

The Influence of Solvent Choice and Coupling Agent on the Morphology of the Silica Phase in Sol-Gel Polyvinylpyrrolidone (PVP) - TEOS Derived Silica Hybrid Films

Kevin Gaw, Masa-aki Kakimoto, Yoshio Imai
Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
Meguro-ku, Tokyo 152, Japan

Introduction

The hydrolysis via a sol-gel process, of silicon-alkoxides for the preparation of silica glass has been studied extensively.¹⁻¹⁵ This process typically involves the spin coating or dipping of a substrate into a TEOS (tetraethoxysilane) alcoholic solution that has achieved some extent of hydrolysis, with further condensation of the TEOS occurring on the substrate. Parameters such as solvent choice, applied electrical fields, rate of solvent removal, process temperatures, the choice of catalyst on these systems has a significant effect on the hydrolysis-condensation behavior and thus, the formation rate and morphology of the desired silica glass.¹ An extensive work on the influence of the carrier solvent chain length on the hydrolysis-condensation behavior of TEOS was performed by Bernards, et al.² If the environment of the reacting TEOS is changed by the use of more polar solvents, such as DMSO and DMAc, we have found that the morphology of the silicate is also substantially altered.

Recently, silicon oxide (SiO₂)-polymeric hybrid films have been synthesized from TEOS and polymers such as poly(oxytetramethylene), poly(oxyethylene), and polyimides³⁻⁷. Preliminary work in our laboratory, by Morikawa, analyzed the formation of hybrid inorganic-organic films of polyvinylpyrrolidone (PVP)-SiO₂ films from alcoholic solutions.⁶

We fabricated thin films of PVP and SiO₂ via a sol-gel method, wherein, the SiO₂ was formed from PVP solutions in various solvents. The affects of the rate of drying, the solvent used and also the incorporation of a coupling agent (CA), aminopropyltriethoxysilane (APTES) on the morphology of the silica phase within the films was analyzed by scanning electron microscopy (SEM) and FTIR.

Experimental

Films were made by casting the solutions on a glass substrate with subsequent solvent removal and hydrolysis-condensation of the TEOS taking place in the cast films. To study the influence of various parameters on the PVP-TEOS system, focusing on the hydrolysis and condensation reactions and the morphology of the SiO₂ phase, the solvents of the system were systematically changed. Alcohols (methanol, ethanol, isopropanol) and more polar solvents, DMAc and DMSO were used. The affects of APTES on the morphology of the SiO₂ phase were also investigated for all solvent systems.

Monolithicity of gels has been found to vary with differences in the concentration of catalyst and molar concentrations of mixture components⁸, so mixtures with molar ratios of TEOS:H₂O of 1:4 were used for all systems. The weight percentage of SiO₂ was kept in the range of 25-40% depending on the amount of coupling agent used. In a closed vessel, PVP was dissolved with vigorous stirring into a 1:9 acidified water-solvent mixture and then TEOS and the coupling agent were added to the mixture. After a constant period of time, the solutions were cast onto a PET sheet and dried.

To investigate if the rate of drying had any affect on the morphology of the SiO₂, the curing of the films was done using a high humidity chamber (90% RH) for the first twenty-four hours of cure and then the films were removed and placed in an oven at 60°C for 24 hours. In a second method, the films were immediately placed into the heated oven.

The percentage of silica in each sample was determined by the use of a Shimadzu TGA at a heating rate of 10°C/min to 800°C. In all systems, the SiO₂ was the minor phase. Upon burnout of the organic PVP, only the inorganic SiO₂ remained. Hence, in the SEM photographs of the heat treated samples only the SiO₂ can be seen. Typical TGA plots of the

samples can be seen in figure 1. The samples analyzed by SEM are from these TGA experiments. FTIR was conducted on a Shimadzu FTIR 8100 on thin films.

