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Synthesis of Melting Gels Using Mono-Substituted and Di-Substituted Alkoxysiloxanes



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Introduction to Organic-Inorganic Hybrid Gels

Hybrid organic-inorganic sol-gel materials containing silica were first called "ORMOSILs" in 1984.¹ Since then, the number of hybrid organic-inorganic combinations has increased rapidly.² Hybrid materials have remarkable features resulting from the synergistic combination of both inorganic and organic components that make them suitable for a wide range of applications such as electrochemical devices, biomedical applications including drug delivery, and electronic and optoelectronic applications including light-emitting diodes, photodiodes, solar cells, gas sensors and field effect transistors.

Generally, organic-inorganic materials are classified in two broad categories: Class I materials where the organic and inorganic components are embedded one within the other and display weak bonds, and Class II materials where there are strong covalent bonds between the inorganic and organic components.³

For more than 25 years hybrid gels have been grown by sol-gel process.⁴ Since sol-gel processing is a low temperature method, it is only natural that sol-gel processing has been extended to hybrid materials with retained organic content. Ordinarily, the outcome of the sol-gel process with the precursor tetraethylorthosilicate (TEOS) (Aldrich Prod. No. 333859) is a 3-dimensional network. TEOS, with 4 identical groups attached to Si, undergoes hydrolysis and polycondensation reactions. The 4 identical groups can be changed to, for example, 3 identical groups and one group with a direct Si-C bond. While the remaining 3 ethoxy groups are reactive to hydrolysis, the substituted group, for example, methyl, is not.

Below is a schematic (Scheme 1) of the number of reactive groups, as the ethoxy group on TEOS is substituted successively by methyl:

Name	Tetraethoxysiloxane	Methyltriethoxy-siloxane	Dimethyldiethoxy-siloxane
Abbreviation	TEOS	MTES	DMDES
Aldrich Product Number	333859	339644	175595
Structure			
Number of Reactive Groups	4	3	2
Number of Nonreactive Substitutions	0	1	2
Relative Reactivity ⁵	Intermediate	Most	Least

Substituting groups besides methyl that have been studied include ethyl, phenyl, and vinyl. The size and polarity of the groups influences the properties. A common precursor among Class II hybrids for thin films is methyltriethoxysiloxane (MTES) (Aldrich Prod. No. 339644), $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$, together with tetraethoxysiloxane (TEOS), $\text{Si}(\text{OC}_2\text{H}_5)_4$.⁶ The retention of the methyl groups in the films reduces tension and lessens cracking. More complicated ORMOSILs are obtained by co-condensation of TEOS with MTES and vinyltriethoxysiloxane (Aldrich Prod. No. 679275) and 3-glycidoxy-propyltrimethoxysiloxane (Aldrich Prod. No. 440167).^{7,8}

In addition to the beneficial effects of retained organic content on mechanical properties, there are interesting effects on hybrid gel surface chemistry, which are reflected in hydrophobicity or hydrophilicity. For example, a water-repelling surface, which has a contact angle greater than 90°, can be tailored through the choice of organic groups on the surface. For silica-based hybrids, the affinity for water can be decreased by reducing the number of the vicinal -OH groups.⁹ Reducing the -OH groups can be achieved by replacing them with hydrophobic groups such as methyl.¹⁰ In this way, organic-inorganic coatings have been developed for anti-graffiti, anti-adhesive and anti-static coatings, among others.¹¹ Since the refractive index and the thickness of hybrid coatings can be adjusted, waveguides based on phenyltriethoxysiloxane (PhTES) (Aldrich Prod. No. 679291), MTES and TEOS have been patterned by microfluidic lithography.¹²

Discovery of Melting Gel Behavior

Recently, it has been found that Class II hybrids, which are mixtures of di-substituted and mono-substituted alkoxysiloxanes, can produce so-called melting gels with a range of softening behaviors and a range of temperatures where the gel flows.¹³ These hybrids originally were investigated to replace low melting temperature sealing glasses that melt around 600 °C. This temperature is too high for most electronic packaging, especially newer devices with organic light emitting diodes (OLED).

