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Phenyl-Substituted Siloxane Hybrid Gels that Soften Below 140°C

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A characteristic of so-called melting gels is that the gels, which are rigid at room temperature, are able to soften and resoften at temperatures around 110°C. However, after consolidation at temperatures higher than 150°C, the gels no longer resoften. Two systems of melting gels were investigated: phenyltrimethoxysilane (PhTMS)–diphenyldimethoxysilane (DPhDMS) and phenyltriethoxysilane (PhTES)–diphenyldiethoxysilane (DPhDES). The influence of disubstituted versus monosubstituted alkoxide on the softening behavior and the temperature of decomposition was studied. The consolidation temperature increased as the amount of disubstituted alkoxide increased, while the decomposition temperature increased only slightly. In general, the ethoxy-containing gels (maximum at 150°C) consolidated at lower temperatures than the methoxy-containing gels (maximum at 180°C).

I. Introduction

HYBRID organic–inorganic materials prepared by the sol–gel process are not simple physical mixtures of inorganic and organic components. This is revealed in the synergistic trends of physical and chemical properties, which are significantly different from mixing models of the individual components.^{1,2} These hybrids have been classified broadly on the basis of the interaction between inorganic and the organic components and have been divided into two main classes.³ Class I refers to materials where the organic and inorganic components are embedded and display weak bonds, such as hydrogen bonds or van der Waals bonds. Class II refers to hybrid materials where strong covalent bonds are present between the inorganic and the organic components. For the second class of hybrid materials, the most common types of precursors are organo-alkoxysilanes with the general formula $R'_n\text{-Si(OR)}_{4-n}$ where $n = 1, 2, \text{ or } 3$ and R' is $-\text{CH}_3$, $-\text{C}_6\text{H}_5$, and $-\text{CH}=\text{CH}_2$, among others.

Schmidt^{4,5} classified the organo-alkoxysilanes as network modifiers (e.g., R' is methyl or phenyl) when the modifiers are stable toward a chemical reaction or as network formers (e.g., R' is vinyl or methacryl) when the modifier can react with itself or another polymerizable group to form additional organic chains. Two common organo-alkoxysilanes, which act as network modifiers, are methyltriethoxysilane (MTES)⁶ and phenyltriethoxysilane (PhTES).⁷ The formation of the molecular species during the hydrolysis-polycondensation of PhTES was studied by Kuniyoshi *et al.*⁷ Using gel permeation chromatography (GPC) and ²⁹Si NMR spectroscopy, they showed that hydrolysis and polycondensation proceeded simultaneously when hydrochloric acid was used as a catalyst. In contrast, hydrolysis went to completion before polycondensation when ace-

tic acid was used as a catalyst. Also, it was shown that the polycondensation rate could be controlled by changing the reaction temperature.

Kamimura *et al.*⁸ determined the activation energy for softening in phenyl polysiloxane glasses prepared using PhTES. The phenyl groups produced domains in the glass that allowed softening at low temperatures. Using PhTES together with diphenyldiethoxysilane (DPhDES) with two steps of catalysis, Masai *et al.*⁹ showed that it is possible to obtain phenyl-modified siloxane with a low softening temperature. In the first step, they used hydrochloric acid, followed by ammonia in the second step for condensation.

The viscoelastic properties of the phenylpolysiloxane network were studied.^{10,11} The flow of the phenylpolysiloxane molecules was related to the molecular volume and the intramolecular structure using a free-volume model. The number of bridging oxygens between silicons was shown to influence the viscosity. An increase in the number of phenyl groups decreased the number of bridging oxygens, leaving only weak interactions between 3D siloxane networks.¹⁰ The intermolecular entanglements played a role in the softening behavior of these materials.¹¹ It was also found that the increase of the elastic modulus with heat treatment was slower when the number of phenyl groups was increased.

The softening behavior of melting gels was initially observed by Matsuda *et al.*,^{12,13} who prepared poly(benzylsilsesquioxane) particles that were then deposited on an ITO substrate by electrophoretic deposition. After heat treatment, continuous thick transparent films were obtained. The softening behavior was mislabeled “melting,” but the name has remained. For cases where hybrid gels are being used to replace low melting temperature glasses, the mislabeling has persisted, which is why these hybrids have come to be known as melting gels.

