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29Si NMR and SAXS investigation of the hybrid organic–inorganic glasses obtained by consolidation of the melting gels†

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This study is focused on structural characterization of hybrid glasses obtained by consolidation of melting gels. The melting gels were prepared in molar ratios of methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMDES) of 75%MTES-25%DMDES and 65%MTES-35%DMDES. Following consolidation, the hybrid glasses were characterized using Raman, 29Si and 13C Nuclear Magnetic Resonance (NMR) spectroscopies, synchrotron Small Angle X-Ray Scattering (SAXS) and scanning electron microscopy (SEM). Raman spectroscopy revealed the presence of Si–C bonds in the hybrid glasses and 8-membered ring structures in the Si–O–Si network. Qualitative NMR spectroscopy identified the main molecular species, while quantitative NMR data showed that the ratio of trimers (T) to dimers (D) varied between 4.6 and 3.8. Two-dimensional 29Si NMR data were used to identify two distinct types of T3 environments. SAXS data showed that the glasses are homogeneous across the nm to micrometer length scales. The scattering cross section was one thousand times lower than what is expected when phase separation occurs. The SEM images show a uniform surface without defects, in agreement with the SAXS results, which further supports that the hybrid glasses are nonporous.

1. Introduction

The concept of melting gels was first introduced in 2001 by Matsuda et al.1 They studied the formation of poly(benzyl-silsesquioxane) particles, which were then deposited on an ITO substrate by electrophoretic deposition. After heat treatment, continuous and uniform transparent thick coatings were obtained. In reality the process called “melting” is a softening process. Melting gels are hybrid organic inorganic materials in which the presence of the covalent bonds between the organic components and inorganic network places the melting gels in the Class II of hybrids.2 The precursors used for preparation of hybrid melting gels are a mixture between a mono-substituted organo-modified alkoxide such as phenyltriethoxysilane3,4 or methyltriethoxysilane5 and a di-substituted organo-modified alkoxide such as diphenyldiethoxysilane3 or dimethyldiethoxysilane.5 Hybrid melting gels differ from classical hybrids through their properties. The defining property of these hybrid melting gels is that they are solid at room temperature, become fluid at a softening temperature \( T_1 \) (\( \sim 110 \) °C), return to rigidity at room temperature, and can be re-softened many times. All the hybrid melting gels also present a consolidation temperature which varies with the composition.3,5 However, after consolidation at a temperature \( T_2 \) (\( T_2 > T_1 \)), the gels no longer soften. The consolidation temperature \( T_2 \) corresponds to cross-linking of the silica chains.5,6 At the consolidation temperature the melting gels are transformed into hybrid glasses.4

The most studied system is the phenyl based melting gel.3,6–8 For this system Kakiuchida et al.6,7 found a correlation between the structure of a melting gel and its viscoelastic properties. Using 29Si MAS NMR and Gel Permeation Chromatography (GPC) they identified the complex nature of the structure of the melting gels. Furthermore, they demonstrated that the softening ability is controlled by the number
of oxygen bridges and the intramolecular structure, and the viscosity follows a free volume model. Despite a growing number of studies on melting gel properties, there are only a few studies that characterize the hybrid glasses obtained from the gel melt consolidation. Masai et al. prepared melting gels and the corresponding low temperature hybrid glasses from phenyltriethoxysilane and diphenyldiethoxysilane. Using \(^{29}\)Si MAS NMR and FT-IR spectroscopy, they identified the phenomena that take place during the thermal transition from melting gels to hybrid glasses. Using the same system and phenyltriethoxysilane along with dimethyldiethoxysilane, we characterized the structure of the hybrid glasses by Raman and FT-IR spectroscopy. The structure and the orientation of the organic groups was found to promote hydrophobicity to the surface of the hybrid glasses.

In our earlier works, hybrid glasses were also obtained using methyl-substituted melting gels. Mainly the focus was on preparation using methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMDES), on their thermal stability, and on their viscoelastic properties. The hybrid glasses obtained from these melting gels were characterized by FT-IR and Raman spectroscopy. These glasses, which are obtained at relatively low temperatures (135–160 °C), perform well as anticorrosive coatings and as hermetic barriers and also have low dielectric constants. While several applications have been pursued for these hybrid glasses, an understanding of their molecular structure is still incomplete.

NMR spectroscopy is among the most powerful techniques for structural studies of the silica-based sol–gel materials. For the sol–gel method, NMR spectroscopy can be used either in solutions to elucidate the early stages of formation of the molecular species of the inorganic or hybrid materials or on solid samples to elucidate the detailed instrumental setup, SAXS can access structural homogeneities, provides statistically significant characterization of the network structure within hybrid gels and glasses. SAXS is based on the elastic scattering of X-rays at scattering angles very close to the direction of the incident beam. Depending on the detailed instrumental setup, SAXS can access structural information in the reciprocal space from sub-nanometer to tens of nanometers (conventional pinhole setup) and even tens of micrometers (Bonse–Hart type setup).

Historically, “horizontal and vertical polymerization in the silane phase” of MTES and DMDES was first studied by Sindorf et al. in comparison with their chlorosilane partners using \(^{29}\)Si and \(^{13}\)C NMR by using cross polarization (CP) and magic angle spinning (MAS). It was found that while that the ethoxysilanes and chlorosilanes have similar chemistries in the silylation reactions of silica surfaces, ethoxysilanes are less reactive than their chlorosilane partners. Pyke et al. studied the copolymerization of the tetraethoxysilane (TEOS) and MTES using two dimensional \(^{1}H/^{29}\)Si NMR correlation, which revealed these two components mixed well in the final gel and no phase separation was induced. Another interesting study on the copolymerization of TEOS along with MTES or ethyltriethoxysilane (ETES) or octyltriethoxysilane (OTES) was carried out by Peeters et al. Using the CP and single-pulse excitation (SPE) MAS NMR, the effect of the length of the organic tail on the degree of condensation was studied. They observed that CP MAS NMR cannot be used to quantitatively obtain reliable data for the system with a long organic tail due to the large distance between the proton and a part of Q or T silicon atoms. For this reason, SPE MAS-NMR was required in quantitative measurements. It was also concluded that the total number of network bonds decreases with the increasing level of substitution.

