

EVOLUTION OF THE VISCOSITY OF MIXED ORGANICALLY MODIFIED SILANE SOLS FOR THE PREPARATION OF ORGANIC-INORGANIC MONOLITHIC GLASS

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Abstract

Organically modified silanes (OMSs) are widely used as starting compounds for the synthesis of organic-inorganic hybrid materials in different shapes by sol-gel processing. The viscosity behaviour of the sols plays an important role in the structure and properties of the final products.

In the present work, we report on the effect of composition, starting compounds and additives on the viscosity evolution of mixed organically modified silane sols and thereby on the feasibility of formation of organic-inorganic glass monoliths from these sols. The experimental results demonstrate that the viscosity increase of the $\text{CH}_3\text{-Si(OCH}_3)_3\text{-CH}_2\text{(O)CHO(CH}_2)_3\text{Si(OCH}_3)_3$ (MG) sols is much faster than the $\text{C}_3\text{H}_7\text{-Si(OCH}_3)_3\text{-CH}_2\text{(O)CHO(CH}_2)_3\text{Si(OCH}_3)_3$ (PG) sols and the base additives are far more effective to the MG sols than to the PG sols. The viscosity-determining silane is $\text{CH}_3\text{-Si(OCH}_3)_3$ (MTMS) in the MG system whereas it is $\text{CH}_2\text{(O)CH=(CH}_2)_3\text{Si(OCH}_3)_3$ (GPTMS) in the PG system. The possibility of forming monolithic gels by a perforation method is closely related to the viscosity behaviour of the sols. Utilization of $\text{C}_2\text{H}_5\text{-Si(OCH}_3)_3$ (ETMS) in replacement of M or P leads to a moderate gelling time and better capability of forming glass monoliths.

Introduction

Organically modified silane precursors, $\text{R}'\text{Si(OR)}_3$, also called trifunctional alkoxy silanes, where R' is an organic group (e.g. $\text{C}_n\text{H}_{2n+1}$, C_6H_5 , $\text{CH}_2\text{=CH-}$ etc.) and R is an alkyl, have been widely used as starting compounds in the synthesis of amorphous materials of different shapes: monoliths, coatings and sheets, as well as fibers via sol-gel processing, aiming at achieving predetermined properties by introducing organic groups into the target materials, for example, contact lens[1], antiscratch coatings[2], thick ($\approx 7 \mu\text{m}$) coatings[3], corrosion resistant coatings with improved adhesion to the substrate[4,5], carbon-containing porous SiO_2 glasses[6,7] and Si-O-N fibers[8]. Improvement of thermal stability and adjustment of refractive

index[9] of the organic-inorganic materials are also possible by the optimization of composition and the introduction of certain additives.

In order to find out suitable matrices for photochromic dyes (e.g. spirooxazine) which need a flexible environment for the ring opening-closure transformation to take place, gels of various compositions were synthesized by the sol-gel method. It has been found[10] that photochromic dyes doped in pure SiO_2 or $\text{Al}_2\text{O}_3\text{-SiO}_2$ gels would either lose their photochromic activity rapidly or change to inverse photochromism. This leads to our new approach to use OMSs as starting precursors. It was also found that a single silane, MTMS or GPTMS, is not suitable to our purpose[11]. In this work, mixed organically modified silanes are used for the preparation of monolithic gels. The viscosity behaviour of the mixed sols is monitored during the early stages in the sol-gel transformation process. The effects of composition, starting precursor and additive on the viscosity evolution and thereby on the possibility of obtaining organic-inorganic monolithic gels are reported and discussed in terms of the competition in hydrolysis and polycondensation between the OMSs.

