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Fiber Drawing from Silicon Alkoxide Solutions in the Sol-Gel Process

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The occurrence of the spinnability in the sols prepared by the hydrolysis and polycondensation of tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane and tetranormalbutoxysilane has been investigated. It has been found that the spinnability appears at high viscosities in all of these solutions when the $H_2O/Si(OR)_4$ mole ratio of the starting solution is 2 and an acid is used in the hydrolysis reaction. It has also been shown that the spinnable solutions show the Newtonian behavior at high viscosities.

Fiber drawing from silicon alkoxide solutions in the sol-gel process is an attractive technique for making silica gel and glass fibers, since the fiber drawing is carried out at room temperature and the resulting gel fibers can be converted to silica glass fibers at 800 - 1000 °C, much lower temperatures than the melting temperature of silica. Sakka and Kamiya[1,2] have investigated the reaction conditions necessary for obtaining spinnable sols and found that the tetraethoxysilane solution exhibits spinnability when an acid catalyst is used and the water to silicon alkoxide mole ratio $H_2O/Si(OC_2H_5)_4$ of the solution is lower than 4. It has been indicated that one-dimensionally developed long particles (called linear particles) are formed in the spinnable solutions. This study has been made to see if the spinnability appears in other silicon alkoxides than tetraethoxysilane (TEOS) and to compare the flow characteristics of the solutions with different alkoxides relative to the spinnability. The solutions of tetramethoxysilane $Si(OCH_3)_4$ (TMOS), tetraisopropoxysilane $Si(i\text{-}OC_3H_7)_4$ (TPOS) and tetranormalbutoxysilane $Si(n\text{-}OC_4H_9)_4$ (TBOS) have been used for the present study.

The starting solutions of the compositions of $Si(OR)_4 : H_2O : ROH : HCl = 1 : 2 : 2 : 0.01$ and $1 : 2 : 7 : 0.01$ in mole were prepared by mixing the starting chemicals at room temperature under vigorous stirring, where R = CH_3, C_2H_5, $i\text{-}C_3H_7$ or $n\text{-}C_4H_9$. To avoid the change of alkoxyl groups on the alkoxide molecules through the ligand exchange reaction between alkoxide and alcohol, ROH with the same R as in the corresponding $Si(OR)_4$ was used. The starting solutions of 21 - 34 cm^3 were kept in a 100 cm^3 beaker without any cover at 40 °C. Viscosity of the solutions was measured at 30 °C by a cone and plate viscometer (Tokyo-keiki Type E) with a teflon cone and stainless steel plate of 53 mm inner diameter equipped with a thermostat. 1.2 cm^3 solution was used. Spinnability of sols was examined by putting a glass rod into the sol and drawing it up.

The immiscibility tendency of the alkoxide with water became evident as the size of the OR group of the alkoxide increased. As shown in Table 1, in TPOS and TBOS systems starting solutions are not homogeneous for ROH/Si(OR)$_4$ = 2, and the amount of alcohol has to be increased up to ROH/Si(OR)$_4$ = 7 to obtain homogeneous solutions.

All the alkoxide solutions investigated in this study showed spinnability just before gelation in the high viscosity range (Table 1). Viscosity change of the TEOS and the TBOS solutions with ROH/Si(OR)$_4$ = 7 is shown in Fig. 1. In either of the solutions the viscosity increased rapidly before gelation and spinnability was observed in a high viscosity range of 1 - 10 Pa s. Viscosities at various shear rates have been measured to characterize the flow behavior of these sols (Figs. 2 and 3). The viscosity had no dependence on shear rate up to the viscosity of 1 - 10 Pa s, where spinnability was observed. This indicates

Table 1. Properties of $Si(OR)_4 - H_2O - ROH - HCl$ solutions. $H_2O/Si(OR)_4$ = 2 and $HCl/Si(OR)_4$ = 0.01. The solutions were kept in a 100 cm^3 beaker without any cover at 40 °C

Alkoxide	ROH/Si(OR)$_4$ in mol	Gelling time / h	Volume loss at gelation / %	Spinnability
$Si(OCH_3)_4$	2	10.0	50	Yes
$Si(OCH_3)_4$	7	13.8	62	Yes
$Si(OC_2H_5)_4$	2	33.3	60	Yes
$Si(OC_2H_5)_4$	7	40.5	86	Yes
$Si(i\text{-}OC_3H_7)_4$	2	immiscible	——	——
$Si(i\text{-}OC_3H_7)_4$	7	40.9	76	Yes
$Si(n\text{-}OC_4H_9)_4$	2	immiscible	——	——
$Si(n\text{-}OC_4H_9)_4$	7	208	84	Yes

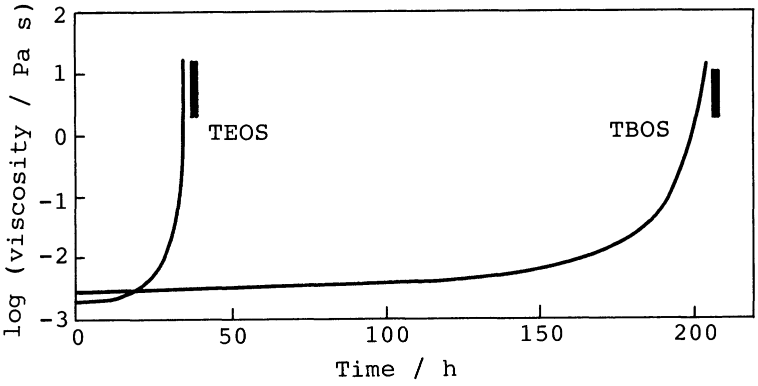

Fig. 1. Viscosity change of the TEOS and the TBOS solutions with ROH/Si(OR)$_4$ = 7. Bars denotes the viscosity range where spinnability was observed.