The formations of silicon-oxycarbide glasses obtained by cohydrolysis and polycondensation of the TEOS along with DMDES or triethoxysilane (TES) along with methyl-diethoxysilane (MDES) or MTES along with methyltrimethoxysilane (MTMS) were investigated by using \(^{29}\)Si and \(^{13}\)C MAS NMR. \(^{29}\)Si and \(^{13}\)C MAS NMR was used for identification of the distribution of the organic groups in the gel phases. In addition, these techniques were used to characterize the evolution between gel and silicon oxy-carbide glasses. Moreover, Suyal et al. showed that the addition of colloidal silica delayed the decomposition of the methyl groups from MTES.

Brus et al. published a series of studies upon co-hydrolysis polycondensation of TEOS with DMDES or TEOs with MTES using \(^{1}H\) MAS NMR \(^{26} 1\)H and \(^{29}\)Si CP/MAS NMR and 2D \(^{1}H-^{29}\)Si heteronuclear experiments. They observed that the dynamic behavior and the nature of the silanol protons in the presence of water are influenced by the amount of methyl groups in the hybrid network. In addition, it was observed that the formation of clusters of OH protons with different strength of hydrogen bond is related to the arrangements of the siloxane units in the final network. Based on the interatomic distances a cage-like model was proposed for the structure of the final copolymer.

Small angle X-ray scattering (SAXS), being a premier, non-destructive technique that probes mesoscopic structure inhomogeneities, provides statistically significant characterization of the network structure within hybrid gels and glasses. SAXS is based on the elastic scattering of X-rays at scattering angles very close to the direction of the incident beam. Depending on the detailed instrumental setup, SAXS can access structural information in the reciprocal space from sub-nanometer to tens of nanometers (conventional pinhole setup) and even tens of micrometers (Bonse–Hart type setup).

As a general technique, SAXS has been used to investigate the microstructures of polymeric gels and glasses. In particular, SAXS was deployed to study the static structure and formation kinetics of a broad range of silicon-based materials, ranging from nanocomposites, nanoparticles, and mesoporous silica films. Notably, SAXS was combined with \(^{29}\)Si to reveal the condensation kinetics of hydrolyzed alkoxides where progressive assembly of small organized units were found to be followed by growth of fractal clusters in tetrahedral TEOS. This study illustrated the potency of combined NMR and SAXS characterizations, where detailed local conformations can be derived from NMR and SAXS reveal global morphological characteristics.

This work will focus on the structure characterization of the hybrid organic–inorganic glasses which contain direct bond between silicon and methyl groups, obtained after consolidation of melting gels. The consolidation of the melting gels represents a new pathway to obtain hybrid organic–inorganic glasses. We seek to provide a comprehensive and cross-length-scale view of the structures by making use of Raman
spectroscopy, $^{13}$C and $^{29}$Si NMR spectroscopy along with synchrotron-based SAXS and scanning electron microscopy (SEM).

2. Experimental

2.1. Melting gel/hybrid glasses preparation

The preparation of the melting gels, reported previously, is briefly discussed below. We used two types of alkoxides, mono-substituted methyltriethoxysilane (MTES) (Sigma-Aldrich, Milwaukee, WI) and di-substituted one dimethyl-diethoxysilane (DMDES) (Sigma-Aldrich, Milwaukee, WI), without further purification. Hydrochloric acid (Fisher Scientific, Atlanta, GA) and ammonia (Sigma-Aldrich, Milwaukee, WI) were used as catalysts while anhydrous ethanol (Sigma-Aldrich, Milwaukee, WI) was used as solvent. Two melting gels presented in Table 1, with compositions of 75% MTES-25% DMDES and 65% MTES-35% DMDES (in mol%) have been investigated in this study. The synthesis was performed in three different steps with predetermined amount of reactants. The molar ratios of MTES:EtOH:H$_2$O:HCl were 1:4:3:0.01. First, water was mixed with hydrochloric acid and half of the ethanol. Separately, MTES was mixed with the other half of ethanol. Then, the mixture between ethanol and MTES was added dropwise to the water solution under continuous stirring. The container was sealed with Parafilm® while the mixture was continuously stirred at room temperature for three hours. In the second step, the di-substituted alkoxide DMDES was diluted with ethanol in a molar ratio of DMDES:EtOH = 1:4. The DMDES-EtOH mixture was added dropwise to the first mixture. This resulting solution was kept under continuous stirring in the sealed container at room temperature for two additional hours. In the third step, ammonia was added to the mixture, which was stirred for one more hour in the sealed container. The molar ratio of (MTES + DMDES):NH$_3$=1:1:0.01. The final solution was continuously stirred for 48 hours at room temperature in an open container until gelation occurred. Ammonium chloride was formed as a byproduct during gelation. To remove this, 10 ml of dry acetone (Spectranal, Sigma-Aldrich) was added to the samples. The ammonium chloride was removed by vacuum filtration. Then the clear solution was stirred until all the acetone evaporated. The obtained gel was treated at 70 °C for 24 hours to remove any remaining acetone and ethanol, followed by another heat treatment at 110 °C for 24 hours to remove of unreacted water. The hybrid glasses were obtained by consolidation of the melting gels on 15 mm × 15 mm mica substrates (Grade V-4 muscovite, SPI Co., West Chester, PA). The consolidation temperatures for each composition are a function of the molar % between MTES and DMDES and are listed in Table 1. At these temperatures the melting gels are transformed into hybrid glasses within a 17 hour consolidation heat treatment.

For the NMR and BET surface area measurements the hybrid glasses were removed from the mica substrates by thermally shocking the samples. The samples were immersed in the liquid nitrogen (77 K) and then very quickly exposed to the room temperature. Repeating this process a few times allowed hybrid glasses to be detached from the substrates. Subsequently, the removed hybrid glasses underwent cryogenic grinding in liquid nitrogen until fine powders were achieved.

For the SAXS and Raman measurements, the hybrid glasses samples as deposited on the mica supports were used. The thickness and density of the coatings are listed in Table 1.

2.2. Sample characterization

The consolidated hybrid glasses were characterized using Raman, $^{13}$C and $^{29}$Si NMR spectroscopy, SAXS and SEM.