In this study, a one-step acid catalyst method was used to synthesize sol–gel hybrids using phenyl substituted alkoxides. Phenyltrimethoxysilane (PhTMS) with diphenyldimethoxysilane (DPhDMS) and PhTES with DPhDES were studied. In effect, the methoxy alkoxide was compared with the ethoxy alkoxide. The consolidation temperature was determined as the ratio between monosubstituted and disubstituted alkoxide was varied. These gels were used to produce ~2-mm-thick coatings on mica, silicon wafers, and polycarbonate substrates.

II. Experimental Procedures

The preparation of two “melting gel” systems was carried out using pairs of mono- and disubstituted alkoxysilanes, PhTMS (Gelest Inc., Morrisville, PA) with DPhDMS (Gelest Inc.) and PhTES (Fluka Chemicals, Milwaukee, WI) with DPhDES (Sigma-Aldrich, Milwaukee, WI). All of the substituted alkoxides were used without further purification. Hydrochloric acid (Fisher Scientific, Atlanta, GA) was used as a catalyst. As solvents, anhydrous methanol (Sigma-Aldrich) was used with PhMTMS–DPhDMS and anhydrous ethanol (Sigma-Aldrich) was used with PhTES–DPhDES system. These gels were prepared using the number of moles of mono- to disubstituted

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Table I. Composition, Consolidation Temperature, Coating Thickness, and Surface Roughness for Phenyltrimethoxysilane (PhTMS)–Diphenyldimethoxysilane (DPhDMS) Gels

Composition moles		Consolidation temperature (°C)	Coating thickness (mm)	Average roughness (mm)
PhTMS	DPhDMS			
1.0	0.25	180	1.57	19.6
1.0	0.20	170	1.39	19.3
1.0	0.15	150	1.62	8.2
1.0	0.10	145	1.88	7.9
1.0	0.0	130	1.79	2.5

alkoxides as indicated in Tables I and II. The synthesis route for PhTMS–DPhDMS is shown in the flowchart (Fig. 1).

For both systems, a two-step synthesis was used. First, the monosubstituted alkoxide and water were mixed together. The molar ratios of PhTMS:H₂O and PhTES:H₂O were 1:1.5. The pH of the water was adjusted to 2.5 using a 0.1 N HCl solution. After the water was added to the PhTMS or to the PhTES, the mixture was stirred continuously at 40°C in a covered beaker. In the absence of a cosolvent, the mixtures initially showed immiscibility between water and monosubstituted alkoxide. With PhTMS, a clear solution was obtained after 30 min of stirring, while with PhTES, a clear solution was obtained after 5 h of stirring. All mixtures were mixed at 40°C for 6 h.

In the second step, the disubstituted alkoxide DPhDMS was diluted with methanol and DPhDES was diluted with ethanol. The molar ratio was 4 mol alcohol to 1 mol disubstituted alkoxide. The disubstituted alkoxide–alcohol mixture was added dropwise to the clear solution of monosubstituted alkoxide and water. This mixture was stirred for another two hours in a closed beaker at 40°C. Then, the clear solution was cooled to room temperature and stirred overnight in an open system until gelation occurred. The gels were then dried at 70°C for 24 h, followed by a heat treatment at 110°C. After these heat treatments, the gels were solid at room temperature, but they resoftened at ~110°C. The consolidation temperatures, after which the gels no longer soften, were determined experimentally and are listed in Tables I and II.

Coatings were deposited by pouring the gels onto different substrates when the gels were fluid. Mica, silicon wafers, and polycarbonate were used as substrates. Following deposition, the coatings were treated at the consolidation temperatures listed in Tables I and II for 24 h.

The thermal behavior of the hybrid gels was studied using differential thermal analysis (Perkin-Elmer DTA-7, Waltham, MA), thermogravimetric analysis (Perkin-Elmer TGA-7), and differential scanning calorimetry (DSC TA-Q-2000, Thermal Analysis Instrument Specialists, Twin Lakes, WI). DTA and TG were recorded at a 5°C/min heating rate in the temperature range between 50° and 800°C under flowing air (20 mL/min). The DSC analyses were recorded using a 5°C/min heating rate between –40° and 200°C in nitrogen flow.

