



Hybrid organic-inorganic gels that are melting gels

L. C. Klein¹ · Andrei Jitianu^{2,3}

Received: 2 July 2024 / Accepted: 15 August 2024

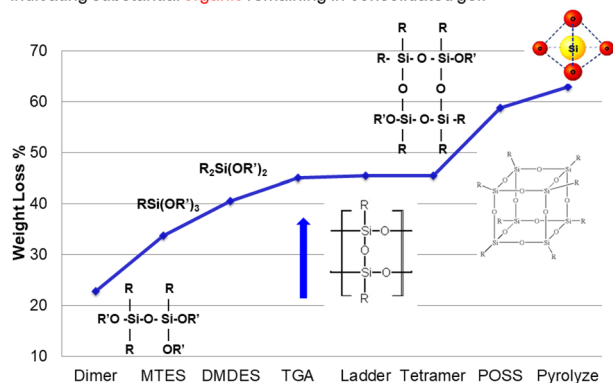
© The Author(s) 2024

Abstract

Ever since the observation in 2001 that some organic-inorganic silica hybrid gels are rigid at room temperature but soften and flow around 100 °C, there has been interest in so-called melting gels. Following heating to 150 °C or higher, the gels no longer soften and are considered consolidated hybrid glasses. The catalog of melting gels has grown over the past 20 years. Longer chain substitutions and other functional groups have been attached to the $\equiv\text{Si-O-Si}\equiv$ molecular species. The substitutions make it possible to adjust the glass transition, the viscosity, and the temperature range of their usefulness.

Graphical Abstract

Estimated Weight Loss for 50%MTES-50%DMEDES in Various Units, indicating substantial **organic** remaining in consolidated gel.



Keywords Melting gels · Glass transition temperature · Consolidation temperature · Organic-inorganic hybrid gels · Substituted siloxanes

Highlights

- Melting gels are mixtures of mono-substituted and di-substituted alkoxy silanes that, along with other additives, are subjected to hydrolysis and condensation polymerization.
- Using differential scanning calorimetry (DSC), glass transition behavior is recorded in unconsolidated melting gels.
- Melting gels consolidate to organic-inorganic glasses when heated to higher temperatures for 24 h.
- The shelf-life for unconsolidated melting gels is longer than one year.

✉ L. C. Klein
licklein@soe.rutgers.edu

¹ Rutgers University, Department of Materials Science and Engineering, 607 Taylor Road, Piscataway, NJ 08854, USA

² Department of Chemistry, Davis Hall, Lehman College-CUNY, 250 Bedford Park Boulevard West, Bronx, NY 10468, USA

³ Chemistry and Biochemistry Program, The Graduate Center of the City University of New York, 365 Fifth Avenue, New York, NY 10016-4309, USA

1 Introduction

An early influence on sol-gel processing was the groundbreaking work of Professor Sakka [1, 2]. While working in the inorganic glass field at the time, he began looking for alternative methods to prepare silicate glasses. He established many of the principles that are followed today in practicing the sol-gel process. The field has expanded since then, even though tetraethyl orthosilicate (TEOS) is still the most common precursor. Hydrolysis of TEOS creates siloxane oligomers consisting of four-fold siloxane rings that are maintained in the network during condensation reactions, although six-fold rings are less strained and more kinetically favorable [3].

A logical development from duplicating silicate glasses with the sol-gel process is the investigation of organically modified silicates (ormosils). Among organically modified silicates with strong covalent bonds, there are so-called melting gels, which have the unusual property of softening around 100 °C when they are first prepared [4]. Following hydrolysis and polymerization, a hybrid silica network forms that contains unhydrolyzed groups. When the melting gels are held isothermally at around 150 °C, the flexible linear chains come closer together and favor further condensation reactions between the chains creating 3D rigid structures [5]. This crosslinking process is irreversible and prevents melting gels from resoftening [6].

One of the melting gel families that has been studied extensively is methyltriethoxysilane (MTES)- and dimethyldiethoxysilane (DMDES)-derived gels [7]. The non-reactive methyl groups cannot hydrolyze, leaving methyl groups grafted on the three-dimensional silica backbone. These melting gels have glass transition temperatures below 0 °C. Subsequently, melting gels were prepared with glass transition temperatures around room temperature using nonreactive phenyl groups [8]. As the catalog of melting gels has expanded, it seems worthwhile to review the state-of-the-art and to integrate the new information. As such, this article is an extension of previous work [9].

2 State-of-the-art of melting gels

Freshly prepared melting gels and unconsolidated melting gels exhibit glass transition behavior, where areas of the network demonstrate relaxation phenomena like organic polymer nanocomposites. Using differential scanning calorimetry (DSC) and rotational rheometry, the glass transition temperatures of the melting gels have been located [10]. With simple extrapolative corrections, by measuring the changes in specific heat, the glass transition temperature is read directly from the DSC plot. In conventional glasses, the glass transition temperature T_g is a

function of cooling rate. The glass transition temperature reflects a temperature range where a viscous metastable material transforms to a rigid, glassy material.

The glass transition temperature in melting gels is correlated with viscosity, dielectric constant and mechanical properties and reflects the degree of cross-linking in the silica network [11]. As the number of oxygen bridges between silicon atoms increases and a more branched structure is formed, the glass transition temperature tends to increase. This trend has been observed in a number of melting gel families, with methyl and phenyl substitutions [10–12].

