

研究速報・Short Communication

Viscosity Change and Spinnability of $\text{Si}(\text{OC}_2\text{H}_5)_4$ - H_2O - $\text{C}_2\text{H}_5\text{OH}$ Solutions on Hydrolysis

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加水分解による $\text{Si}(\text{OC}_2\text{H}_5)_4$ - H_2O - $\text{C}_2\text{H}_5\text{OH}$ 溶液の粘度変化と曳糸性

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It has been reported¹⁾ that the alcoholic solutions of silicon tetraethoxide $\text{Si}(\text{OC}_2\text{H}_5)_4$ added with water increase in viscosity through hydrolysis and polymerization, showing the remarkable spinnability just before gelling when the molar ratio of the added water to the alkoxide (m) is less than 2 and the reaction is catalyzed by HCl. At 30°C, it takes 3 to 6 days for the solutions with $m=1.0$ and 2.0 to become viscous enough for drawing fibers and the spinnable state lasts only for a few hours at most. This makes it difficult to apply the fiber-drawing from the alkoxide solutions for practical purpose. In the present work, it is shown that the spinnable viscous state of the $\text{Si}(\text{OC}_2\text{H}_5)_4$ - H_2O - $\text{C}_2\text{H}_5\text{OH}$ solution is attained within several hours and held for longer than 10 hours by adjusting the water content of the solution and conducting the hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ at 80°C.

125 g of $\text{Si}(\text{OC}_2\text{H}_5)_4$ (supplied by Nakarai Chem. Co.) was diluted with 18.2 ml of 95 vol% ethanol, followed by the addition of 18.2 ml of the ethanol containing given amounts of water and HCl under stirring at room temperature. The water and HCl were added slowly, taking one and a half hour or more, so that no precipitation occurred. The molar ratio of HCl to the alkoxide was kept at 0.01

and that of water (m) was 2.0, 1.7 and 1.0 for solutions No. 1, No. 2 and No. 3, respectively. The resultant clear $\text{Si}(\text{OC}_2\text{H}_5)_4$ - H_2O - $\text{C}_2\text{H}_5\text{OH}$ solutions were kept open to air under stirring at 80°C for hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$.

The changes of the viscosity of three solutions with time measured at 25°C are shown in Fig. 1. A part of the solution (5~10 ml) was transferred to a small container and rapidly cooled to 25°C from 80°C by immersing the container in ice water to measure the viscosity.

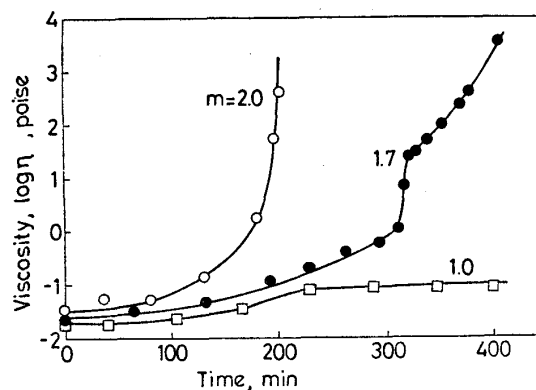


Fig. 1. The viscosity change of $\text{Si}(\text{OC}_2\text{H}_5)_4$ - H_2O - $\text{C}_2\text{H}_5\text{OH}$ solutions at 80°C.

- : Solution No. 1 with the mole ratio of water $m=2.0$,
● : No. 2 with $m=1.7$,
□ : No. 3 with $m=1.0$.

The cooling rate was so large that the viscosity of the solution little changed during the above process. An Ostwald type viscometer was used for viscosities lower than several centipoise, and a balanced sphere viscometer for higher viscosities.

Differences in viscosity change among the three solutions are noted in Fig. 1. Solution No. 1 with $m=2.0$ increases in viscosity rapidly. It gels in about 3 h, much faster than at 25°C and 30°C where the gelation occurred in 350 h and 165 h, respectively. The fibers could be drawn from the solution cooled to 25°C after the viscosity reached several poise. The fiber drawing could be continued for a few hours until the viscosity reached about hundred poise. Solution No. 3 with $m=1.0$ increases in viscosity very slowly and levels off at about 10 cp. Viscous state and gelling were not observed even if the solution was kept standing at 80°C for a longer time.

The water in the alkoxide solution is consumed for the hydrolysis reaction to give polymerized products, and as a result the viscosity of the solution increases. Some of the water as well as alcohol evaporate during the hydrolysis, while the alkoxide and the polymerized products are scarcely lost at 25°C²⁾. It is possible that the evaporation of water from solution No. 3 is faster than the consumption for the hydrolysis, and the polymerization of the alkoxide is stopped, the viscosity levelling

off at about 10 cp. The two different viscosity changes seen in solutions No. 1 and 3 imply that the solution with a m value between 1.0 and 2.0 may show the viscosity change suitable for fiber drawing for a long time. This may be solution No. 2 with $m=1.7$.

As shown in Fig. 1, the viscosity of solution No. 2 increases up to about several tens of poise like solution No. 1, then its change becomes smaller above this value possibly because of loss of water by evaporation. The smaller increase in viscosity occurring above the turning point might be due to the slower progress of hydrolysis and polymerization caused by the water absorbed from ambient atmosphere. The solution remained spinnable for about 2 hours even at 80°C and 10 or more hours at 25°C.

A steplike change of the viscosity was observed in solution No. 1 kept at 45°C but not in solutions No. 2 and No. 3. However, such a steplike change was not seen at 30°C and 25°C in all the three solutions investigated.

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References

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訂 正

窯業協会誌 90 [8] 481-84 (1982) 掲載の, “1 000°Cにおける北朝鮮産カオリンのムライト化反応に及ぼす数種の鉱化剤の効果” の著者は, 小山田 了三・角 和博です。お詫びして訂正致します。