Experimental

The preparation procedure of the organic-inorganic monolithic gels using mixed OMSs as starting precursors is similar to that described in a previous paper[12]. The final molar ratio between water and silanes is 3.0, while the volume ratio of EtOH to silanes is 0.3. Additives, NaAc and NaF, were added 3h prior to the onset of the viscosity monitoring. The samples are labelled with $X_{g_{mn}}$, where X may be methyltrimethoxysilane (MTMS), ethyltrimethoxysilane (ETMS) and n-propyltrimethoxysilane (PTMS), G represents 3-glycidyloxypropyltrimethoxysilane (GPTMS), and m/n denotes the X-to-G molar ratio.

For monitoring the viscosity evolution during the early stages of the sol-gel transformation, the viscosity at a rotation rate of 500 s^{-1} was taken at appropriate time intervals using a Z_1 measuring system of a computer-controlled PHYSICA rotation viscosimeter. The perforation method with one hole per day was used for the observation of the monolithic gel-forming capability, starting from the third day after wet gels were formed.

Results and discussion

Using MTMS, ETMS, PTMS and GPTMS as starting precursors, sols in MG, EG and PG systems having various m/n ratios were prepared for monitoring the variation of viscosity with holding time in airtight glass containers at room temperature (RT). Figs. 1 and 2 show the viscosity evolution of the sols in the MG system with and without NaAc as a base additive. It can be seen from these figures that the higher the content of MTMS, the faster the increase of the viscosity. Even in the case of sols without NaAc, the MG82 and MG64 sols would become very viscous within 50 h and 75 h, respectively, making the viscosity measurement difficult to go further. On the other hand, the MG01 (pure GPTMS) and MG28 sols exhibit very slow viscosity increase. With the addition of NaAc at a molar ratio (MR) of 10^{-2} to the silanes, the viscosity increase is greatly accelerated, the MG37 and MG46 sols show very steep viscosity increases within 20 h and 30 h, respectively, and it was impossible to further monitor the viscosity of the MG64 and MG82 sols 10 h after preparation.

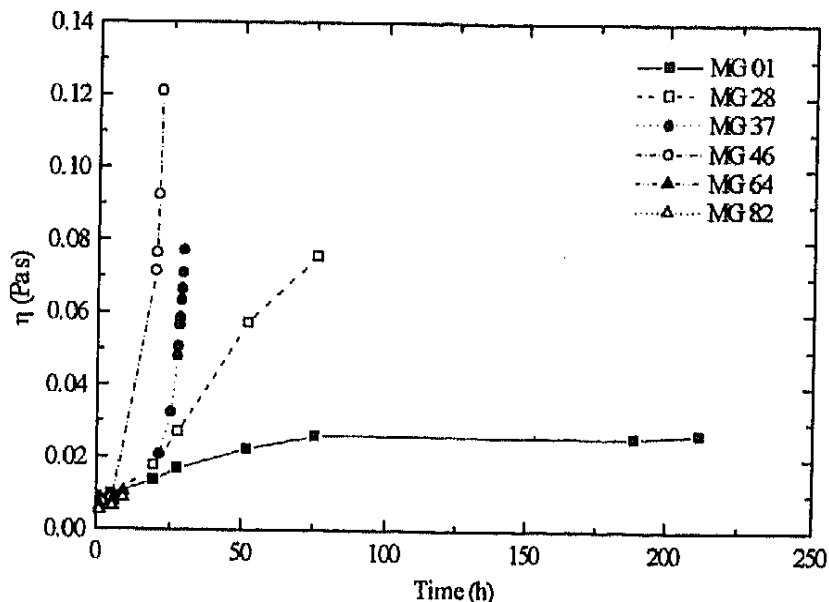


Fig. 1 Viscosity evolution in the early stages of sol-gel transformation in the MG system ($MR_{NaAc} = 10^{-2}$)

All the sols in the PG system, with or without NaAc, would remain in liquid state for a very long time period (> 0.5 year) under the airtight condition. Nevertheless the effect of composition and NaAc-addition on the viscosity evolution can still be clearly witnessed from Figs. 3 and 4. If no NaAc is added, the viscosity would always decrease with increasing P/G molar ratio, whereas in the case of NaAc-addition, it varies in a somewhat complicated manner: decreases with increasing P/G molar ratio within 70 h, but increases with increasing P/G molar ratio after 80 h RT-holding.