When thermogravimetric analysis (TGA) was used to study methyl-containing melting gels made with DMDES and MTES, weight loss percentage increased as the DMDES content increased [13]. The weight loss occurred in two steps. The first step was due to the removal of ethoxy and hydroxy groups. The second step was due to the pyrolysis of methyl groups. Differential thermal analysis (DTA) also showed an exothermic peak that confirmed the combustion of methyl groups identified by TGA. A broad exothermic peak indicated a uniform distribution of methyl-groups throughout the silica network, while a narrow peak arose from methyl-groups on the surface of the gel.

When FT-IR spectra of evolved gases were collected from melting gels during heating and isothermal treatment at the consolidation temperature, which was determined when the sample was heated isothermally for 17–24 h and the sample lost its ability to resoften, only CO₂ was identified in the evolved gasses. The fact that CO₂ was released during this process indicates the decomposition of unreacted organic groups. At the same time, no water was identified in the evolved gasses [14].

As expected, the weight loss during heating was higher when the organic content increased. The consolidation temperature is determined by the degree of crosslinking of the hybrid silica network [15]. Di-substituted alkoxides have only two ethoxy-groups available to create bonds with a silica network. A decrease in the amount of di-substituted precursor leads to a decrease of the consolidation temperature, which is the opposite direction in temperature from what is observed for glass transition.

The evolution from gel to rigid hybrid glass raises the question about what structures exist in the rigid gel. For mixtures of precursors with two reactive groups and three reactive groups, the simplest structures that will form are dimers, tetramers and silsesquioxanes, species of formula $R\text{SiO}_{3/2}$ [16]. Assuming that melting gels contain mostly chains that can move when heated above the softening temperature, the chains are flexible up to their consolidation temperature. By increasing the temperature, the chains can move to a favorable position that allows them to react further through condensation reactions of the hydrolyzed

parts of the chains. The final condensation reactions create a denser, cross-linked network which is the final product of the melting gel synthesis, a hybrid glass. Using a simple calculation of the species present in a model gel, assuming 50% MTES and 50% DMEDES, the weight loss expected for various species are indicated in Fig. 1. For example, if a dimer forms and all of the methyl groups are pyrolyzed the weight loss would be about 22%. On the other hand, the polyhedral oligomeric silsesquioxanes (POSS) structure experiences a weight loss of around 59%. Full conversion to SiO_2 corresponds to around 62% weight loss. The actual recorded weight loss from TGA was around 45%, which is close to that for ladder structures.

Initially, seven families of melting gels shown in Figs. 2 and 3 were studied systematically. The glass transition temperatures were determined directly from the DSC

Estimated Weight Loss for 50%MTES-50%DMEDES in Various Units, indicating substantial organic remaining in consolidated gel.

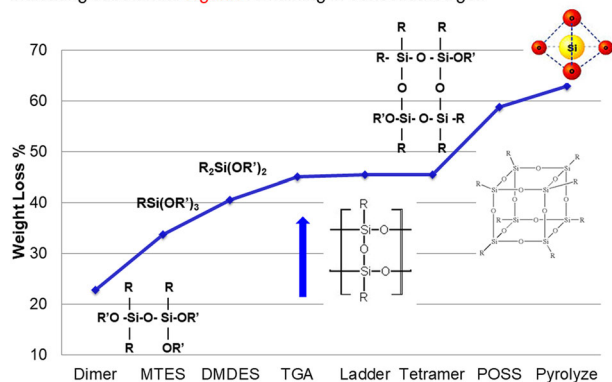
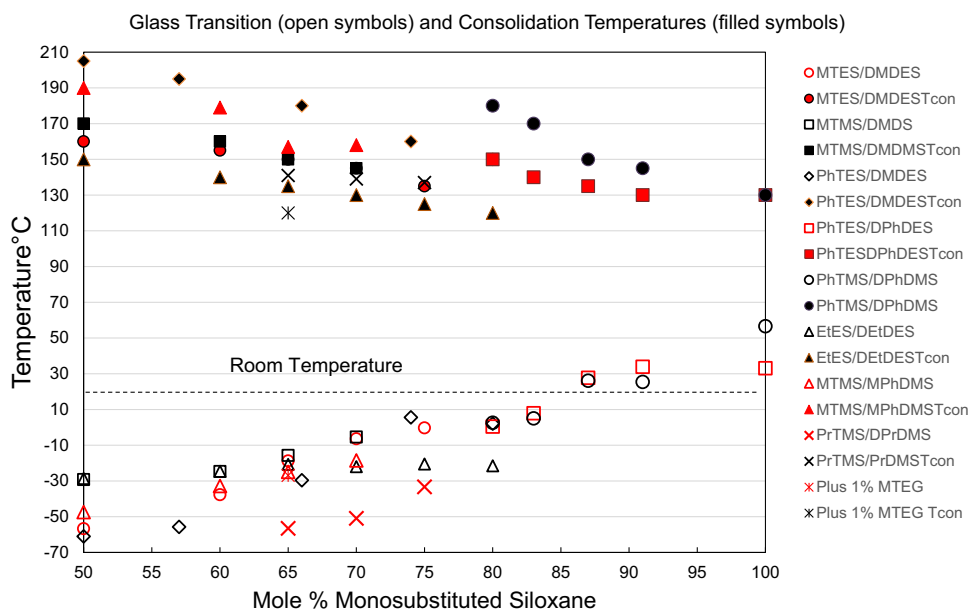