Raman spectra were recorded using Renishaw® in Via Raman Microscope (Renishaw, Gloucestershire, UK) equipped with 765 nm laser between 4000–200 cm$^{-1}$. The spectra were acquired under a Leica optical microscope at 20× magnification.

NMR $^{13}$C and $^{29}$Si quantifications and $T_1$ measurements were conducted at 7.0 T on a Bruker spectrometer equipped with a 4 mm double resonance probehead. The MAS frequency was set at 12 kHz. $T_1$ longitudinal relaxation time measurements were conducted with a saturation-recovery approach, using 10 saturation pulses for both $^{13}$C and $^{29}$Si experiments with a saturation train of 10 pulses spaced by delays decreasing step by step from 50 to 5 ms. Quantitative measurements were collected with an echo-MAS sequence and a short echo duration of two rotor periods. Full magnetization recovery was ensured by recycling delays at least quintupling the longest $T_1$ measured under the same conditions. The number of scans was adjusted for each recovery delay to optimize the experimental time while maintaining good signal-to-noise. The peak intensities were extracted from sets of peak-profile parameters (positions, widths and Gaussian to Lorentzian ratios), allowing only the amplitudes to vary. These sets of parameters were obtained, for each sample and experimental condition, from a simultaneous fit of multiple spectra, including the echo-MAS spectra with the highest signal to noise and CP-MAS spectra collected with different contact times, which ensures the robustness of the spectral decomposition into individual components. Uncertainty evaluation was performed with a Monte-Carlo approach using an in-house MATLAB program. Random noise within the experimental standard deviation was introduced to the experimental data to produce a large number of datasets, which were subsequently fitted. Statistical analysis was conducted on the fitting parameters to yield the uncertainty of the measured $T_1$ value.

Two-dimensional $^{29}$Si/$^{29}$Si dipolar double quantum (DQ) experiments were conducted on sample 2 using a 9.4 T Bruker spectrometer with a 7 mm double-resonance probe, using symmetry-based$^{43}$ SR26$^{41}$ recoupling, at the MAS frequency of

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$^\dagger$ Certain commercial equipment, instruments, software or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the Department of Commerce or the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
5.5 kHz and a $^{29}\text{Si}$ nutation frequency of 35.7 kHz (optimized for maximum recoupling efficiency). Heteronuclear $^1\text{H}$ decoupling was achieved using CW decoupling at a $^1\text{H}$ nutation frequency of 60 kHz during the recoupling, and SPINAL64 at 60 kHz during acquisition in both dimensions. The DQ creation and reconversion blocks used 5 recoupling supercycles each, corresponding to 7.1 ms blocks. A two-rotor-period echo was added at the end of the pulse sequence to ensure a flat baseline. The indirect dimension was collected with 48 $t_1$ increments using the States procedure, with 7424 scans and a recycle delay of 1.5 s (total duration: 6 days). The spectral width in the indirect dimension was 5500 Hz (to ensure synchronization with the rotor rotation). This is too small to observe the full range of the DQ dimension, where cross-peak frequencies correspond to the sum of the individual sites that are coupled (such that the width is typically twice the width of the standard spectrum) and lead to a folding of the peaks. An unfolded spectrum can nevertheless be obtained by a “shearing” transformation that yields a SQ–SQ spectrum, instead of the double-quantum – single-quantum (DQ-SQ) 2D spectrum that is obtained after standard Fourier transformation. This is done by first performing Fourier transform on the direct dimension of the 2D time-domain signal, and then applying a first-order phase correction of the indirect-time domain signal with a coefficient that varies linearly with the frequency in the direct dimension, and finally applying the Fourier transform in the indirect dimension to obtain the sheared SQ–SQ spectrum. All chemical shifts are given relative to (neat) tetramethylsilane (TMS).

The densities of the samples were measured on the ground hybrid glasses using a pycnometer with helium AccuPyc II 1340 (Micromeritics, Norcross, GA).

The BET surface area of the samples was determined by absorption/desorption of nitrogen at 77 K using a Tristar II 3020 BET surface analyzer. Samples were previously outgassed at 110 °C in a nitrogen flow overnight. Surface areas were determined using the Brunauer–Emmett–Teller (BET) method.

SAXS scattering experiments were conducted at the ultrasmall angle X-ray scattering (USAXS) instrument at the Advanced Photon Source, Argonne National Laboratory. This instrument makes use of Bonse–Hart type of crystal optics to access a scattering $q$ range that is normally unavailable to a conventional pinhole based small angle scattering camera. Here $q$ is the magnitude of the scattering vector, and is defined as $q = 4\pi\lambda/\sin(\theta)$, where $\lambda$ is the X-ray wavelength and $\theta$ is one half of the scattering angle. The USAXS instrument has a $q$ resolution of $\approx 1 \times 10^{-4}$ Å$^{-1}$. Coupled with an add-on Pilatus 100 K detector, the USAXS instrument can access a $q$ range from $1 \times 10^{-4}$ Å$^{-1}$ to 1 Å$^{-1}$. Particularly, it is worth noting that the USAXS instrument is primary-calibrated, i.e., the measured intensity is directly related to the differential scattering cross section, a physical property of the material being studied.

1D-collimated USAXS experiments were conducted in fly-scan mode using monochromatic 17.5 keV X-rays ($\lambda = 0.708481$ Å). The beam size was 0.8 mm × 0.8 mm. The X-ray flux density was $\approx 10^{13}$ photon per s per mm$^2$. The high X-ray flux ensures that weak scattering signals, commonly expected from a melting gel system, be captured. Total scan time was 120 s. The sample was placed on a standard sample holder. SAXS experiments were conducted twice on some of the samples as a check of damage to the samples caused by the X-ray beam. It was found that in these hybrid glasses, the exposed X-ray dosage does not alter the materials microstructures.

To visually examine the materials microstructures, the surface and the cross-sections of the fractures of the hybrid glasses were evaluated using a Hitachi S-2700 SEM. The SEM was operated at 25 keV acceleration voltage. The SEM was equipped with and AMT digital camera system.