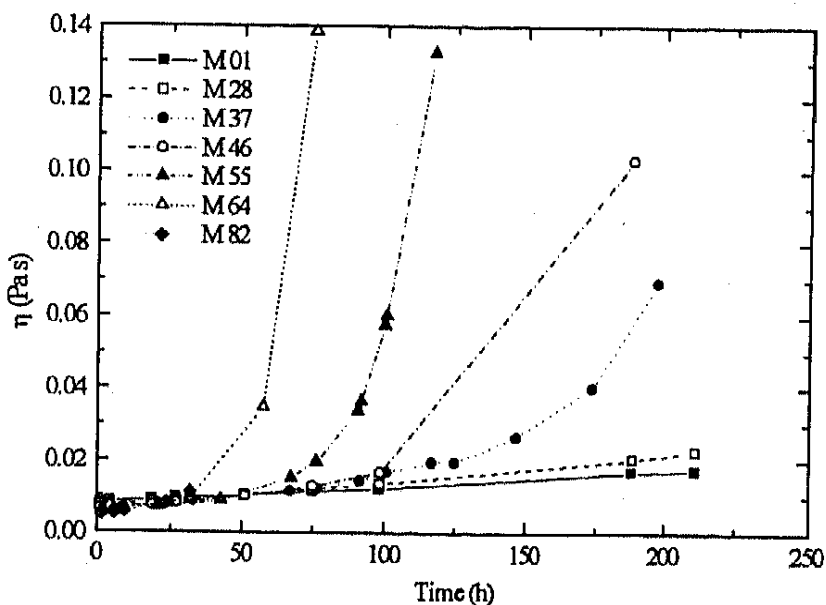


Fig. 2 Viscosity evolution in the early stages of sol-gel transformation in the MG system ($MR_{NaAc} = 0$)

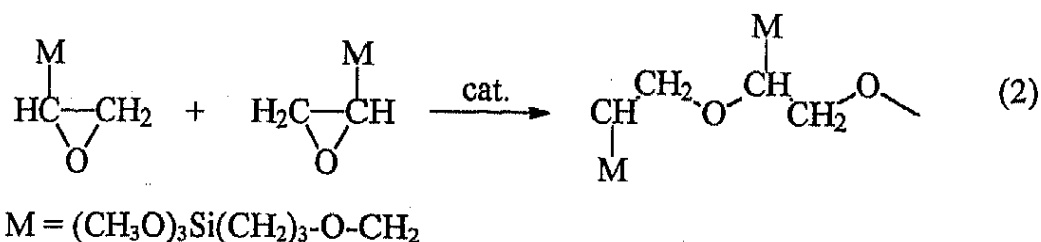
It turns out from the above results that under the same experimental conditions the viscosity increase of the MG sols is much faster than the PG sols and the base

additive, NaAc, is far more effective as a catalyst to the MG system than to the PG system in promoting the hydrolysis-polycondensation reactions. It can also be extracted from these results that the viscosity-determining silane precursors are different in the two systems: MTMS in the MG system and GPTMS in the PG system in the beginning stage.

The hydrolysis and polycondensation of OMSs can be expressed as:



In general, the longer the chain of R', the slower the hydrolysis-polycondensation reaction of the alkoxy groups (OR), but if R' contains some hydrolyzable or polymerizable groups, additional cross-linking may occur under certain conditions. For example, the epoxy group in GPTMS may undergo polyaddition reaction, resulting in a viscosity increase.



This is the reason for the result that the higher the content of GPTMS, the higher the viscosity in the PG sols without NaAc. The addition of NaAc into the PG sols would lead to enhanced hydrolysis-polycondensation reaction (eqn. (1)) of the OR groups preferentially in PTMS, contributing to the viscosity increase. After certain period of RT-holding (ca. 75 h in this work) this enhancement effect becomes predominant over that of the additional cross-linking, as a result, the higher the P/G molar ratio, the higher the viscosity as shown in Fig. 3.