Melting gels are rigid at room temperature, soften at around 110 °C and consolidate at temperatures above 130 °C. The process of (a) softening, (b) becoming rigid and (c) re-softening can be repeated many times, until heated above 130 °C after which the gel no longer softens.¹³

While the softening behavior has been called melting, it is not melting in a thermodynamic sense.¹⁴ At the same time, it is not thixotropic behavior either, as the material cannot be caused to flow by shearing. Instead, the ability to soften and flow is a behavior seen in some but not all combinations of mono-substituted and di-substituted alkoxysiloxanes, indicating incomplete crosslinking. In fact, melting gels show glass transition behavior at temperatures below 0 °C.

One of the first mentions of "melting gels" involved poly(benzyl-silsesquioxane) (POSS) particles, which were deposited onto an indium-tin oxide (ITO) (Aldrich Prod. Nos. 749745, 749796) coated substrate by electrophoretic deposition. After heat treatment at very low temperatures, continuous thick transparent films were obtained.¹⁴ Using a different approach with PhTES and DPhDES (diphenyldiethoxysiloxane) (Aldrich Prod. No. D83532), poly-silsesquioxanes were obtained that showed a low softening point. PhTES-DPhDES hybrids could be formed with or without ethanol as monodisperse particles, and the glass transition temperature of these hybrids varied with ratio of PhTES and DPhDES.¹⁵⁻¹⁷



In comparing the methyl substituted melting gels with ethoxy (MTES/DMEDES), with methoxy (MTMS/DMDMS) and their phenyl-substituted melting gel analogs (PhTES/DPhDES and PhTMS/DPhDMS), it was found that melting gels occurred for different mixtures, depending on the system. The methyl-substituted alkoxy siloxanes show melting gel behavior over a wide range of compositions, while the phenyl-substituted compositions are a majority of the mono-substituted alkoxy siloxane, going so far as to have melting gels with only PhTES or PhTMS.¹³

Now that melting gel behavior has been studied in a more systematic way, a family of organically modified silica gels made up of mixtures of mono-substituted alkoxy siloxanes and di-substituted alkoxy siloxanes has been characterized and their properties such as contact angle with water¹⁰, density¹⁸, and hermeticity have been investigated.¹⁸

Precursors for Melting Gels

While the catalog of alkoxy siloxanes is almost limitless, two typical precursors for melting gels are listed in **Table 1**, along with TEOS for comparison. Note that all of the precursors are liquids at room temperature, and are described as reacting slowly with water at room temperature.

Table 1: Precursors Investigated for Melting Gels, with TEOS for comparison.

Chemical Name	Formula	Molecular Weight (g/mol)	Melting Point (°C)	Boiling Point (°C)	Specific Gravity	% Oxide
DMEDES	C ₆ H ₁₆ O ₂ Si	148.28	-97	114	0.865	40.5
MTES	C ₇ H ₁₈ O ₃ Si	178.3	-50	142	0.895	33.7
TEOS	C ₈ H ₂₀ O ₄ Si	208.33	-77	169	0.9335	28.8

Synthesis of Melting Gels Using Mono-Substituted and Di-Substituted Alkoxysiloxanes

In a typical synthesis, the MTES and DMEDES are used without further purification. Hydrochloric acid and ammonia are used as catalysts. Anhydrous ethanol is the solvent. A total of 5 gels were prepared with the indicated mol% of MTES and DMEDES listed in **Table 2**. The synthesis flowchart is shown in **Figure 1**, and described step-by-step.