For surface Raman analysis, a Renishaw® in-via Raman Microscope (Renishaw, Gloucestershire, UK) equipped with a

Table II. Composition, Consolidation Temperature, Coating Thickness, and Surface Roughness for Phenyltriethoxysilane (PhTES)–Diphenyldiethoxysilane (DPhDES) Gels

Composition moles		Consolidation temperature (°C)	Coating thickness (mm)	Average roughness (mm)
PhTES	DPhDES			
1.0	0.25	150	1.56	20.9
1.0	0.20	140	1.25	6.3
1.0	0.15	135	1.64	6.8
1.0	0.10	130	2.04 [†]	8.5
1.0	0.0	130	cracked	

[†]only on polycarbonate.

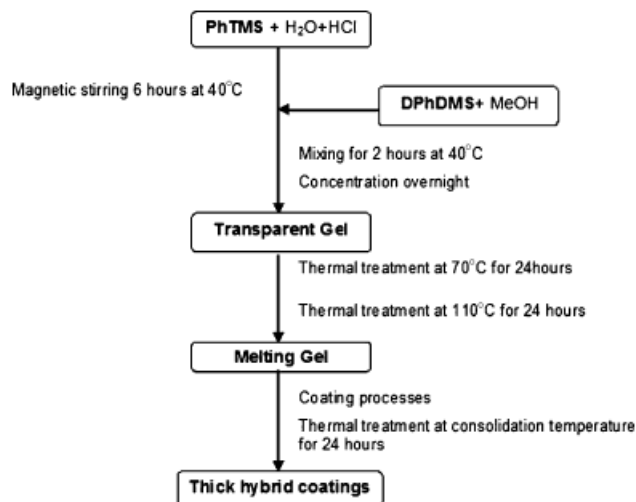


Fig. 1. Flowchart of the synthesis of the melting gels in the phenyltrimethoxysilane (PhTMS)–diphenyldimethoxysilane (DPhDMS) system and the coating process.

765 nm laser was used. The Raman spectra were recorded between 100 and 4000 cm⁻¹. The mappings of the surface were recorded at 50 × magnification under an optical microscope.

The AFM images were acquired in a tapping mode using a Nanoscope IV Scanning probe microscope (Veeco®, Planiview, NY). The contact angle between a water droplet and the film was measured, and the angle was calculated using KSV CAM Optical Contact Angle and Pendant Drop Surface Tension Software 3.80 (Monroe, CT). Five measurements were made for each composition and averaged. The error for this measurement is ±2.0°.

III. Results

When the acidified water was added to the monosubstituted alkoxide, the mixture exhibited a water-in-oil phase separation, due to the immiscibility of PhTMS and PhTES with water. During mixing at 40°C, all solutions became clear, indicating that the reactions of hydrolysis and polycondensation were occurring and releasing methanol or ethanol upon formation of hydroxylated species.¹⁴ Clear solutions were achieved sooner with PhTMS than the PhTES, due to the higher reactivity of the methoxy alkoxides, compared with ethoxy alkoxides.¹⁵ Compositions with more than 0.25 mol of disubstituted alkoxide to 1 mol of monosubstituted alkoxide did not form clear solutions and were not investigated further.

In the second step, the disubstituted alkoxide diluted in alcohol was added. After gelation, the samples were treated at 70°C to eliminate alcohol and at 110°C to remove surface water. The gels were solids at room temperature, but they softened at temperatures around 110°C. The consolidation temperature was established empirically by going through heating and cooling cycles until the temperature was 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 temperature increased with increasing amounts of disubstituted alkoxide, as listed in Tables I and II.

Figure 2 shows the TGA and DTA curves for the samples with PhTMS:DPhDMS = 1:0.2 and PhTES:DPhDMS = 1:0.2, the same molar ratio of monosubstituted to disubstituted alkoxide. The TGA curves show that both samples have two stages of weight loss. For the methoxy-containing sample, the first weight loss is between 200° and 400°C, which is likely due to the burning of methoxy groups and elimination of hydroxyl. For the ethoxy-containing samples, the first weight loss is between 200° and 300°C. The second weight loss between 500° and 660°C corresponds to removal of the phenyl groups. The second weight