### Table 1. The starting compositions of the melting gels, their temperatures of consolidation and the thicknesses and densities of the hybrid glasses obtained by consolidation of the melting gels

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (mol%)</th>
<th>Temperature of consolidation (°C)</th>
<th>Thickness of coatings (mm)</th>
<th>Density (g cm$^{-3}$)</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75 65</td>
<td>135</td>
<td>1.284</td>
<td>0.86</td>
<td>0.0255</td>
</tr>
<tr>
<td>2</td>
<td>25 35</td>
<td>150</td>
<td>1.252</td>
<td>1.06</td>
<td>0.0141</td>
</tr>
</tbody>
</table>

3. Results and discussion

In this study we focused on the two compositions listed in Table 1 for two reasons. First, the melting gel with 75% MTES-25%DMDES composition is the gel with the highest content of MTES which retains the melting properties. On the other hand, the melting gel with 65%MTES-35%DMDES composition is the borderline gel between solid and liquid state at room temperature. Second, the hybrid organic inorganic glasses obtained using those compositions proved to be the best anticorrosive coatings.

The Raman spectra of the investigated hybrid glass samples are presented in Fig. 1a while the assignments of the peaks are listed in Table 2.

3.1. Raman characterization

Although more than 60% of the studied hybrid glasses contain $\text{SiO}_2$, the characteristic peaks for the presence of the Si–O–Si bonds, identified at 790 cm$^{-1}$ (assigned to $\nu_{\text{sym}}$ Si–O–Si) and at 1090 cm$^{-1}$ (assigned to $\nu_{\text{asym}}$ Si–O–Si), have very low intensity. On the other hand, the characteristic peaks for the Si–O–Si ring breathing mode, identified at 461 cm$^{-1}$ (attributed to the 8-member ring structure) and at 202 cm$^{-1}$ (characteristic...
Fig. 1 The Raman spectra of the hybrid glasses. (a) Complete Raman spectra; (b) partial spectra between 600 cm\(^{-1}\) and 900 cm\(^{-1}\) which illustrate an increasing of Si–C bonds in the hybrid glass with a higher amount of DMDES (sample 2).

The peak intensities are given in parentheses as (s) for strong, (m) for medium, (w) for weak, (vw) for very weak and (sh) shoulder.

### Table 2: The Raman peak assignments of the hybrid glasses obtained by consolidation of the melting gels

<table>
<thead>
<tr>
<th>Raman Shift/cm(^{-1})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2971 (w)</td>
<td>(\nu_{\text{asym}}) CH(_3)</td>
</tr>
<tr>
<td>2901 (s)</td>
<td>(\nu_{\text{sym}}) CH(_3)</td>
</tr>
<tr>
<td>2808 (vw)</td>
<td>Overtones</td>
</tr>
<tr>
<td>1413 (vs)</td>
<td>(\delta_{\text{asym}}) Si–O–Si</td>
</tr>
<tr>
<td>1223 (sh)</td>
<td>(\delta_{\text{sym}}) CH(_3) (Si–CH(_3))</td>
</tr>
<tr>
<td>1097 (sh)</td>
<td>(\nu_{\text{asym}}) Si–O–Si</td>
</tr>
<tr>
<td>860 (m)</td>
<td>(\delta_{\text{asym}}) Si–O–C (alkoxi)</td>
</tr>
<tr>
<td>797 (w)</td>
<td>(\nu_{\text{sym}}) Si–O–Si</td>
</tr>
<tr>
<td>743 (w sh)</td>
<td>(\rho) CH(_3)</td>
</tr>
<tr>
<td>704 (m)</td>
<td>(\nu) Si–C (Si–CH(_3))</td>
</tr>
<tr>
<td>589 (w)</td>
<td>Si–O–Si ring breathing vibration for 6 member</td>
</tr>
<tr>
<td>461 (s)</td>
<td>Si–O–Si ring breathing vibration for a 8 member ring</td>
</tr>
<tr>
<td>202 (s)</td>
<td>(\sigma) Si–O–Si</td>
</tr>
</tbody>
</table>

\(\nu\) Si–C, Si–O–Si, and \(\delta\) Si–O–Si, are high in intensity.\(^{53-55}\) These results demonstrate that the main structure of the matrix is formed by an 8-member ring structure. Additionally, we identified a very weak peak at 589 cm\(^{-1}\) that is characteristic of a 6-member ring structure,\(^{53}\) which suggests that small amount of this structure is also present. Raman spectroscopy also reveals the presence of Si–C bonds. These was identified at 705 cm\(^{-1}\) and was assigned to the \(\nu\) Si–C at ref. 52 and 55.

Besides the peaks mentioned above, the most intense peaks belong to the methyl groups bonded to the silica backbone. These were identified at 2971 cm\(^{-1}\) and 2901 cm\(^{-1}\), which were assigned to \(\nu_{\text{asym}}\) CH\(_3\) and \(\nu_{\text{sym}}\) CH\(_3\), respectively. In addition, Raman bands placed at 1413 cm\(^{-1}\), 1223 cm\(^{-1}\) and 743 cm\(^{-1}\) were assigned to \(\delta_{\text{asym}}\) CH\(_3\), \(\delta_{\text{sym}}\) CH\(_3\) and \(\rho\) CH\(_3\), respectively.\(^{55}\)

The high intensity of the peaks assigned to the organic groups can be credited to the presence of the methyl groups to the surface of the hybrid glasses investigated.\(^{4,5,12}\) Moreover, in the Raman spectra of the both samples, we also identified a very weak peak at 864 cm\(^{-1}\) which was assigned to the \(\delta\) Si–O–C. The existence of this band demonstrates that few ethoxy groups from the original alkoxides remain unreacted and are entrapped in the hybrid glasses.

Fig. 1b details the normalized Raman spectra of the two hybrid glasses investigated in this study. It can be observed that the Raman intensity of the band assigned to the \(\nu\) Si–C is increasing for sample 2, which has a higher amount of DMDES (35 mol%) than sample 1 (25 mol%). Here, the higher amount of the DMDES leads to a higher number of Si–C bonds, which is reflected by the higher intensity of the \(\nu\) Si–C peak in the sample 2.