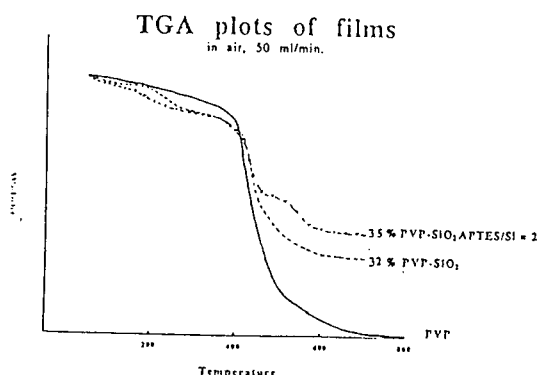


Figure 1
Typical TGA plots

Film SiO₂ Domain Morphology

Solvent	APTES:Si (molar ratio)	Domain shape/size (in micrometers)	Pore size (in micrometers)
Alcohols (Methanol, Ethanol, Isopropanol)	0	Sheets	----
	2/3	Spheres/ d<0.1	----
	1-2	Spheres/ d<1	----
	3	Connected Spheres/ d<2	<200
	5	Isolated Spheres/ d>3	----
DMSO	0	Sheetlike	<50
	2/3-1	Spheres/ d<1	<100
	2	Spheres/ d<1	<100
	3	Spheres, d<1/ plates	<500
	5	Spherically sheetlike	<500
DMAc	0	Sheets	50
	2/3	Spheres, d<1	----
	1	Ribbons, d<1	----
	1	Ribbons, d<1	----
	5	Sheets and spheres, d<1	----

Table 1
Morphology of Si phase
in different solvents

Results

Changing the solvent and the addition of coupling agent in the mixtures had a dramatic effect on the morphology of the SiO₂ phase as is itemized in Table 1. Some samples formed unanalyzable powders upon the heating of the films to the burnout temperature. This is because the silica phase formed non-interconnected domains in the PVP matrix.

In all the systems containing no coupling agent, the SiO₂ formed a sheet-like structure. This agrees with previous work done by Iyoku.⁸ These sheets typically contained micropores that ranged in size from 10 nm to 1 μm in diameter as can be seen in Fig 2. These pores were round in all the samples with a spaces between pores ranging from 10 nm to several μm. All systems with no coupling agent had a similar morphological character and also formed clear films of uniform thickness.

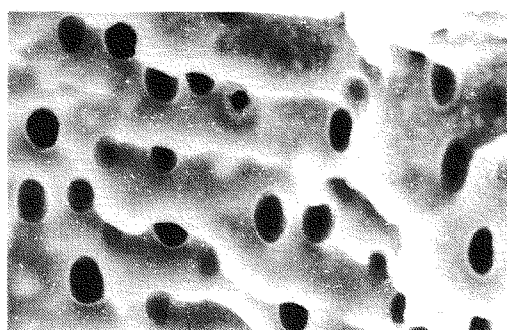


Figure 2
DMAc solvent
Pores in sheet-like structure
No coupling agent

However, for solutions that contained coupling agent, vast differences in processability occurred. Systems that had high amounts of coupling agent (molar ratio CA:Si >5:1) became cloudy, extremely viscous and rapidly became an intractable, uncastable gels.

The addition of the coupling agent to the systems has a dramatic effect on the morphology of the SiO₂. When APTES was added, the SiO₂ domains changed from sheet-like to particulate in nature. From FEM back-scattering and SEM, it can be seen that for methanolic

systems of all CA:Si ratios, the particle size of the Si domains was much smaller and thus, were more numerous than they were when heavier alcohols were used (Fig. 3). Moreover, for all alcoholic systems with high CA:Si ratios (>3:1), there were significantly less Si domains and these domains were larger than in samples with low levels of CA (Figs. 4,5).

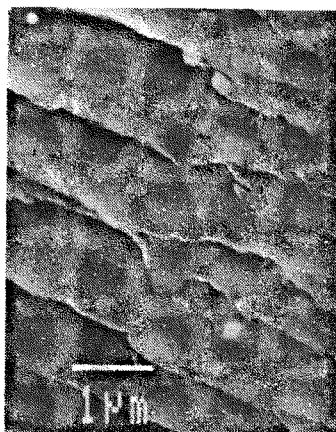


Figure 3
Methanol Solvent
No coupling agent

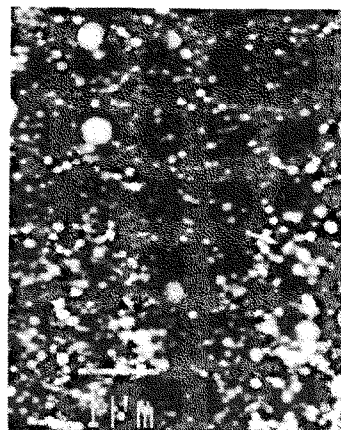


Figure 4
Methanol Solvent
CA:Si = 2



Figure 5
Methanol Solvent
CA:Si = 2

The most dramatic morphological effect of replacement of alcohols with more polar solvents is that the overall SiO₂ phase becomes more monolithic in nature as the individual SiO₂ domain size shrinks. For DMAc samples, as seen in Figure 5, it is evident that some of the SiO₂ tends to form a mixed plate-like and a particulate phase morphology. For both DMAc and DMSO solvent systems, the coupling agent had the effect of changing the coalescent behavior of the Si which manifested itself in the concurrent appearance of particulate and sheet-like morphologies. Carda, et al.⁹, using highly polar DMAc, found that the polarity of the solvent also had an effect on the gelation kinetics of a TEOS system. These influences can be seen in the resulting SiO₂ phase morphology of the polar solvent systems.