Fig. 1 Approximate thermal weight loss corresponding to possible species in a model melting gel composition with 50% MTES – 50% DMEDES

Fig. 2 Glass transition temperature (T_g) and consolidation temperature (T_{con}) for all investigated melting gel compositions vs. mol % mono-substituted siloxane, with ethyl, methyl, phenyl and mixed substitutions, including those plotted in Fig. 1 (2019)



plot, as the intersection of tangents as the heat flow versus temperature curve bends. The consolidation temperature was determined when the sample lost its ability to resoften following 17–24 h of heating. The trends for all seven families are that the glass transition temperatures increase and the consolidation temperatures decrease as the mol% mono-substituted siloxane approaches 100%. Note there are no melting gels with more than 50 mol% of the di-substituted siloxane.

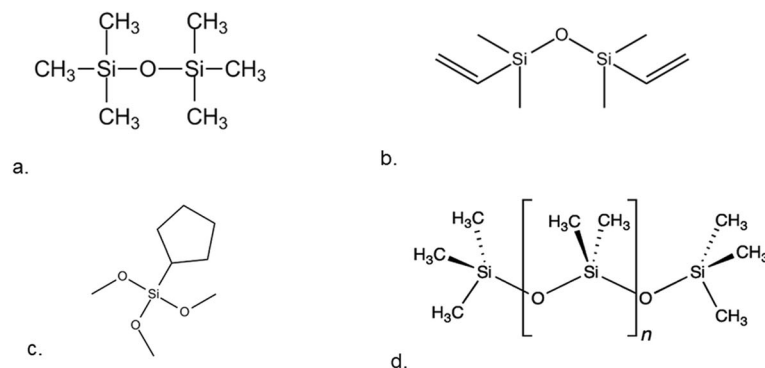
Thin films and monoliths have been made from precursors with different levels of substitution groups. The thermal analysis showed that combinations of alkyl groups did not affect significantly the endothermic process of removing solvent or water. However, precursors with large substituted groups, such as phenyl-groups, required higher temperature to remove the bulkier groups. The alkyl group caused a decrease in the temperature of the exothermic peak as the size of the group reduced. MTES with TEOS samples showed that the methyl group is easier to remove than the ethoxy-groups according to DSC measurements [6].

A one-step acid catalysis method was used to synthesize melting gels using phenyltrimethoxysilane (PhTMS) with diphenyldimethoxysilane (DPhDMS), along with phenyltriethoxysilane (PhTES) with diphenyldiethoxysilane (DPhDES) [6, 15]. The consolidation temperature increased with an increase in di-substituted siloxane for both systems, while the glass transition temperature demonstrated the opposite trend. Subsequently, this system was modified with additions of TEOS and TMOS. By including a precursor with 4 hydrolyzable groups, it was thought that the network would be stronger. However, there were dilution effects and concerns about phase separation [17].

Figure 2 is an updated compilation of glass transition temperatures and consolidation temperatures. The previous version has been expanded to include data obtained since 2017 [9]. An updated listing of many of the precursors that have been incorporated into melting gels is given in Table 1. The compositions are grouped according to the number of components. First there are the single precursor

compositions that result in melting gels. Second, there are the two precursor compositions that include a mono-substituted and a di-substituted melting gel, or TEOS plus a mono- or di-substituted precursor. Last, there are three precursor compositions, where the third precursor is tetra-functional and added in small amounts. Generally, the alkyl groups have 1, 2 or 3 carbons. Mono-substituted siloxanes

Fig. 3 Molecular structures of some recent additions to melting gels: **a** Hexamethyldisiloxane, **b** 1,3-Divinyltetramethyl disiloxane **c** Cyclopentyl trimethoxysilane, **d** PDMS poly(dimethylsiloxane)



Molecular structures of some recent additions to melting gels:

(a) Hexamethyldisiloxane, (b) 1,3-Divinyltetramethyl disiloxane (c) Cyclopentyl trimethoxysilane, (d) PDMS poly(dimethylsiloxane)

Table 1 Reagents used in the Synthesis of Oligomeric Silsesquioxanes and Melting Gels (Those marked with * are illustrated in Fig. 2)

Name	Abbreviation	Chemical Formula	Number of Hydrolyzable Groups
1-Component			
Methyl triethoxysilane	MTES	$C_7H_{18}O_3Si$	3
Phenyl triethoxysilane*	PhTES	$C_{12}H_{20}O_3Si$	3
Cyclohexyl trimethoxysilane or Phenyl trimethoxysilane	PhTMS	$C_9H_{14}O_3Si$	3
Cyclopentyl trimethoxysilane*	PenTMS	$C_8H_{18}O_3Si$	3
2-Components - Mono- and di-substituted			
Ethyl triethoxysilane with	EtES	$C_8H_{20}O_3Si$	3
Diethyl diethoxysilane	DEtDES	$C_4H_{12}O_2Si$	2
Methyl triethoxysilane with	MTES	$C_7H_{18}O_3Si$	3
Dimethyl diethoxysilane	DMDES	$C_6H_{16}O_2Si$	2
Methyl trimethoxysilane with	MTMS	$C_4H_{12}O_3Si$	3
Dimethyl dimethoxysilane	DMDMS	$C_4H_{12}O_2Si$	2
Methyl trimethoxysilane with	MTMS	$C_4H_{12}O_3Si$	3
Methyl phenyl dimethoxysilane	MPhDMS	$C_9H_{14}O_2Si$	2
Phenyl triethoxysilane with	PhTES	$C_{12}H_{20}O_3Si$	3
Diphenyl diethoxysilane	DPhDES	$C_{16}H_{20}O_2Si$	2
Phenyl trimethoxysilane with	PhTES	$C_{12}H_{20}O_3Si$	3
Dimethyl diethoxysilane	DMDES	$C_6H_{16}O_2Si$	2
Phenyl trimethoxysilane with	PhTMS	$C_9H_{14}O_3Si$	3
Diphenyl dimethoxysilane	DPhDMS	$C_{14}H_{16}O_2Si$	2
Propyl trimethoxysilane with	PrTMS	$C_6H_{16}O_3Si$	3
Dipropyl dimethoxysilane*	Diso-PDMS	$C_8H_{20}O_2Si$	2

