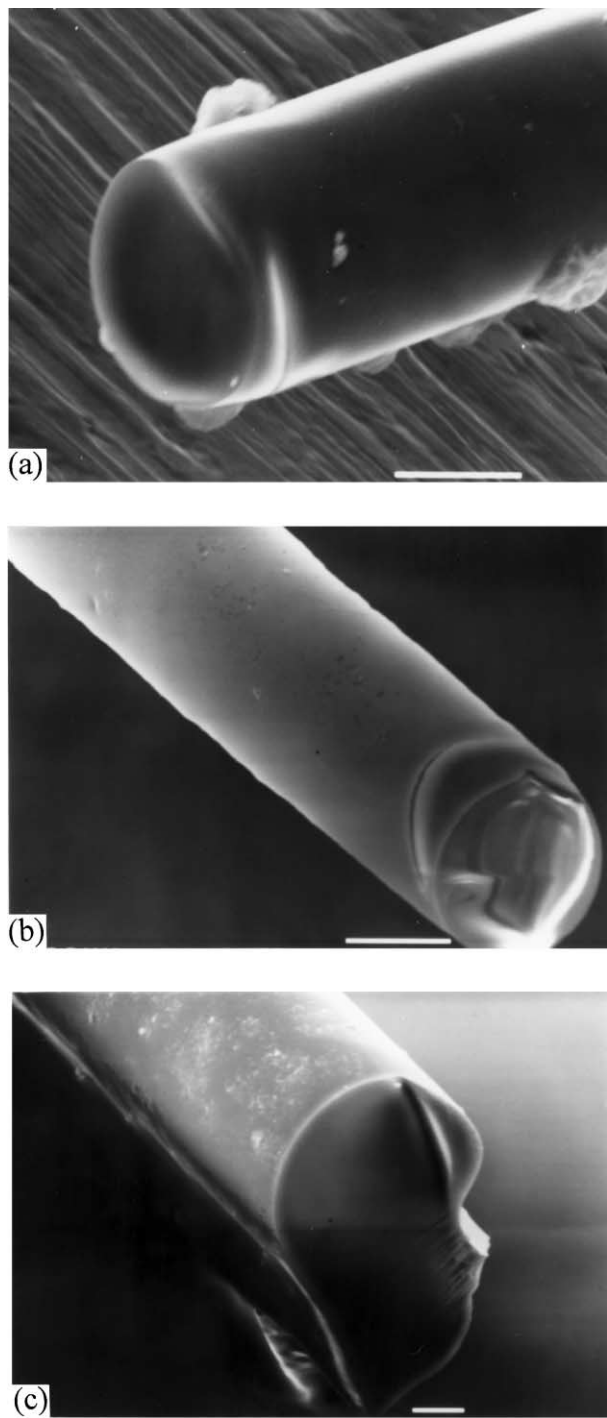


Fig. 8. Scanning electron micrographs of processed gel fibers dried at room temperature (a) F1, (b) F2, and (c) F3. Bars = 10 μm .

uniformity, the morphologies of the three gel fibers did not appear to be very different. These fibers drawn from the spinnable sols led a rapid increase in the surface area/volume ratios, resulting in rapid evaporation of remaining volatiles, and immediate gelation thus the fibers were coherent.^{1,2} However, gel fiber prepared from the excess ethanol condition showed a lower uniformity of the surface. The specific surface areas of

dried fibers F1, F2, and F3 were about 85, 72, and 128 m^2/g , respectively.

4. Conclusions

This study has shown that a sol-gel process can provide a simple and feasible route for the preparation of forsterite gel fibers. Optimizing a few main preparation parameters, e.g. the amount of acetic acid, water, and ethanol, gel fibers could be drawn from the viscous sols. These parameters significantly affected the gelation time and spinnability of the precursor sols, with acetic acid predominating the spinnability. The content of water and ethanol also strongly affected the molecular structures of the gel fibers. IR study confirmed that acetic acid could act as a ligand and modify the molecular structure of the polymeric species. It was considered that the acetate ligands promoted the formation of linear-type polymers and thus played an important role on inhibiting the hydrolysis-condensation reaction and enhancing the spinnability. The rheological measurements indicated that the viscous sols were essentially Newtonian or near Newtonian flow in the spinnable viscosity ranges.

The replacement of alkoxy groups by acetate anions and the length of gel fibers were also strongly dependent on the amount of water and ethanol in the spinnable sols. The length of gel fibers increased with increasing the amount of acetic acid, and decreased as the content of water and ethanol increased for a given solution composition. Presumably, higher water content could reduce the type and the degree of acetate ligands, which probably gave rise to the polymeric species with a more extent of branched or crossed-linked structures, thus shortening the length of drawn fiber and the time of gelation. Excessive ethanol could also reduce the degree of acetate ligands, which probably led to the polymeric species with a lower degree of linear-type structures or a greater extent of branched structures, thus decreasing the length of drawn fiber; moreover, its dried gel fiber exhibited a lower uniformity of the surface as compared with the low ethanol condition.

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