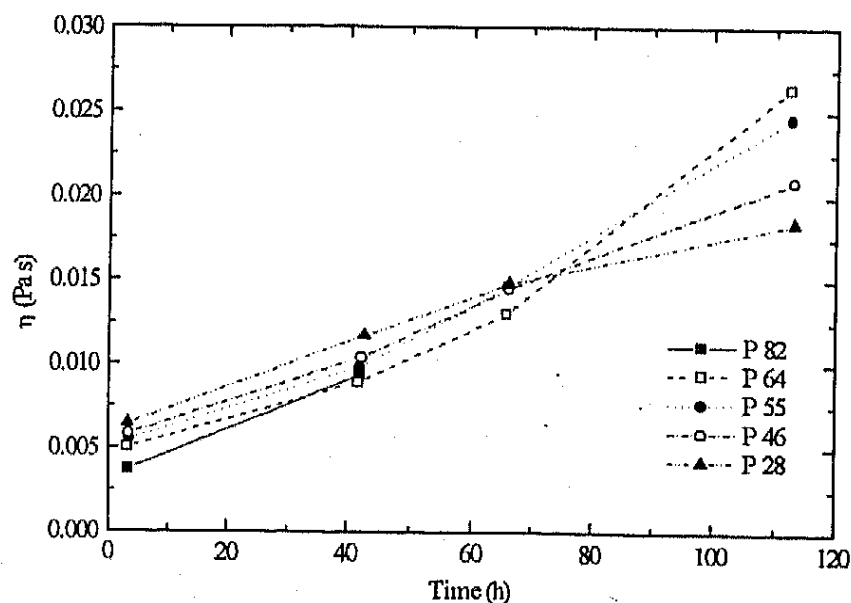


Fig. 3 Viscosity evolution in the early stages of sol-gel transformation in the PG system ($\text{MR}_{\text{NaAc}} = 10^{-2}$)

The viscosity evolution behaviour of EG sols is between the MG and PG systems but closer to the former. The effect of NaF on the viscosity evolution was also found to be milder than NaAc.

All the results obtained suggest that it is possible to tailor the viscosity of sols by optimizing composition and employing certain additives to achieve desired shapes of organic-inorganic glassy materials via the sol-gel method. For instance, a moderate viscosity increasing speed towards the expected viscosity is required for the production of monolithic gels, while a viscosity „window“, i.e. a low viscosity increasing speed, is needed for the manufacture of coatings. These requirements and needs can be fulfilled based on the above results. In another paper published in this proceedings, xerogels in EG system are employed as matrices for photochromic dyes. This system possesses moderate gelling time (100-200 h) and acceptable volume shrinkage (around 50%) and renders it possible to monitor the variation of photochromism during the sol-wetgel-xerogel transformation.