### 3.2. NMR peak assignments

\(\text{\(^{29}\)}\)Si NMR measurements are used to distinguish between the different Si environments formed in the hybrid glasses on the basis of the number of attached carbons and the degree of condensation. The notation T\(^{n}\) and D\(^{n}\) are used to designate \(\text{CSi(OSi)}\)\(_{n}\)(OR)\(_{3-n}\) and \(\text{C}_{2}\text{Si(OSi)}\)\(_{n}\)(OR)\(_{2-n}\) units originating from MTMES and DMDES monomers, respectively, with \(R = H\) corresponding to silanol groups or \(R = \text{CH}_2\text{CH}_3\) corresponding to unreacted Si–O–CH\(_2\text{CH}_3\) functions from the alkoxide. Quantitative \(\text{\(^{29}\)}\)Si NMR spectra recorded at room temperature for the hybrid glasses samples are shown in Fig. 2a. Assignments of the different signals to D\(^1\), D\(^2\), T\(^2\), and T\(^3\) signals can be made based on literature data.\(^{56-59}\) The variations of relative intensities between T\(^n\) and D\(^n\) sites in the materials of the sample 1 and 2 reflect the different compositions of their synthesis mixtures, with larger proportions of DMDES in the sample 2 leading to higher relative intensities of the D\(^n\) sites.

At room temperature, different conformations of the polymer chains are dynamically averaged on the NMR timescale (fast exchange regime) since they are frozen. The line-widths in the slow motional regime are typically of the order of 5 ppm (full width at half maximum, FWHM) corresponding to 300 Hz for \(\text{\(^{29}\)}\)Si at 7.0 T. The characteristic time corresponding to the intermediate exchange regime for a pair of peaks with a
frequency difference \( \Delta \nu \) between 2 sites is given by \( 1/(\pi \Delta \nu) \).\(^{10}\) Thus, in order for chemical shift dispersions on the order of 5 ppm to be dynamically averaged out, it typically requires the chain reorientation dynamics to be significantly faster than \( 10^{-3} \) s. The fast motional regime is clearly reached at room temperature. Some chemical shift dispersion nevertheless remains for each type of \( T^n \) or \( D^n \) environment, which points to chemically distinct local environments. This is particularly clear for \( D^5 \) sites, which show two clearly-resolved peaks, but also for the \( T^4 \) and \( T^3 \) peaks which show more or less pronounced shoulders (more clearly visible on \( ^{29}\text{Si}[^1\text{H}] \) cross polarization MAS spectra that have better signal to noise, data not shown). The deconvolution of spectra in individual components are shown in ESI (Fig. S1†). These different components may be due to differences in the nature of the neighboring Si sites (\( D^1, D^2, T^2 \) or \( T^3 \)) or, for \( T^2 \) species, to the nature of the R group of uncondensed O atoms (O−H or unreacted O−CH\(_3\)−CH\(_3\) moieties). Attempts to assign these different contributions are discussed further below.

The \( ^{29}\text{Si} \) NMR spectra of the hybrid glasses, samples 1 and 2, shown in Fig. 2a, are very similar and their assignments are presented in Table 3. This is more clearly reflected in a quantitative analysis of the \( ^{29}\text{Si} \) NMR data shown in Fig. 2b, which are based on the spectral decompositions shown in ESI (Fig. S1†).

Another important observation from these quantitative analyses is the discrepancy between the overall populations of \( D^n \) and \( T^n \) sites and the relative amounts of DMDES and MTES used for the synthesis. The stars in Fig. 2b indicate the populations expected based on the composition of the synthesis mixtures. They reveal that a significant proportion of the \( D \) sites have been lost in the course of the synthesis procedure or during the thermal treatments necessary to remove the solvent (70 °C/24 h), to remove the water (110 °C/24 h) or to consolidate the hybrid glasses (temperature of consolidation is listed in Table 1). This effect is significantly more pronounced in the case of the sample 2, which has the highest DMDES content (35%) in the synthesis mixture. As shown in Table 4, this different behavior appears to be due to a very subtle difference of \( D^6 \) and \( T^n \) relative proportions, with \( T^n/D^6 \) ratios varying between 4.6 and 3.8 in hybrid glass samples 1 and 2, respectively, compared to MTES/DMDES ratios of 3.0 and 1.9 in the synthesis mixtures.

These unexpected results are corroborated by quantitative \( ^{13}\text{C} \) NMR data, which also shed some light on the nature of uncondensed O atoms. Fig. 3a shows quantitative \( ^{13}\text{C} \) NMR spectra recorded at room temperature for hybrid glasses 1 (in blue) and 2 (in red). The signatures of (\( \text{CH}_3 \))\(_2\text{SiO}_3 \) species originating from DMDES monomers (at \( -3 \) ppm) and \( \text{CH}_3=\text{SiO}_3 \) species originating from MTES monomers (at \( -1 \) ppm) are well resolved in all \( ^{13}\text{C} \) spectra. Changes in relative amplitudes reflect again to some extent the relative ratios of monomers in the synthesis mixtures and confirm the assignments. Two other peaks are detected in the \( ^{13}\text{C} \) NMR spectra, at 18 and 58 ppm, which may be assigned to \( \text{CH}_3=\text{CH}_2=\text{O} \) and \( -\text{CH}_2=\text{O} \) environments (respectively) corresponding to partially unreacted ethoxy groups, Si−O−CH\(_3\)−CH\(_3\) functions carried by \( D^1 \) or \( T^2 \) Si atoms. Those data are in good agreement with the Raman results which also show the presence of some unreacted ethoxy groups.