Table 1 (continued)

Name	Abbreviation	Chemical Formula	Number of Hydrolyzable Groups
2-components -Mono-or di-substituted With TEOS			
Methyltriethoxysilane with	MTES	C ₇ H ₁₈ O ₃ Si	3
Tetraethoxysilane	TEOS	C ₈ H ₂₀ O ₄ Si	4
Phenyl triethoxysilane with	PhTES	C ₁₂ H ₂₀ O ₃ Si	3
Tetraethoxysilane	TEOS	C ₈ H ₂₀ O ₄ Si	4
Dimethyl diethoxysilane with	DMDDES	C ₆ H ₁₆ O ₂ Si	2
Tetraethoxysilane	TEOS	C ₈ H ₂₀ O ₄ Si	4
3-Components			
Phenyl triethoxysilane with	PhTES	C ₁₂ H ₂₀ O ₃ Si	3
Diphenyl diethoxysilane	DPhDES	C ₁₆ H ₂₀ O ₂ Si	2
Tetraethoxysilane	TEOS	C ₈ H ₂₀ O ₄ Si	4
Phenyl trimethoxysilane with	PhTMS	C ₉ H ₁₄ O ₃ Si	3
Diphenyl dimethoxysilane	DPhDMS	C ₁₄ H ₁₆ O ₂ Si	2
Tetramethoxysilane	TMOS	C ₄ H ₁₂ O ₄ Si	4
Methyl triethoxysilane with	MTES	C ₇ H ₁₈ O ₃ Si	3
Dimethyl diethoxysilane	DMDDES	C ₆ H ₁₆ O ₂ Si	2
Tetraethoxygermane	TEG	C ₈ H ₂₀ O ₄ Ge	4
Phenyl triethoxysilane with	PhTES	C ₁₂ H ₂₀ O ₃ Si	3
Hexamethyldisiloxane*	HMDS	C ₆ H ₁₈ OSi ₂	-
1,3-Divinyltetramethyldisiloxane*	DVMDS	C ₈ H ₁₈ OSi ₂	-

may be diluted and co-hydrolyzed with tetrafunctional alkoxysilanes, such as TEOS. There is a subset of ormosils where a bridge is formed between two Si atoms producing arylene or alkylene-bridged polysilsesquioxanes [16].

One interesting point in Fig. 2 is the one showing the effect of substituting 1% of the silica with germania, through a substitution of 1% MTEG for MTES. The substitution of 1% MTEG caused a decrease in the glass transition temperature from -18.8 to -26.9 °C, along with a decrease in the consolidation temperature from 150 to 120 °C. This is a sizable decrease for such a small substitution, and is attributed to shorter, less crosslinked molecular chains. The substitution was intended to increase the thermal stability of the network and to decrease the time of consolidation. This work using a more electronegative species such as Ge instead of Si is not yet published.

Organically modified polysilsesquioxanes with melting behavior were obtained by using hydrochloric acid first to hydrolyze the mixture, followed by ammonia for condensation [18]. This two-step process produced melting behavior using PhTES alone. When DPhDES or DMDDES was added as a second component, the gels continued to show softening. The trend was that the gels showed a decrease in network connectivity by incorporation of di-substituted siloxanes, making it possible to obtain melting gels over a range of compositions [19].

The trends in behavior of substitutions with 1, 2, 3 or 4 carbons in the substitution has been confirmed in a number of cases [20]. When the number of carbons is increased to 6, 7 and 8, the tendency is towards aggregation into cage-like structures and increased steric hindrance. The glass transition temperatures recorded using DSC were as low as -77 °C for 8 carbons and -97 °C for 6 carbons. Further increase in the number of carbons to 10, 12, 16 and 18 carbons encouraged self-assembly and lamellar structures. In these samples, no glass transition behavior was observed. This study is valuable for placing a limit on the species that can be incorporated into a melting gel [21].

3 Characterization techniques

In addition to studies using thermal analysis, melting gels have been characterized using rotational viscometry [22]. The glass transition temperature measured in both cases are very close. Most of the studies have used infrared spectroscopy to identify species in gels, and this has been expanded to other spectroscopies.

For example, ²⁹Si-NMR has been used to characterize molecular structures in the PhTES-DPhDES and MTES-DMDDES systems. ²⁹Si-NMR spectra showed that the molecular structures of the gels were three-dimensional

siloxane networks with phenyl groups that interacted weakly with each other. The number of bridging oxygens between silicons and the intramolecular structure was shown to influence the viscosity [23].