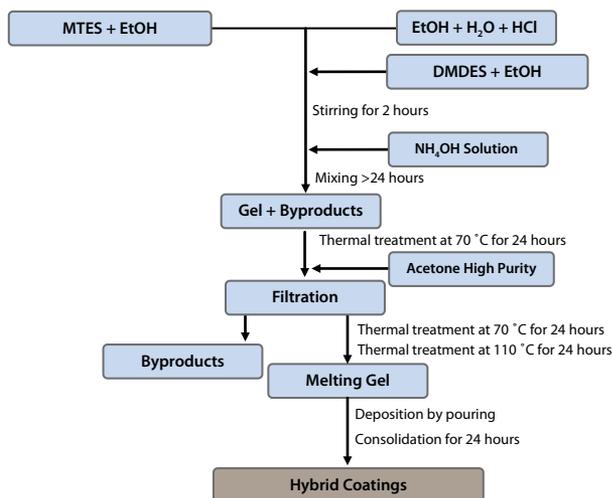


Figure 1. Flow chart of the synthesis of melting gels using MTES and DMEDES.

The synthesis has three steps. First the water is mixed with hydrochloric acid and half of the ethanol. The MTES is mixed with the other half of the ethanol separately. Then, the ethanol mixed with MTES is added dropwise to the water solution under continuous stirring. The beaker is covered tightly, and the mixture is stirred at room temperature for 3 hours.

In the second step, DMEDES is diluted with ethanol. The DMEDES in ethanol mixture is added dropwise to the mixture from the first step. This solution is kept in a closed beaker at room temperature for another two hours of stirring.

In the third step, ammonia is added to the reaction mixture and the solution is stirred for another hour in a closed beaker. Then the clear solution is stirred for 48 hours at room temperature in an open beaker until gelation occurs. The gels are heat treated at 70 °C overnight to remove excess ethanol. During this process, a white powder of ammonium chloride forms on the gels. To remove the ammonium chloride, 10 mL of acetone are added to the samples, followed by removal by vacuum filtration. Again, the gels are heat treated at 70 °C for 24 hours, followed by a last heat treatment at 110 °C for removal of un-reacted water.

After this heat treatment, the gels are rigid at room temperature. However, when heated above ~110 °C, the gels soften and become fluid, in some cases as fluid as water. To locate the consolidation temperature, samples were subjected to heating and cooling cycles until the minimum temperature is found after which the gels could not be softened. Once the gel had been heated to the consolidation temperature, the behavior was no longer reversible. The consolidation temperatures (T_{CON}) are listed in **Table 2**.

The thermal behavior of the hybrid gels before consolidation was studied using differential thermal analysis (Perkin-Elmer DTA-7), thermogravimetric analysis (Perkin-Elmer TGA-7) and differential scanning calorimetry (DSC TA-Q-2000).¹⁹ The glass transition temperatures were determined and are listed in **Table 2**.

Table 2: Relationship between composition and properties of melting gels.

Monosubstituted (mol %) MTES	Disubstituted (mol %) DMEDES	T_g (°C)	T_{CON} (°C)	Total Weight Loss (%)	Calculated Weight Loss (%)
50	50	-56.7	160	45	62.9
60	40	-37.7	155	37	63.6
65	35	-18.8	150	35	63.9
70	30	-6.4	145	34	64.3
75	25	-0.3	135	30	64.6

Results and Discussion

The weight loss for all gels occurred in two temperature ranges. At lower temperatures between about 150 °C and 300 °C, the weight loss is attributed to the removal of the ethoxy and hydroxyl groups. The second weight loss occurs between about 350 °C and 500 °C due to the combustion of the methyl groups. For all samples, the differential thermal analysis shows an exothermic peak accompanying the high temperature weight loss, confirming the combustion of the methyl groups.

The measured weight loss increases with the concentration of the di-substituted alkoxysiloxane. Considering that the calculated weight loss, based on formula weight and full oxidation to silica, varies little among the compositions, it is interesting to see the measured trend. The consolidation temperature trends in the same direction as the weight loss, as shown in **Table 2**.

The consolidation temperatures listed in **Table 2** decreases with a decrease in the amount of di-substituted alkoxysiloxane. This decrease in the consolidation temperature is consistent with the fact that di-substituted alkoxysiloxanes have only two reactive sites available to create new bonds with the rest of the silica network, while mono-substituted alkoxysiloxanes have three. Without the mono-substituted alkoxysiloxane, the di-substituted alkoxysiloxanes remain liquid after hydrolysis and polycondensation reactions because only linear chains are formed. When mono-substituted alkoxysiloxanes are mixed with the di-substituted alkoxysiloxanes, the di-substituted alkoxysiloxanes act as bridges between the molecular species formed when the mono-substituted alkoxysiloxanes hydrolyze.