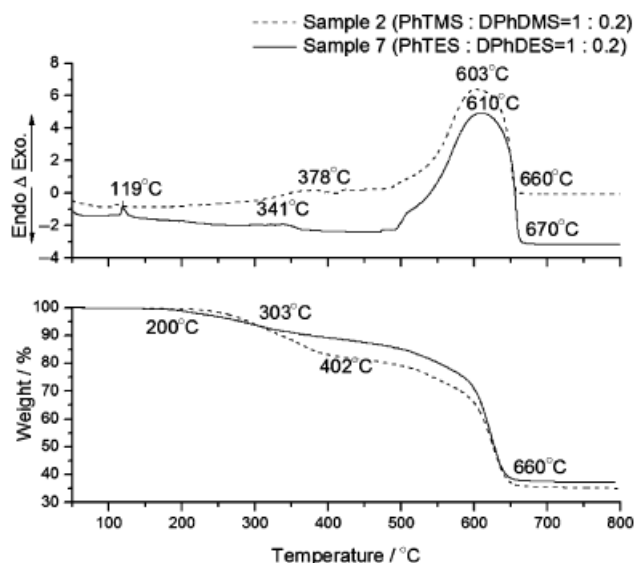


Fig. 2. Thermogravimetric analysis and differential thermal analysis curves of the samples prepared using phenyltrimethoxysilane (PhTMS):diphenyldimethoxysilane (DPhDMS) = 1:0.2 and PhTES:DPhDES = 1:0.2.

loss is similar for both the methoxy-containing and the ethoxy-containing gels, supporting the assignment of this weight loss to the phenyl groups that the samples have in common.

The DTA curves show an exothermic peak at 378°C for the methoxy-containing sample and at 340°C for the ethoxy-containing sample. Combustion of the methoxy or the ethoxy groups gives rise to an exothermic peak. However, the major exothermic peak for both samples occurs at ~600°C, which is associated with the burning of the phenyl groups. For the samples containing only the monosubstituted alkoxides, the exothermal peak attributed to the burning of the phenyl groups occurs at slightly lower temperatures than samples containing both mono- and disubstituted alkoxides.

Glass transition temperatures were determined from DSC plots for gels before consolidation. The T_g values are listed in Tables III and IV. The T_g varied from 2.6° to 41.6°C for the methoxy-containing gels, and from 0.4° to 33.1°C for the ethoxy-containing gels. The glass transition temperature increased as the amount of the disubstituted alkoxide decreased. A decrease in the amount of disubstituted alkoxide and the corresponding increase in the monosubstituted alkoxide would indicate a greater capacity for crosslinking and an increase in T_g .

The results of the thermal analysis are summarized in Tables III and IV. For both systems, the weight loss decreases with decreasing amount of disubstituted alkoxide. The smaller weight loss reflects the decrease in the number of phenyl groups, and an increase in the silica content.

In addition to the consolidation temperatures, Tables I and II list the characteristics of the coatings after consolidation of the gels. Gels prepared with PhTMS–DPhDMS gave continuous coatings on all three substrates, mica, silicon wafers, and polycarbonate. Gels prepared with PhTES:DPhDES gave continu-

Table IV. Composition and Thermal Characteristics of Phenyltriethoxysilane (PhTES)–Diphenyldiethoxysilane (DPhDES) Gels

Composition moles PhTES	Moles DPhDES	Glass transition T_g (°C)	Total loss (%)	Weight peak of exotherm (°C)
1.0	0.25	0.4	64.5	603
1.0	0.20	7.9	63.5	607
1.0	0.15	27.7	61	598
1.0	0.10	33.9	60	603
1.0	0.0	33.1	57	602

ous coatings on mica, silicon wafers, and polycarbonate, when the content of DPhDES was 0.15M or greater. The gel with 0.10M DPhDES only gave continuous coatings on polycarbonate, and the gel with only PhTES produced cracked films.

The coatings deposited by pouring the softened gel onto the substrates are between 1.3 and 2.0 mm thick. The thickness increases as the amount of the disubstituted alkoxide is decreased. This reflects an increase in the viscosity of the melting gels when the amount of DPhDMS or DPhDES is decreased.

Tables I and II list the values of the average roughness determined in AFM scans of the coatings. The trend is a decrease in roughness with a decrease in the amount of the disubstituted alkoxide. Figure 3(a) shows the AFM image of a coating using PhTMS:DPhDMS = 1:0.2, and Fig. 3(b) shows the AFM image of a coating using PhTES:DPhDES = 1:0.2. The surfaces of the coatings are free of cracks.