^{13}C and ^{29}Si NMR spectroscopy along with synchrotron-based small angle x-ray scattering (SAXS) have been used to characterize the structure in detail. In particular, the SAXS results show that the glasses are homogeneous from the nm to μm length scales [24].

4 Applications

Originally, melting gels were developed to replace low melting temperature sealing glasses, which melt around $600\text{ }^\circ\text{C}$ [25, 26]. Because this temperature is too high for electronic packaging, for organic light emitting diodes (OLED) and thin film transistors (TFT), it was important to find materials with lower processing temperatures. Successful applications are mainly optical materials, especially those that require texturing and patterning, coatings that are corrosion barriers and protective layers, and hosts for optically active species.

4.1 Optical applications

Among melting gels that were developed to replace low melting inorganic glasses, it was found that the refractive index of hybrid coatings varied according to the quantity of the organic bonded to the inorganic network, making them candidates for waveguides [27]. To test this idea, a waveguide was prepared by microfluidic lithography, based on PhTES, MTES and TEOS [28]. Using this method, patterned microstructures with a linewidth of 20 and $35\text{ }\mu\text{m}$ were obtained. Pregrooves $1.6\text{ }\mu\text{m}$ in pitch and 86 nm in depth were patterned on a 130 mm diameter glass disk substrate for optical data storage using MTES and TEOS [29]. Since then, several composition have been developed that facilitate imprint lithography [30–32].

The earliest reports of softening gels focused on continuous, transparent thick films on indium tin oxide (ITO) coated glass substrates applied by electrophoretic deposition of phenylsilsesquioxane particles. The morphology of the thick films changed after heat treatment, from aggregates of particles to continuous thick films. Softening behavior was observed in films, prepared with poly(benzylsilsesquioxane) particles, as well [19].

Melting gels consisting of MTES and DMEDES were investigated for hermetic barriers for electronic devices to protect them from humidity and atmospheric gasses [6]. Nitrogen sorption BET surface area measurements showed that these gels were non-porous. In a comparison of melting gels from MTES–DMEDES and methyltrimethoxysilane

(MTMS)–dimethyldimethoxysilane (DMDMS) systems and their ability to form hydrophobic hybrid glass coatings, both systems showed melting gel behavior and formed hybrid glass coatings on mica substrates of $\sim 1\text{ mm}$ thickness with no visible cracks, and contact angles greater than 90° [4].

When the thermal behavior of melting gels in the MTES–DMEDES system was studied, it was found that the consolidation temperature increased with an increase in the number of non-hydrolytic groups [7]. In the 50 mol% MTES–50 mol% DMEDES composition a dielectric constant as low as 3.3 was measured by impedance spectrometry at frequencies greater than 1 kHz. As direct Si–C bonds are less polarizable than $\equiv\text{Si–O–Si}\equiv$, the di-substituted siloxane, DMEDES, contributes to decreasing the dielectric constant [11]. Another study showed that varying the ratio of mono-substituted to di-substituted siloxane or varying the substituted group from aromatic to aliphatic made it possible to adjust the temperatures for softening and consolidation. The range between glass transition temperature and consolidation temperature is relevant to microfabrication of optoelectronics or chemical sensors that require pattern transfer and imprinting [30–32].

A typical result of the capillary molding process is that walls maintain a high aspect ratio of 5:1. Silsesquioxane glasses are being developed for more applications where the softening behavior facilitates their use for patterning. When prepared without solvent from a single precursor, such as cyclopentyl or cyclohexyl trimethoxysilanes, it is possible to obtain clear glasses that are transparent in the deep-UV. The glass transition temperature can be as high as $70\text{ }^\circ\text{C}$. The viscosity behavior is classified as fragile according to the Vogel-Fulcher-Tammann equation [33].

Over the past 20 years, more and more uses for melting gels have been found. For example, hybrid gels described as silsesquioxanes with $\equiv\text{Si–O–Si}\equiv$ backbones and lateral organic groups are being used as hydrogen scavengers in fiber optic cables [34]. In cases where a high refractive index is needed, alkoxy silanes modified with naphthyl and phenanthrenyl groups have been processed into melting gels in order to reach a refractive index greater than 1.6 and still maintain transparency [35, 36].

It should be mentioned that unconsolidated gels stored in closed containers for more than a year exhibited softening when warmed up. It is not surprising that the samples with no water in them are stable at room temperature.

4.2 Corrosion barriers

Melting gels from MTES and DMEDES have been used as anticorrosive coatings for AISI 304 stainless steel [37, 38] and magnesium [39]. Thick, hydrophobic, crack-free and nonporous coatings were formed. The coatings showed some plasticity in scratch tests and good adhesion to the

substrate through hydroxyl bonds. Electrochemical tests showed excellent performance of the coatings against corrosion with no sign of degradation even after several months of immersion in 3.5% sodium chloride solution.

Some treatments with mixtures of TEOS and MTES have been applied to 304 stainless steel by spraying [40] or dipping [41]. Some sprayed layers were followed by dip coatings to decrease the surface roughness. In addition to the organically modified sol-gel coatings, some coatings have been prepared with TEOS, 3-methacryloxy propyl trimethoxysilane (MPTS) followed by thermal curing with methyl methacrylate on mild steel [42]. Besides the studies on steels, there are studies of organic-inorganic coatings for aluminum alloys. For example, TEOS and triethoxy octylsilane (TEOCS) has been tested on aluminum alloys such as AA2024 [43].