The glass transition temperatures listed in **Table 2** show the opposite trend to the consolidation temperature. The T_g values increase with decreasing amount of di-substituted alkoxysiloxanes. The glass transition is generally thought of as the interval of transition between liquid states and glassy, amorphous states. Put another way, the glass transition reflects a number of macroscopic properties, such as viscosity, dielectric constant, and mechanical properties. Using the approach developed for traditional organic polymers and applied to inorganic silica-based polymers, the glass transition temperature is considered a measure of the degree of cross-linking in the silica network. In other words, the T_g increases with an increase in the number of oxygen bridges between silicon atoms.

After gelation and heat treatment to remove solvents and water, the gels are rigid. An example of a melting gel is shown in **Figure 2**. A beaker with a rigid layer of gel on the bottom is turned on its side. This is the appearance of the melting gel after gelation, but before consolidation. Then, the beaker is placed on a hot plate and warmed to a modest 110 °C. The tilted beaker with the softened gel is shown in **Figure 3**. The gel has softened and is beginning to flow because the beaker is tilted. Most of the combinations soften to a viscosity between water and syrup, making pouring easy. When the fluid gel was poured onto a variety of substrates, including glass, mica, silicon, copper and aluminum, the gel adhered well to all surfaces. Thick films were about 1 mm thick and relatively smooth. In addition, the films are transparent and show no tackiness. The thick films have been heated to their consolidation temperatures, after which a variety of physical properties, such as contact angle, hardness and permeability, have been measured and reported.²⁰



Figure 2. Beaker containing melting gel before heating on its side.



Figure 3. Beaker tilted after warming to soften the gel so that it can be poured.

Applications of Melting Gels for “low- κ ” Dielectrics

The property requirements for low- κ materials in integrated circuits for simple metal-oxide semiconductor field effect transistors (MOSFET) include structural uniformity, low dielectric constant ($\kappa \sim 2$), low dielectric loss, high hardness, high adhesion strength, thermal stability, and low moisture absorption.²¹ Many of these characteristics can be satisfied by melting gels. The network structure in organically modified silica melting gels helps them achieve the structural uniformity and hardness. Also, the fact that SiO_2 has a low κ by itself means that the dielectric constant of the melting gel can be close to 2 with appropriate amount of organic component and possibly some closed porosity. In addition, the silica content of the hybrid gives thermal stability to the low κ material. Melting gels have low viscosity at their softening temperature, so they can be applied by spin coating. The coatings show good adhesion to silicon substrates, and melting gels show very low vapor transport values.²² For all of these reasons, melting gels are interesting materials to consider for multilevel interconnect structures.

One composition that looks promising for low- κ dielectrics is the 65% MTES - 35% DMDES gel, which has a high value of the contact angle ($\theta = 100^\circ$), negligible BET surface area (0.0138 m^2/g) and a low density (1.252 g/cm^3). The dielectric constant is about 4.2 at 1KHz.²³

Conclusions

A combination of mono-substituted and di-substituted alkoxysilanes, reacted using a three-step synthesis, results in a so-called melting gel. The alkoxysilanes undergo hydrolysis and condensation polymerization similar to a conventional sol-gel process. Hydrochloric acid in the first step promotes the formation of linear polymer chains. Ammonia in the third step serves to neutralize the hydrochloric acid and to promote cross-linking between the polymer chains, which leads to gelation. Incomplete cross-linking is reflected in the glass transition temperature T_g of the gels before consolidation. The melting gels can be softened repeatedly. However, once the gels have been heated to their consolidation temperature, they no longer soften. After consolidation, the gels are hard and impermeable.