The Raman spectra for gels with PhTMS:DPhDMS = 1:0.2 and PhTES:DPhDES = 1:0.2 are shown in Fig. 4. The spectra have the characteristic peaks for the phenyl groups at 3043 cm^{-1} ($\nu_{\text{sym}} \text{CH}$ from C_6H_5), 2920 cm^{-1} ($\nu_{\text{asym}} \text{CH}$ from C_6H_5), the pair from 1591 and 1569 cm^{-1} ($\nu \text{C}_6\text{H}_5$, ring stretching), 1090 and 1032 cm^{-1} ($\delta_{\text{sym}} \text{CH}$ and $\delta_{\text{asym}} \text{CH}$), 1054 cm^{-1} (ring breathing mode) and the most intense pairs at 1030 and 1000 cm^{-1} (in plane C_6H_5 ring deformation).¹⁶ The silica network was evidenced by the presence of very weak peaks located at 1067 cm^{-1} ($\nu_{\text{asym}} \text{Si-O-Si}$),¹⁷ 850 cm^{-1} ($\delta_{\text{asym}} \text{O-Si-O}$), and 790 cm^{-1} ($\nu_{\text{sym}} \text{Si-O-Si}$)¹⁸ and at 580, 460, and 400 cm^{-1}

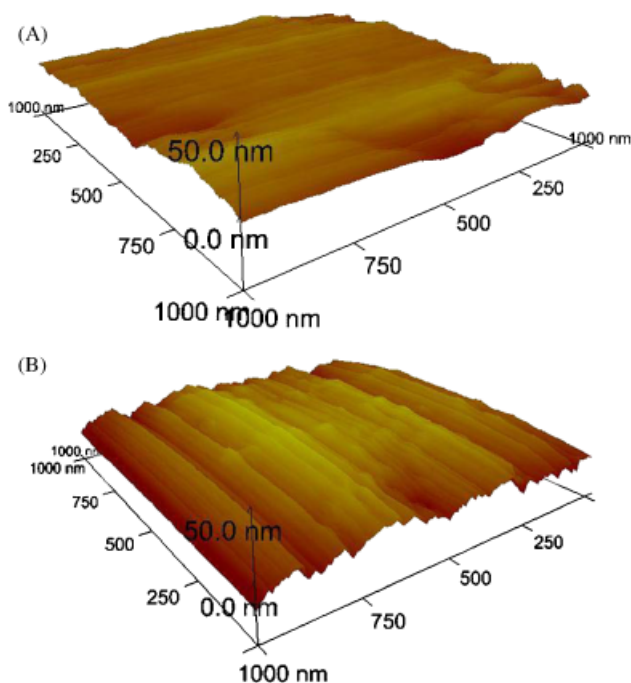


Fig. 3. (A) The AFM image of the coating with phenyltrimethoxysilane (PhTMS):diphenyldimethoxysilane (DPhDMS) = 1:0.2 ($R_a = 19.35 \text{ nm}$). Figure 3(B) The AFM image of the coating with PhTES:DPhDES = 1:0.2 ($R_a = 6.31 \text{ nm}$).

Table III. Composition and Thermal Characteristics of Phenyltrimethoxysilane (PhTMS)–Diphenyldimethoxysilane (DPhDMS) Gels

Composition moles PhTMS	Moles DPhDMS	Glass transition T_g (°C)	Total loss (%)	Weight peak of exotherm (°C)
1.0	0.25	2.6	65	608
1.0	0.20	5.0	64.5	603
1.0	0.15	26.1	60.5	602
1.0	0.10	25.4	59.5	602
1.0	0.0	41.6	56.6	596

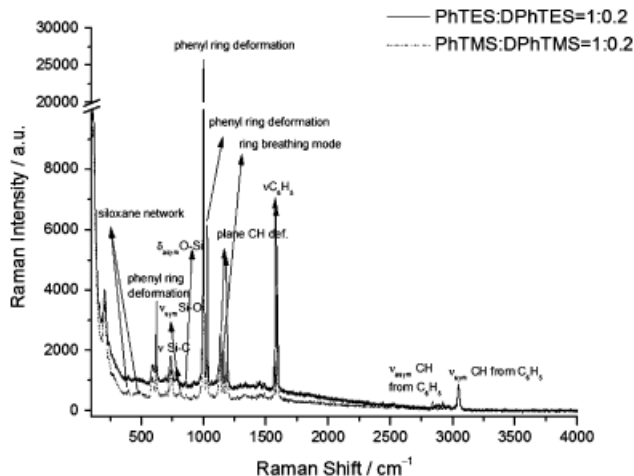


Fig. 4. Raman spectra of the samples with phenyltrimethoxysilane (PhTMS):diphenyldimethoxysilane (DPhDMS) = 1:0.2 and PhTES:DPhDES = 1:0.2.