4.3 Nanoparticle hosts

Melting gels are a suitable host material for nanoparticles. In particular, gold nanoparticles are used for their chemical stability and their electromagnetic confinement that produces localized surface plasmon resonance [44, 45]. These localized surface plasmon resonances result in amplification of light by orders of magnitude enabling chemical sensors based on surface plasmon resonance, as well as sensors based on surface enhanced Raman spectroscopy (SERS).

Functionalized gold nanoparticles have been encapsulated in sol-gel hybrid silica. In some cases, the nanoparticles were used as dopants for the hybrid silica gel offering the property of localized surface plasmon resonance. To ensure dispersion in the glass matrix, the nanoparticles were functionalized by a polymer mixture of organosilanes [45]. The final nanocomposite showed shifts in the plasmonic behavior that were attributed to size effects and the properties of the matrix, rather than surface plasmon resonance coupling indicative of particle agglomeration.

Gold nanoparticles suspended in acetone were introduced easily into a 65 mol% MTES – 35 mol% DMDES melting gel during the purification step [46]. For this composition, the glass transition temperature is $-18.8\text{ }^{\circ}\text{C}$ and the consolidation temperature is $150\text{ }^{\circ}\text{C}$. While the gel solution was stirred at high speed, the acetone suspension of gold nanoparticles was added. The gels were heated at $70\text{ }^{\circ}\text{C}$ for 24 h for the removal of the remaining organic solvents, ethanol and acetone, after which they were heated to $110\text{ }^{\circ}\text{C}$ to remove any remaining water.

The doped sample had a light violet color. UV-Vis spectra indicated that when gold citrate nanospheres were incorporated in the melting gel, there was a plasmon shift in the spectra for the consolidated sample. Melting gels with gold nanoparticles showed a broad plasmon peak at around 568 nm, compared to the undoped coating, which showed

no peak. The plasmon peak confirmed that the gold nanoparticles were incorporated in the melting gel without modification [46].

4.4 Related systems

Some different but related systems have been investigated for showing glass transition behavior well below room temperature. For example, silica-poly(dimethylsiloxane) (PDMS) composites have been prepared. In this case, hydride-terminated PDMS (MW = 17,200) was mixed with 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane in the presence of a catalyst. Films of this composition was allowed to swell in TEOS in the presence of a catalyst. In this way, composites with up to about 23.5 weight % were achieved. The glass transition temperature was around $-115\text{ }^{\circ}\text{C}$ and did not vary much with silica content, although increased silica content made crystallization of the PDMS more difficult [47].

Recently, a similar behavior to melting gels has been observed in solutions more commonly associated with metal organic framework (MOF) systems. Titanium and zirconium alkoxides were hydrolyzed in the presence of some β -diketones. A low temperature thermomechanical analyzer was used to measure glass transition temperatures over a wide range, from $-30\text{ }^{\circ}\text{C}$ for titanium with a succinic anhydride chelating agent to $20\text{ }^{\circ}\text{C}$ for zirconium with an ethyl benzoylacetate chelating agent. The behavior was attributed to clusters forming with M-O-M bonds surrounded by weakly bonded organic ligands [48].

As the original focus of melting gels was to find an alternative to low-temperature sealing glasses, there continue to be studies beginning with PhTES which can be modified in many ways, with for example hexamethyl disiloxane and divinyltetramethyldisiloxane, to improve its mechanical properties [49]. The important feature of this system is the near total absence of silanol groups. In fact, the ability to remove silanols in the final step of preparing melting gels is an important quality of these materials as the number of applications expands.

5 Summary

Melting gels generally contain a mono-substituted and a di-substituted siloxane. Depending on the substitution, both the glass transition and the consolidation temperature varies, and consequently the temperature window between the two changes in a systematic way. The window represents the temperature range where the gels can be manipulated in a number of ways to make thin and thick films, to prepare textured surfaces, and to employ imprint lithography.

Many combinations of mono-substituted and di-substituted siloxanes have been processed into melting gels. The gels can be used in bulk form and applied as thin and thick coatings. The gels typically have no measurable porosity, because the organic groups fill in spaces in the silicate network. These properties make it possible to use melting gels and their corresponding hybrid glasses for corrosion barriers, low temperature sealing glasses, dielectric layers, hydrophobic coatings, and hosts for optical devices.

Data availability

Data is provided within the manuscript.

Acknowledgements Financial support was received from NSF Award 1313544 Materials World Network-SusChEM and Ministerio de Economía y Competitividad, SPAIN (PCIN-2013-030).