The interconnectedness of the SiO₂ domains increased with increasing polarity of the solvent. In Figures 3 and 4, for alcoholic solvent systems, the domains are separated and appear as islands in the PVP matrix, but for DMAc systems (Fig. 5) the domains are connected as if they are sintered together.

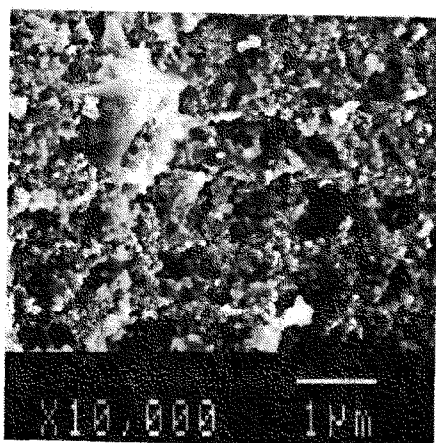


Figure 6
DMAc solvent
CA:Si = 2

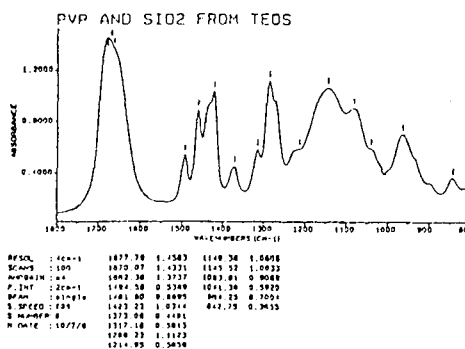


Figure 7
FTIR PVP-SiO₂
MeOH solvent

Discussion

The influence of the polarity of the solvent used in previous studies has been found to affect the initial and final rates of condensation but the SiO₂ moieties created were found to be identical.¹⁰ Also, the microstructural evolution of the SiO₂ has been found to be modified by organics within the system and is related to the degree of network linkage in the system.¹¹ Clearly, as seen in figures 4-6, the incorporation of a polymer (PVP), and a coupling agent (APTES) to a reacting TEOS system, changes the nature of the SiO₂ moieties formed. In systems with no APTES, the SiO₂ formed sheets in all solvents. Using APTES, the size of SiO₂ spheres and the size of the pores in the sheets formed was heavily influenced by the concentration of coupling agent. The drying conditions of the films were found to have no influence on the final morphology of the SiO₂ domains.

Since the nascent SiO₂ domains could have differing solubilities in the different solvents they could separate from the reaction mixture earlier and thus act as nucleation sites earlier in the reaction process and this could influence the final SiO₂ morphology.¹² This change in structure can be seen in the widespread interconnectedness of the SiO₂ domains in the systems using the more polar solvents DMSO and DMAc. Also, since micro-spheres formed in a ethanol-base catalyzed system were found to be perfectly round and grew by an Ostwald ripening mechanism¹³, this could explain the size difference of the SiO₂ domains in the systems with APTES. If the nucleation of Si domains is retarded by the addition of APTES, then, the domains would be less numerous and would be larger for equivalent weight percentage SiO₂ films as was seen in the films made here.

The size of spherical domains in TEOS systems was also found to be dependent on the amount of progress the reaction has been allowed to achieve.¹⁴ The extent of reaction for the TEOS can be seen in the FTIR plot (Fig. 7) of a methanolic system. The presence of SiOH groups is indicated by the broad peak centered around 964 cm⁻¹. This peak was seen for all systems regardless of APTES content and is indicative of incomplete condensation of the partially reacted TEOS. This TEOS reaction inhibition was caused by the interference of the reacting TEOS by the PVP and was also seen by Morikawa in his NMR work.⁶ The changes in the behavior of the reacting systems by the formation of bonds between the PVP, TEOS and the APTES could be responsible for the radical changes in morphological and coalescent character of the SiO₂. Moriya et al.¹⁵, found that the nature of the incorporated polymer in a hybrid polymer inorganic gel, effected the overall pore size and distribution of the Si phase. They attributed this to the differences in the hydrophobic or the hydrophilic groups of the polymers used. We think that similar mechanisms are at work in the PVP-TEOS system.

Acknowledgments

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