Quantitative analyses of \( ^{13}\text{C} \) NMR data, shown in Fig. 3b and Table 4, confirm the loss of a significant proportion of the DMDES monomers (or of their products) in the course of the materials synthesis. These data provide very reliable results since solid nature of the hybrid glasses allowed the use of faster MAS spinning rates (typically 12 kHz as compared to 5.5 kHz for gel samples). The ratios between the area of the peak assigned to \( \text{CH}_3=\text{SiO}_3 \) species (at \( -3 \) ppm) and half the area of the peak assigned to (\( \text{CH}_3 \))\(_2\text{SiO}_3 \) species (at \( -1 \) ppm) are 4.8 and 3.7 for gel samples 1 and 2, respectively. These results are

![Fig. 2](image)

**Table 3** The assignments of the \( ^{29}\text{Si} \) MAS NMR Spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical shift/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D^0 )</td>
</tr>
<tr>
<td>1</td>
<td>-17.2</td>
</tr>
<tr>
<td>2</td>
<td>-16.4</td>
</tr>
</tbody>
</table>
in quantitative agreement with the ratios between the cumulated areas of T² and D² ²⁹Si NMR peaks (4.6 and 3.8, respectively), and considerably higher than the MTES/DMDES ratios of the synthesis mixture (3.0 and 1.9, respectively). As already observed from ²⁹Si NMR data, the loss of DMDES moieties is more severe in the sample 2 containing the higher amount of these monomers in the synthesis mixture, which tends to even out the contrast of compositions between the two samples. Quantifications of the areas of the two resonances assigned to the –O–CH₂–CH₃ groups reveal the nature of the incompletely condensed D¹ and T³ Si environments detected in ²⁹Si NMR data. Combining both quantitative ²⁹Si and ¹³C NMR data (see details in ESI†), we find that 24% of non-polymerized Si–O sites are in the form of Si–O–CH₂–CH₃ rather than Si–OH moieties, calculated from the combination of ¹³C and ²⁹Si quantitative NMR data (see details in ESI).

3.3. The network analysis of the hybrid glasses

One-dimensional ²⁹Si NMR spectra resolve a certain number of local Si environments, or “molecular motifs” characterized by the number of Si–C bonds and the number of Si neighbors connected via bridging O atoms as shown in Fig. 2. More extended motifs can however be identified by recording two-dimensional correlation spectra that probe the connectivities between Si atoms, in the hope to better understand in particular the fine structures of the ²⁹Si spectra. Examples of these fine structures are highlighted on the top Fig. 4 by the spectral decomposition of a ²⁹Si[¹H] CP-MAS NMR spectrum collected for the sample hybrid glass 2, with individual components shown as grey lines. Between 2 to 3 different types of D², T², and T³ environments are thus distinguished, which are designated thereafter as D₃⁺, D₅⁻, D₇, T₄⁻, T₆⁻, T₈⁻, T₆⁺, T₈⁺, and T₁₀⁺. The two-dimensional spectra shown in Fig. 4 were collected to try to better understand the origins of these different features. They were obtained with a sequence of radio-frequency pulses designed to reintroduce the homonuclear dipole–dipole couplings between nearby ²⁹Si nuclei to probe their spatial proximities. This experiment was conducted in conditions specifically optimized to yield intense cross peaks for the short Si–Si distances of ca. 3 Å between connected ²⁹Si–O–²⁹Si pairs and weak or negligible cross peaks for the longer distances associated with non-connected pairs. The result of such an experiment (after the “shearing” transformation, see details in Experimental section) is a 2D map in which pairs of correlation peaks appear on both parts of the spectrum diagonal at horizontal and vertical ²⁹Si frequencies corresponding to the nuclei that are connected. Because of severe signal to noise limitations in the original 2D spectrum (shown in blue), a symmetrization procedure was applied to gain signal to noise (in principle by the square root of 2) by adding up the regions on D¹ sites. It seems instead that the more hydrophobic character of the sample of hybrid glass 2 stabilizes these Si–O–CH₂–CH₃ moieties (both on D¹ and T³ sites), which may well contribute to their inherent flexibility and hydrophobicity. The amount of uncondensed Si sites (whether in the form of Si–OH or Si–OEt) D¹ and T³ was used to calculate the probability for a Si–O bond to remain uncondensed. We find that, in both hybrid glasses, this probability is between 11 and 12% for Si–O bonds in T sites as compared to 3 to 5% for D sites. This means that DMDES precursors tend to condense more easily than MTES.

### Table 4 Summary of the quantitative ¹³C and ²⁹Si NMR analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>MTES (%)</th>
<th>DMDES (%)</th>
<th>MTES/DMDES</th>
<th>NMR quantifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>25</td>
<td>3.0</td>
<td>(6.6/8.0)/I(D⁶¹)</td>
</tr>
<tr>
<td>2</td>
<td>65</td>
<td>35</td>
<td>1.9</td>
<td>I(CH₃–SiO₂)/I(CH₃)</td>
</tr>
</tbody>
</table>

* Proportion of incompletely condensed Si [D¹ or T² sites] forming Si–O–CH₂–CH₃ rather than Si–OH moieties, calculated from the combination of ¹³C and ²⁹Si quantitative NMR data (see details in ESI).
Fig. 4 Dipolar -mediated $^{29}$Si–$^{29}$Si correlation NMR spectra for the sample hybrid glass 2 65%MTES-35%DMDES, revealing close proximities between Si atoms characteristic of Si–O–Si framework connectivity. The blue contours correspond to the original spectrum (sheared from SQ–DQ to DQ–DQ representation, see experimental section for details) whereas the red contours correspond to a spectrum obtained by symmetrization with respect to the diagonal (shown as a black dashed line) of the former, to increase signal to noise. Only the upper-left half of this symmetric spectrum is shown to better see the original spectrum underneath. 1D spectra shown in black on top and right side of the 2D spectrum are $^{29}$Si [$^1$H] CP-MAS spectra recorded with identical contact time as the 2D experiment. The 1D model obtained by decomposition of this $^{29}$Si [$^1$H] CP-MAS spectrum in individual contributions (shown as grey lines) is shown in red.

both sides of diagonal. The resulting 2D spectrum is shown in red in Fig. 4, overlaid with the original spectrum. Because of the symmetry of this spectrum with respect to the diagonal, only its upper-left half is shown to better illustrate the original (blue) spectrum underneath (the symmetric representation can sometimes be misleading by making high noise level points look like correlation peaks).