Author contributions The authors contributed equally to the experimental work reported in the paper. Klein prepared the manuscript and Jitianu reviewed the manuscript.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Sakka S, Kamiya K (1982) The sol-gel transition in the hydrolysis of metal alkoxides in relation to the formation of glass fibers and films. *J Non-Cryst Solids* 48:31–46
- Sakka S (1988) Fibers from the sol-gel process in Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes, ed. Klein LC, Noyes Publications, Park Ridge, NJ, pp. 140–161
- West JK, Zhu BF, Cheng YC, Hench LL (1990) Quantum chemistry of sol-gel silica clusters. *J Non-Cryst Solids* 121:51–55
- Jitianu A, Amatucci G, Klein LC (2008) Organic-inorganic sol-gel thick films for humidity barriers. *J Mater Res* 23:2084–2090
- Matsuda A, Matsuno Y, Tatsumisago M, Minami T (1998) Fine patterning and characterization of gel films derived from methyltriethoxysilane and tetraethoxysilane. *J Am Ceram Soc* 81:2849–2852
- Jitianu A, Amatucci G, Klein LC (2009) Phenyl-substituted siloxane hybrid gels that soften below 140 °C. *J Am Ceram Soc* 92:36–40
- Jitianu A, Doyle J, Amatucci G, Klein LC (2010) Methyl modified siloxane melting gels for hydrophobic films. *J Sol-Gel Sci Technol* 53:272–279
- Jitianu A, Gonzalez G, Klein LC (2015) Hybrid sol-gel glasses with glass-transition temperatures below room temperature. *J Am Ceram Soc* 98:3673–3679
- Klein LC, Kallontzi S, Fabris L, Jitianu A, Ryan C, Aparicio M, Lei L, Singer JP (2019) Applications of melting gels. *J Sol-Gel Sci Technol* 89:66–77
- Jitianu M, Jitianu A, Stamper M, Aboagye D, Klein LC (2013) Melting gel films for low temperature Seals, MRS Spring 2013 Meeting Symposium M: Solution Synthesis of Inorganic Functional Materials – Films, Nanoparticles, and Nanocomposites, eds. Jain M, Jia Q, Puig T and Kozuka H. Vol. 1547, Materials Research Society, Warrendale, PA, pp. 81–86
- Gambino L, Jitianu A, Klein LC (2012) Dielectric behavior of organically modified siloxane melting gels. *J Non-Cryst Solids* 358:3501–3504
- Kuniyoshi M, Takahashi M, Tokuda Y, Yoko T (2006) Hydrolysis and polycondensation of acid-catalyzed phenyltriethoxysilane (PhTES). *J Sol-Gel Sci Technol* 39:175–183
- Klein LC, Jitianu A (2010) Organic-inorganic hybrid melting gels. *J Sol-Gel Sci Technol* 55:86–93
- Jitianu A, Lammers K, Arbuckle-Kiel GA, Klein LC (2011) Thermal analysis of organically modified siloxane melting gels. *J Therm Anal Calor* 107:1039–1045
- Kakiuchida H, Takahashi M, Tokuda Y, Masai H, Kuniyoshi M, Yoko T (2006) Viscoelastic and structural properties of a phenyl-modified polysiloxane system with a three-dimensional structure. *J Phys Chem B* 110:7321–7327
- Shea KJ, Loy DA, Webster OW (1989) Aryl-bridged polysilsesquioxanes-new microporous materials. *Chem Mater* 1:572–574
- Al-Marzoki K, Klein LC, Jitianu A (2020) Effect of tetraethoxyethoxysilane on melting gel. *Behav J Am Ceram Soc* 103:4140–4149
- Katagiri K, Hasegawa K, Matsuda A, Tatsumisago M, Minami T (1998) Preparation of transparent thick films by electrophoretic sol-gel deposition using phenyltriethoxysilane-derived particles. *J Am Ceram Soc* 81:2501–2503
- Matsuda A, Sasaki T, Hasegawa K, Tatsumisago M, Minami T (2001) Thermal softening behavior and application to transparent thick films of poly(benzylsilsesquioxane) particles prepared by the sol-gel process. *J Am Ceram Soc* 84:775–780
- Picard Q, Akalonu G, Mercado J, Mosa J, Aparicio M, Klein LC, Jitianu A (2018) Electrodeposition of hybrid sol-gel glass coatings on 304 stainless steel for corrosion protection, *Ceramic Transactions 265: Advances in Materials Science for Environmental and Energy Technologies V*, eds. Ohji T, Kanakala R, Matyas J, Manjoran NJ, Wong-Ng WK, American Ceramic Soc., Westerville, OH, pp. 205–220
- Pohl S, Kickelbick G (2023) Influence of alkyl groups on the formation of softenable polysilsesquioxanes. *Sol-Gel Sci Tech* 107:329–346
- Kamimura Y, Kurumada K, Asaba K, Banno H, Kambara H, Hiro M (2006) Evaluation of activation energy of viscous flow of sol-gel derived phenyl-modified silica glass. *J Non-Cryst Solids* 352:3175–3178
- Kakiuchida H, Takahashi M, Tokuda Y, Masai H, Yoko T (2007) Effects of organic groups on structure and viscoelastic properties of organic-inorganic polysiloxane hybrid system. *J Phys Chem B* 111:982–988