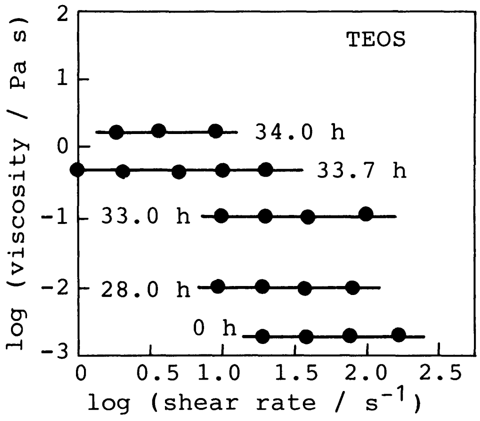

Fig. 2. Viscosity measured at various shear rates in the TEOS solution with $C_2H_5OH/Si(OC_2H_5)_4$ = 7. The time denotes the reaction time.

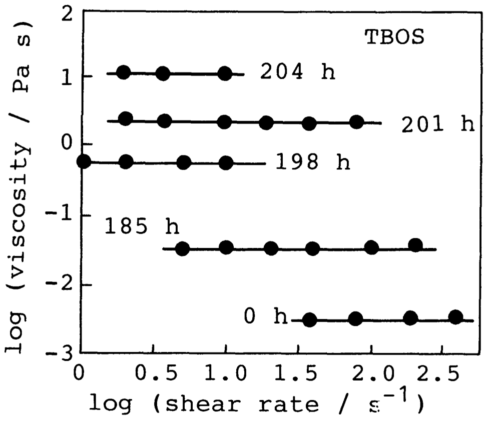

Fig. 3. Viscosity measured at various shear rates in the TBOS solution with $n-C_4H_9OH/Si(n-OC_4H_9)_4$ = 7. The time denotes the reaction time.

that these sols behave as Newtonian liquids. In other words, the Newtonian flow is an important character of the spinnable sols, whatever the starting alkoxides are. It was reported[3)] that no spinnability appears when the viscous solution exhibits non-Newtonian behavior. It can be proposed that the increase of viscosity found in these solutions should occur by the increase in the concentration of the linear particles than by the formation of network structure throughout the solutions.

The time required for a starting solution to become a spinnable sol of high viscosities depended on the kind of alkoxide. As shown in Table 1, the gelling time increases with increasing size of the OR group of the alkoxide, which means that the time needed for obtaining spinnable sols also increases with the size of the OR group. This can be clearly seen in Fig. 1 showing viscosities of the TEOS and the TBOS solutions.

The volume change of the solution in the gelation process is shown in Fig. 4 for the TMOS, TEOS, TPOS,and TBOS solutions with $ROH/Si(OR)_4$ = 7, where the volume is expressed in terms of the volume per mole of Si. It is assumed that the volume of the solution decreases with time due to vaporization of the solvent. Figure 4 shows that the gelation takes place when the volume of the solution reaches 40 - 65 cm^3/Si-mol accompanied with the 60 - 90% volume loss. It is likely that there is a certain critical volume at which the viscosity becomes high enough for gelation. These indicate that the time needed for the formation of the spinnable sol and for gelation depends on the initial volume of the solution and the rate of vaporization of solvents. Since the solution of the alkoxides with larger OR groups have larger initial volumes and smaller rates of vaporization, longer time is needed to obtain highly viscous spinnable sols or gels.

It can be pointed out that there are differences in the rate of increase of viscosity among the solutions studied. As can be seen in Fig. 2, the viscosity of the TBOS solution increases more slowly than that of the TEOS solution and the TBOS sol lies in the viscosity range of spinnability for a longer time than the TEOS sol. It may be due to a slower rate of vaporization in the TBOS solution than in the TEOS solution. It can be said that the fiber drawing can be performed for a longer time for the solution of the alkoxide with larger OR groups.

In conclusion, the spinnable sols could be made from the solutions of tetramethoxysilane, tetraisopropoxysilane and tetranormalbutoxysilane as well as tetraethoxysilane by hydrolyzing these alkoxides with water of $H_2O/Si(OR)_4 = 2$ in mole under acidic conditions. These spinnable sols have been found to behave as Newtonian liquids up to the viscosity range of 1 - 10 Pa s. The time needed for obtaining these spinnable sols depends mainly on the rate of vaporization during gelation reaction and increases as the size of the OR group of the alkoxide increases. Fiber drawing was found to be performed for a longer time in the solution with a lower rate of vaporization, that is, of the alkoxides with larger OR groups.

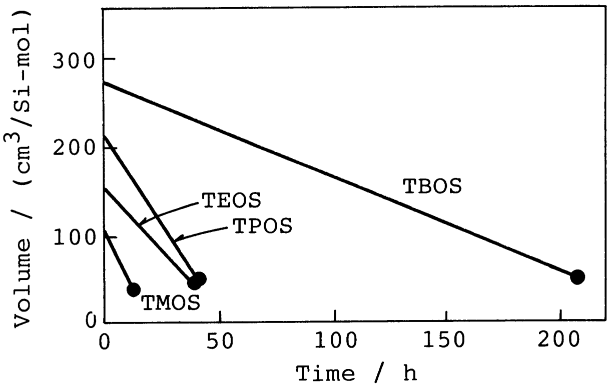

Fig. 4. The change of the volume per mole of Si during gelation reaction for the TMOS, TEOS, TPOS and TBOS solutions with $ROH/Si(OR)_4 = 7$. ● denotes the gelling point.

References

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