The main features of the correlation spectrum reveal extended molecular motifs centered on Si–O–Si pairs that are depicted schematically in Fig. 4 (using the same color code as in Fig. 2), and which point to different levels of network ramification, with 4-fold-branched T$_3$–T$_4$ pairs, 3-fold-branched T$_3$–T$_4$ and D$_2$–T$_3$ pairs, linear D$_2$–T$_2$, D$_2$–T$_2$ and D$_2$–D$_2$ pairs. The 2D spectrum shows a higher intensity of D$_2$–D$_2$ correlations as compared to D$_2$–T$^*_2$ correlations, which barely point out of the noise level after symmetrization (and only at the D$_2$–T$^*_2$ position). The quantitative 1D spectra of all samples show D$_2$ intensities comparable to the D$^*_1$ intensities, suggesting that the D$_2$ position ($-17$ ppm) could be a signature of a D$_2$–D$_2$ end chain.

Semi-quantitative estimations of the conditional probability for each site to be correlated with another may be calculated assuming that (i) Si–Si distances between connected Si–O–Si sites are all identical (resulting in equal efficiencies of the double-quantum excitation during the NMR sequence) and (ii) that signal losses during the sequence are the same for all sites. The results indicate that site T$_3^a$ environments are primarily connected to T$^*_3$ environments (primarily to other T$_3^a$), with only ca. 12% probability to be connected to T$^*_3$ sites and ca. 11% probability to be connected to D$^2$ sites. They are hence indicative of strongly reticulated regions. In contrast, T$_3^b$ environments have higher probabilities to be connected to T$^*_3$ sites (17%) and 10% to be connected to D$^2$ sites. They are nevertheless connected primarily to other T$_3^a$ sites and to T$_3^b$ environments (49% and 23%, respectively), indicating that they may well correspond to edges of these strongly interconnected domains.

The quantitative analyzes of 1D $^{29}$Si NMR spectra of samples may be re-examined in the light of this difference of reticulation degrees around T$_3^a$ and T$_3^b$ Si environments. In both samples the more reticulated T$_3^a$ sites appear to account for ca. 46% of the total amount of T$^*_3$ sites, in hybrid glass sample 1, 75%MTES-25%DMDES and 51% in hybrid glass sample 2, 65%MTES-35%DMDES.

Other 2D peak intensities are less intense and thereby less reliable, making it difficult to understand the differences between different types of D$^2$ sites and different types of T$^*_2$ sites.

We observe however that D$^2$ sites in general tend to have a stronger probability to be connected to other D$^2$ sites rather than to T$^*_2$ sites, whereas T$^*_2$ sites are connected to other T$^*_2$ sites rather than to D$^2$ sites. Both have comparable (and rather high) probabilities to be connected to T$^*_3$ sites.

While NMR provides deep insights regarding the structure at the molecular level, the microstructural morphologies of the sol–gel materials are also known to affect materials properties. SANS, due to its nature of being a nondestructive and statistically significant technique, is applied to probe the possible segregation, separation, and presence of micro/nano-pores within the consolidated hybrid glasses. In particular, we made use of the high-brilliance synchrotron X-ray beam to ensure that weak scattering intensities can be captured.

The SANS profiles of both hybrid glass samples are shown in Fig. 5. It is clear that these profiles bear much resemblance. First, the reduced (slit-smeared) differential scattering cross section $d \Sigma(q)/Vd\Omega$ is very low in intensity and noisy, which indicates that the scattering contrast that gives rise to the scattering signal is weak. This high degree of noise originates from data reduction, whereas the sample scattering, although weak, is unmistakably evident from the raw scattering data (not shown). Second, a broad scattering feature at $q$ below 0.01 A$^{-1}$ exists, which indicates certain degree of microphase separation. This scattering feature also does not appear to have a strong dependence on the molar ratio between MTES and DMDES.

NMR results of these hybrid glass materials strongly indicate that they possess a network structure. To fully account for
the scattering profiles, we made use of the Debye-Bueche model,\textsuperscript{44} which describes scattering from a randomly distributed two-phase system, a situation very similar to the hybrid glasses. This model assumes that the pair-correlation function $\gamma(r)$ follows a simple exponential decay,

$$\gamma(r) = \exp \left( -\frac{r}{\xi} \right)$$  \hspace{1cm} (1)

where $r$ is the interatomic distance, and $\xi$, the correlation length, is a measure of the average separation distance between the separated phases.

The scattering cross section, following eqn (1), is

$$\frac{d\Sigma(q)}{d\Omega} = \frac{8\pi(\Delta\rho)^2 \phi_1 \phi_2 \xi^2}{[1 + (q\xi)^2]^{2}}$$  \hspace{1cm} (2)

Here, $\Delta\rho$ is the scattering contrast; $\phi_1$ and $\phi_2$ are the volume fraction of the two phases, respectively.

Fig. 5 shows that despite the high degree of noise, the Debye-Bueche model describes the scattering intensity profiles very well. The correlation lengths were found to be $10.3 \pm 0.8$ nm for sample 1 and $7.5 \pm 0.1$ nm for sample 2, respectively. This result indicates that higher MTES-to-DMDES ratio leads to a larger phase-separation distance. We also note that our observed scattering profiles are similar to those acquired by Hagiwara et al.\textsuperscript{45} in a similar hybrid organoalkoxide material prepared using sol-gel synthesis. Instead of characterizing possible phase separation, these authors opted to view the gels as fractal structures, perhaps due to the limited $q$ range of their SAXS camera. In our case, the broad $q$ range of the USAXS instrument leaves little doubt about the bend of scattering curve near 0.01 Å$^{-1}$, which prompted our analysis of a phase-separated network structure that is consistent with NMR findings. Such type of separation was also visually confirmed by atomic force microscopy in a study of nanohybrids containing 1,8-bis(triethoxysilyl)octane.\textsuperscript{46}

![Fig. 5 Synchrotron SAXS data and fit using Debye-Bueche model of sample 1 (75%MTES + 25%DMDES) and sample 2 (65%MTES + 35%DMDES).](image)

We also evaluated the degree of phase separation following eqn (2). For this purpose, we calculated the scattering length densities of both MTES and DMDES, which are tabulated in Table 5. Assuming complete phase separation, the theoretical X-ray scattering contrast between MTES and DMDES is $2.31 \times 10^{20}$ cm$^{-4}$. Empirically, the ratio between the experimental and theoretical scattering contrasts could serve to gauge the phase separation. Here, following the fitting results from Fig. 5, we found that the experimental scattering contrasts for samples 1 and 2 are $8.35 \times 10^{16}$ cm$^{-4}$ and $1.97 \times 10^{17}$ cm$^{-4}$, respectively. In other words, the experimental contrasts are on the order of $10^{-3}$ of the theoretical contrast. This result shows that MTES and DMDES are fairly homogenously mixed and do not phase separate to form well-defined phase structures. In other words, from an electron density point of view, the hybrid glass materials possess a high degree of uniformity across nm to micrometer length scales.