(Si–O–Si in the plane vibration of a 6-member ring, an 8-member ring, and a 10-member ring, respectively).¹⁹ The vibration assigned to Si–C or Si-phenyl bonds was identified at 630 cm^{-1} .^{18,20}

Using an optical microscope with the Raman spectrometer, the chemical uniformity of the surface was investigated, by mapping the surface of the sample with PhTMS:DPhDMS = 1:0.25, after consolidation at 180°C . Seven Raman spectra have been recorded along the $\sim 200\text{ }\mu\text{m}$ line shown in the inset in the Fig. 5. The spectra are identical.

The contact angle is plotted versus the molar ratio monosubstituted to disubstituted alkoxides for both systems in Fig. 6. In all but one case, the coatings exhibit hydrophobic surfaces with a contact angle $\theta > 90^\circ$. The contact angle increases with an increase in the amount of disubstituted alkoxide. All melting gels have BET surface areas lower than $1\text{ m}^2/\text{g}$ after their consolidation, as determined by standard nitrogen sorption techniques.

IV. Discussion

The interesting property of these hybrid gels is that they are rigid at room temperature, become fluid at a temperature T_1 ($\sim 110^\circ\text{C}$), and can be resoftened many times. However, after consolidation at a temperature T_2 ($T_2 > T_1$), the gels no longer soften. The consolidation temperature appears to correspond to crosslinking of the silica chains in 3D networks.²¹ Heating of these gels to temperature T_2 increases the reactivity of retained organic or hydroxyl groups, which allows crosslinking to proceed to the point of forming an irreversible network. As a result

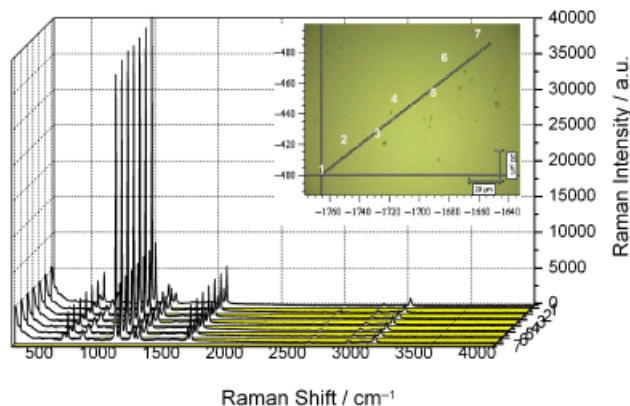


Fig. 5. Raman-mapping spectra for coatings with phenyltrimethoxysilane (PhTMS):diphenyldimethoxysilane (DPhDMS) = 1:0.25 after its consolidation at 180°C . The inset shows an optical micrograph of the coatings at a magnification of $\times 50$.

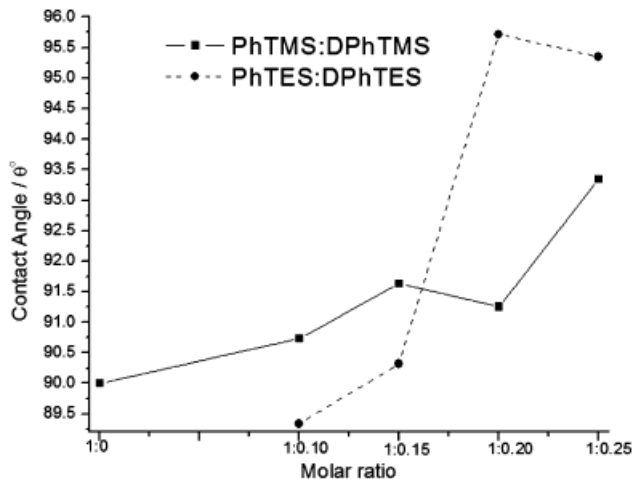


Fig. 6. Variation of the contact angle θ° versus molar ratio monosubstituted to disubstituted alkoxides.

of the heat treatment for 24 h at the consolidation temperature, the gels crosslink and densify. The softening-becoming rigid-resoftening process can be repeated many times, as long as the crosslinking is not completed by increasing the temperature to T_2 .