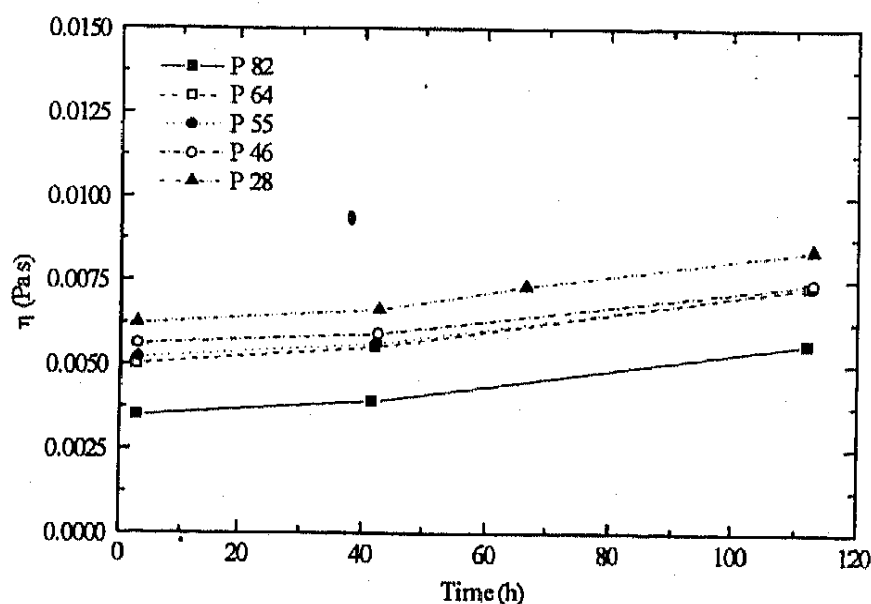


Fig. 4 Viscosity evolution in the early stages of sol-gel transformation in the PG system ($MR_{NaAc} = 0$)

Finally, the capability of forming monolithic xerogels via the perforation method is closely related to the viscosity evolution behaviour of the sols. Gelling time of sols which contain > 50 mole% MTMS and with NaAc as catalyst ($MR_{NaAc} = 10^{-2}$) are too short for them to convert into big monolithic xerogels without cracking during air drying, while the gelling times of the PG sols are too long for them to become wetgels unless being exposed directly to air to allow evaporation of the solvent even if NaAc is added ($MR_{NaAc} = 10^{-2}$). EG sols with NaF as catalyst ($MR_{NaF} = 2 \times 10^{-4}$) exhibit medium gelling times between the MG and PG sols. Xerogel rods and discs of high transparency in this system have been successfully produced through careful control of the perforation process.

Conclusions

Different shapes of xerogels, rod, disc and coating, can be prepared starting from mixed organically modified silanes in the XTMS-GPTMS systems, where X = M (CH₃-), E (C₂H₅-) or P (C₃H₇-), by optimizing the composition and using appropriate base additives when necessary.

MG sols with high content of MTMS and catalysed by NaAc exhibit very short gelling times and little possibility to become monolithic xerogels, while the gelling times of PG sols are too long to allow formation of wetgels under the airtight conditions. MG sols with lower content of MTMS and EG sols catalysed by NaF possess moderate gelling times (100-200 h) and high possibility to convert into monolithic xerogels.

References

- [1] G. Philipp and H. Schmidt, *J. Non-Cryst. Solids* **63** (1984) 283
- [2] H. Schmidt, B. Seifering, G. Philipp, in: *Ultrastructure processing of Advanced Ceramics*, ed. J. D. Mackenzie & D. R. Ulrich (John Wiley and sons, 1988) P 651
- [3] M. Mennig, G. Jonschker and H. Schmidt, *SPIE* **1758**, Sol-gel Optics II (1992) 105
- [4] V. Izumi, H. Tanaka, Y. Uchida, N. Tohge and T. Minami, *J. Non-Cryst. Solids* **147 & 148** (1992) 428
- [5] Idem., *J. Mater. Sci. Lett.* **12** (1993) 724
- [6] K. Kamiya, T. Yoko, T. Sano and K. Tanaka, *J. Non-Cryst. Solids* **119** (1990) 14
- [7] C. Liu, H. Zhang, S. Komanoni and C. G. Pantano, *J. Sol-gel Sci. Techn.* **1** (1994) 141
- [8] K. Kamiya, M. Ohta and T. Yoko, *J. Non-Cryst. Solids* **83** (1986) 208
- [9] H. Schmidt, *Mat. Res. Symp. Proc.* **171** (1990) 3
- [10] L. Hou, B. Hoffmann, M. Mennig and H. Schmidt, *J. Sol-gel Sci. Techn.* **2** (1994) 635
- [11] L. Hou, M. Mennig and H. Schmidt, *SPIE* **2288**, Sol-gel Optics III (1994) 328
- [12] L. Hou, M. Mennig and H. Schmidt, *Chimica Chronica*, New Series **23** (1994) 175