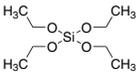
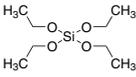
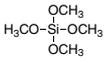
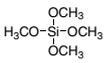
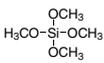
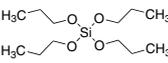
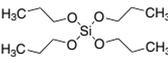
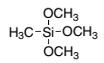
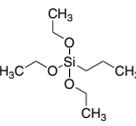
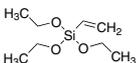
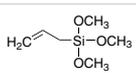
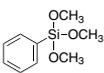


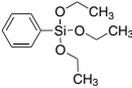
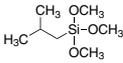
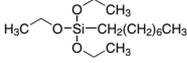
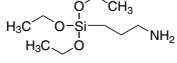
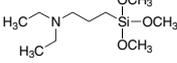
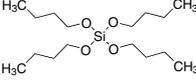
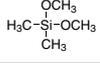
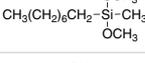
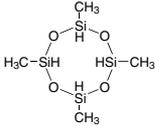
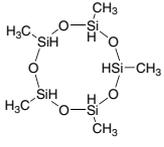
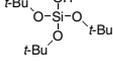
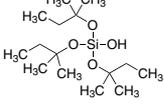
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Silicon Precursors for Hybrid and Melting Gels: Silicates and Siloxanes

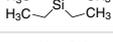
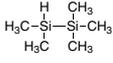
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Name	Structure	Purity	Prod. No.
Tetraethyl orthosilicate		99.999% trace metals basis	333859-25ML 333859-100ML
Tetraethyl orthosilicate		98%	131903-25ML 131903-250ML 131903-500ML 131903-1L 131903-2.5L 131903-4L
Tetramethyl orthosilicate		≥98% ≥99.9% trace metals basis	679259-50G
Tetramethyl orthosilicate		≥99%	341436-25G 341436-100G
Tetramethyl orthosilicate		98%	218472-100G 218472-500G
Tetrapropyl orthosilicate		≥98%	679240-50G
Tetrapropyl orthosilicate		95%	235741-25G 235741-100G
Trimethoxymethylsilane		≥98%	679232-50G
n-Propyltriethoxysilane		≥98%	679321-50G
Triethoxyvinylsilane		≥98%	679275-50G
Allyltrimethoxysilane		≥98%	679267-50G
Trimethoxyphenylsilane		≥98%	679313-50G

Name	Structure	Purity	Prod. No.
Triethoxyphenylsilane		≥98%	679291-50G
Isobutyl(trimethoxy)silane		≥98%	679364-50G
Triethoxy(octyl)silane		98% 99.99% trace metals basis	679305-50G
(3-Aminopropyl)triethoxysilane		≥98.0%	741442-100ML 741442-500ML
[3-(Diethylamino)propyl]trimethoxysilane		≥98%	679356-50G
Tetraethyl orthosilicate		97%	T5702-100G
Tetramethylammonium silicate solution	$(\text{CH}_3)_4\text{N}(\text{OH}) \cdot 2\text{SiO}_2$	≥99.99% trace metals basis	438669-100ML 438669-500ML
Dimethoxydimethylsilane		≥99.5% 99.999% metals basis	556688-25ML
Dimethoxy(methyl)octylsilane		≥95.0%, GC	68215-25ML
2,4,6,8-Tetramethylcyclotetrasiloxane		≥99.999% trace metals basis ≥99.5%	512990-25ML 512990-100ML
2,4,6,8,10-Pentamethylcyclopentasiloxane		96%	517801-25ML
Tris(<i>tert</i> -butoxy)silanol		99.999%	553468-5G 553468-25G
Tris(<i>tert</i> -pentoxy)silanol		≥99.99%	553441-5G 553441-25G

Silicon Precursors for Hybrid and Melting Gels: Silanes

For a complete list of available materials, visit aldrich.com/mnel

Name	Structure	Purity	Prod. No.
1,1,2,2-Tetramethyldisilane		98%	445126-1G
Tetramethylsilane		≥99.99% trace metals basis	523771-100ML
Tetraethylsilane		99%	510874-5ML 510874-25ML
Pentamethyldisilane		97%	557641-5ML