The consolidation temperatures listed in Tables I and II decrease with a decrease of the amount of disubstituted alkoxide, for both systems. This decreasing of the consolidation temperature can be explained by the fact that disubstituted alkoxides have only two functionalities available to create new bonds with the rest of the silica network. Without the monosubstituted alkoxide, the disubstituted alkoxides remain liquids after the hydrolysis and polycondensations reactions because only linear chains are formed. The linear chains are not able to form 3D networks. When monosubstituted alkoxides are mixed with the disubstituted alkoxides, the disubstituted alkoxides act as bridges between the molecular species formed when the monosubstituted alkoxides hydrolyze. The substituted phenyl groups occupy a higher volume than the ethoxy or the methoxy groups. When more disubstituted alkoxide is present, the high number of phenyl groups creates a steric hindrance to the crosslinking process, which leads to an increase of the consolidation temperature.

The glass transition temperatures listed in Tables III and IV show trend opposite to the consolidation temperature. The T_g values increase with decreasing amount of disubstituted alkoxides. The glass transition is generally thought of as the interval of transition between liquid states and glassy, amorphous states.^{10,22} Put another way, the glass transition is associated with a temperature T_g , which is influenced by 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,²² the glass transition temperature is considered a measure of the degree of crosslinking in the silica network. In other words, the T_g increases with an increase in the number of oxygen bridges between silicon atoms. The highest T_g values are for samples with only monosubstituted alkoxides, 41.6°C for PhTMS and 33.1°C for PhTES. The T_g values for the methoxy-substituted alkoxide are higher than the T_g values for the ethoxy-substituted alkoxide, given that the methoxy groups are more reactive and achieve a higher degree of polycondensation than for the samples, that contain ethoxy groups.

Takahashi *et al.*²³ showed that the T_g decreases with an increase of the amount of cosolvent. In the present study, the amount of solvent decreases with a decrease in the amount of the disubstituted alkoxide, in agreement with this trend.

The thickness of the consolidated coatings, listed in Tables III and IV, increases as the amount of disubstituted alkoxides is decreased. That is, the thickness increases with increasing T_g ,

reflecting the higher viscosity when the gel is poured. The average roughness decreases as the thickness increases, again reflecting the higher viscosity at the time of pouring. Put another way, the compositions with more disubstituted alkoxide are more fluid, and give thinner, rougher coatings.

The Raman spectra in Fig. 4 have intense, sharp peaks assigned to the phenyl groups. The characteristic vibrations for the silica network and for Si–C bonds have a low intensity. These spectra have been acquired under a microscope where the penetration of the laser beam is $\sim 0.5 \mu\text{m}$. The high intensity of the phenyl peaks appears to be due to their concentration on the surface of the coatings. Raman mapping showed identical spectra with strong phenyl peaks, indicating a chemically uniform surface of the coatings after their consolidation.

The phenyl groups on the surface give rise to hydrophobic behavior. When a water droplet was placed on the surface, the contact angle was generally $>90^\circ$, and the contact angle increased with an increase in the amount of the disubstituted alkoxide, DPhDMS or DPhDES, as the number of phenyl groups increased. The contact angle increase was not linear, with the highest value $\theta = 95.7^\circ$ measured for the sample with PhTES:DPhDES = 1:0.2. The values for the methoxy-containing system were lower than the ethoxy-containing samples, due to the higher reactivity of the methoxy groups, leading to fewer phenyl groups on the surface.

V. Conclusions

Melting gels were prepared using monosubstituted and disubstituted alkoxides. The consolidation temperature, after which melting gels no longer soften, increased with an increase in disubstituted alkoxide for both systems, the highest being 180°C for the sample with PhTES:DPhDES = 1:0.25. The glass transition reflected the degree of crosslinking. The T_g values decreased toward 0°C as the amount of disubstituted alkoxide increased. Continuous, thick coatings were obtained by pouring the softened gels onto mica, silicon wafer, and polycarbonate substrates, followed by consolidation. Raman spectra showed strong peaks for phenyl groups, which were concentrated on the surface of the gels. The concentration of phenyl groups on the surface is also seen in the hydrophobic character of the surface.

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