24. Jitianu A, Cadars S, Zhang F, Rodriguez G, Picard Q, Aparicio M, Mosa J, Klein LC (2017) ^{29}Si NMR and SAXS investigation of the hybrid organic–inorganic glasses obtained by consolidation of the melting gels. *Dalton Trans* 46:3729–3741
25. Kurumada K, Ashraf KM, Matsumoto S (2014) Effects of heat treatment on various properties of organic–inorganic hybrid silica derived from phenyltriethoxysilane. *Mat Chem Phys* 144:132–138
26. Masai H, Takahashi M, Tokuda Y, Yoko T (2005) Gel-melting method for preparation of organically modified siloxane low-melting glasses. *J Mater Res* 20:1234–1241
27. Macan J, Tadanaga K, Tatsumisago M (2010) Influence of copolymerization with alkyltrialkoxysilanes on condensation and thermal behavior of poly(phenylsilsesquioxane) particles. *J Sol-Gel Sci Technol* 53:31–37
28. Kuniyoshi M, Takahashi M, Tokuda Y, Yoko T (2007) Thermosoftening phenyl siloxane glasses prepared via sol concentration. *J Non-Cryst Solids* 353:4162–4169
29. Mah SK, Chung IJ (1995) Effects of dimethyldiethoxysilane addition on tetraethylorthosilicate sol-gel process. *J Non-Cryst Solids* 183:252–259
30. Jeong S, Ahn S-J, Moon J (2005) Fabrication of patterned inorganic-organic hybrid film for the optical waveguide by microfluidic lithography. *J Am Ceram Soc* 88:1003–1036
31. Back F, Bockmeyer M, Rudigier-Voigt E, Lobmann P (2013) Hybrid polymer sol-gel material for UV-nanoimprint: Microstructure and thermal densification. *J Sol-Gel Sci Technol* 66:73–83
32. Kim E, Xia Y, Whitesides GM (1996) Micromolding in capillaries: applications in materials science. *J Am Chem Soc* 118:5722–5731
33. Kajihara K, Suzuki R, Seto R, Itakura H, Ishijima M (2023) Poly(cyclohexyl-silsesquioxane)-based hydrophilic thermoset-resistant deep-ultraviolet-transparent glasses with low melting temperatures. *ACS Appl Mater Interfaces* 15:31880–31887
34. Stolov AA, Li J, Hokansson AS, Hines MJ (2022) Effects of hydrogen scavenging cable gel on the strength and attenuation of optical fibers. *J Lightwave Technol* 40:6264–6271
35. Briesenick M, Gallei M, Kickelbick G (2022) High-refractive-index polysiloxanes containing naphthyl and phenanthrenyl groups and their thermally cross-linked resins. *Macromolecules* 55:4675–4691
36. Huang S-Y, Wang J-S (2017) Thermally stable conformal encapsulation material for high-power ultraviolet light-emitting diodes. *Optical Eng* 56:077105-1-5
37. Aparicio M, Jitianu A, Rodriguez G, Degnah A, Al-Marzoki K, Mosa J, Klein LC (2016) Corrosion protection of AISI 304 stainless steel with melting gel coatings. *Electrochim Acta* 202:325–332
38. Aparicio M, Jitianu A, Rodriguez G, Al-Marzoki K, Jitianu M, Mosa J, Klein LC (2017) Thickness-properties synergy in organic–inorganic consolidated melting-gel coatings for protection of 304 stainless steel in NaCl solutions. *Surf Coat Technol* 315:426–435
39. Aparicio M, Mosa J, Rodriguez G, Guzman J, Picard Q, Klein LC, Jitianu A (2019) Consolidated melting-gel coatings on AZ31 magnesium alloy with excellent corrosion resistance in NaCl solutions – an interface study. *ACS Appl Mater Interfaces* 11:3493–3505
40. Hwang T, Lee HY, Kim H, Kim GT (2010) Two layered silica protective film made by a spray-and-dip coating method on 304 stainless steel. *J Sol-Gel Sci Technol* 55:207–212
41. Nikrooz B, Zandrahimi M, Ebrahimifar H (2012) High temperature oxidation resistance and corrosion properties of dip coated silica coating by sol-gel method on stainless steel. *J Sol-Gel Sci Technol* 63:286–293
42. Hammer P, dos Santos FC, Cerrutti BM, Pulcinelli SH, Santilli CV (2012) Highly corrosion resistant siloxane-polymethyl methacrylate hybrid coatings. *J Sol-Gel Sci Technol* 63:266–274
43. Pan X, Wu J, Ge Y, Xiao K, Luo H, Gao S, Li X (2014) Preparation and characterization of anticorrosion Ormosil sol-gel coatings for aluminum alloy. *J Sol-Gel Sci Technol* 72:8–20
44. Lunden H, Liotta A, Chateau D, Lerouge F, Chaput F, Parola S, Brannlund C, Ghadyani Z, Kildemo M, Lindgren M, Lopes C (2015) Dispersion and self-orientation of gold nanoparticles in sol–gel hybrid silica – optical transmission properties. *J Mater Chem C* 3:1026–1034
45. Chateau D, Liotta A, Gregori D, Lerouge F, Chaput F, Desert A, Parola S (2017) Controlled surface modification of gold nanostructures with functionalized silicon polymers. *J Sol-Gel Sci Technol* 81:147–153
46. Kallontzi S, Fabris L, Jitianu M, Hernandez A, Jitianu A, Klein LC (2019) Gold nanoparticles in melting gels. *J Sol-Gel Sci Technol* 91:189–197
47. Fragiadakis D, Pissis P, Bokobza L (2005) Glass transition and molecular dynamics in poly(dimethylsiloxane)/silica nanocomposites. *Polymer* 46:6001–6008
48. Tsuitsui R, Oda S, Suzuki K, Nakano H, Emi Y, Yamazaki S, Kozuka H (2024) Glass transition of amorphous materials composed of organically modified metal oxo-oligomers. *Mater Chem Phys* 314:128845.
49. Liu F, Zeng X, Lai X, Li H (2017) Synthesis and characterization of polyphenylsilsesquioxane terminated with methyl and vinyl groups low-melting glass. *J Adhes Sci Technol* 31:2399–2409