Last but not least, we note that the low scattering intensities also confirm that micro- and nano-pores are completely absent in these hybrid glasses, as the pores have the highest possible X-ray scattering contrast and their presence would have been eminently captured by the scattering methods. From a mechanical property point of view, the lack of pore-related defects is beneficial in improving fracture toughness and reducing fatigue cracks.

### 3.4. The BET surface area analysis

The N$_2$ physisorption data are summarized in the Table 1. Both samples demonstrate very low BET surface areas with values on the order of 0.01 m$^2$ g$^{-1}$, which is in good agreement with SAXS findings, which show a level of porosity below detection limit. Furthermore, these results suggest that samples with higher amount of disubstituted alkoxide have a lower BET surface areas.

<table>
<thead>
<tr>
<th>Mass density (g cm$^{-3}$)</th>
<th>Scattering length density (10$^{20}$ cm$^{-2}$)</th>
<th>Scattering contrast (10$^{20}$ cm$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTES</td>
<td>1.332</td>
<td>11.66</td>
</tr>
<tr>
<td>DMDES</td>
<td>1.122</td>
<td>10.14</td>
</tr>
</tbody>
</table>

*Mass densities of MTES and DMDES are estimated from a series of mass densities of hybrid glasses containing different molar ratios of MTES and DMDES.*

### 3.5. The SEM analysis

The SEM images of the surface fractures and the cross sections of the fractures of both studied hybrid glass samples are presented in Fig. 6. The images of the surface Fig. 6a and b show a smooth surface without defects or glass domains. Because the surfaces are defect-free, and hence featureless, we opted to show SEM results near the fracture, where the defects that emerged during the fracture process are also highlighted. The images of the cross sections of the fracture (Fig. 6c–f) show homogenous structures without formation of any domains or
without any visible phase separation which is in agreement with the previous data. No micro- or macro-pores were detected in the hybrid glasses. These surface-sensitive SEM data are in very good agreement with the SAXS data, which are connected to the bulk microstructure. The cross section of the fracture of the hybrid glass with composition 65%MTES-35%DMES presented in Fig. 6d and f display a flaky area which shows also a certain orientation of the material. The presence of the flakes can be correlated with the higher concentration of the organic content in this sample. On the other hand, the

Fig. 6 The SEM images of the surfaces of (a) 75%MTES-25%DMDES; and (b) 65%MTES-35%DMES hybrid glass samples (c) and (e) show the cross-sections of fracture for the 75%MTES-25%DMDES sample; (d) and (f) show the cross-sections of fracture for the 65%MTES-35%DMDES sample.
images of the cross section of the hybrid glass with composition 75%MTES-25%DMDES presented in Fig. 6c and e show a clear fracture with longitudinal lines. This aspect of the fracture can be correlated with higher content of Si–O–Si bonds in sample 1 as it was revealed by the NMR analysis. The highest content of Si–O–Si bonds is increasing the rigidity of the sample which can determine a clearer fracture.

4. Conclusions

The structure and morphology of hybrid glasses prepared with different ratios of MTES and DMDES have been investigated in this study using Raman, one- and two-dimensional $^{29}$Si and one dimensional $^{13}$C NMR spectroscopy, SAXS and SEM microscopy.

The Raman spectroscopy showed that the structure of the matrix is formed mainly by 8-member ring structures. In addition, the Raman measurements revealed that organic groups are placed at the surface of the hybrid glasses.

The $^{13}$C and $^{29}$Si NMR spectroscopy offered information about the molecular structures of the hybrid glasses. The main molecular species were quantitatively identified. Quantitative $^{29}$Si NMR of the hybrid glasses samples shown characteristic signals to $D_1^1$, $D_2^1$, $T_1^1$, and $T_2^1$. The quantitative measurements identify the final ratio between the mono substituted species CH$_3$-SiO$_3$ and the di-substituted species (CH$_3$)$_2$-SiO$_2$ which are present in each studied hybrid glass. This points out a loss of DMDES precursors during the synthesis. Our data reveal the presence of unhydrolyzed Si-OEt groups which was also identified in the Raman spectra. These Si-OEt groups, seem to be stabilized when higher amounts of DMDES are present, and may increase the inter-chain mobility by acting as lubricant owing to their inherent flexibility and hydrophobicity, in contrast with Si-OH groups that form hydrogen bonds. This can explain the higher rigidity of sample 1.

Two-dimensional $^{29}$Si NMR data show more extended structural motifs within the framework, which seem to reveal that two distinct types of $T^4$ Si environments (the dominant type of Si sites in both materials) exist, that correspond to Si atoms located in regions with different extents of framework condensation.

The SAXS data revealed that the mono substituted species (CH$_3$-SiO$_3$) and the di-substituted species (CH$_3$)$_2$-SiO$_2$ that are coming from hydrolysis and polycondensation of the MTES and DMDES are homogeneously mixed and do not separate to form a well-defined phase structure. In addition, the SAXS data confirmed the absence of any nano- or micro-pores.

The absence of the pores was confirmed also by the BET and SEM analyses. The SEM images of the fractures confirmed that the sample 1 (75%MTES-25%DMDES) has higher rigidity than sample 2(75%MTES-25%DMDES) which contains a higher amount of DMDES. Based on the NMR data it was concluded that the samples with higher amount of DMDES retain a higher amount of unhydrolyzed Si-OEt groups which can increase the flexibility of the hybrid glass 2.

We have performed a thorough investigation of the structure of hybrid glasses at both a molecular level and a micro-structure level. We envisage that our findings in this study would serve as a bridge to connect the molecular arrangements of the hybrid glasses to their physical characteristics, and potentially impact the synthesis and design of a broader range of hybrid glass materials by consolidation of melting gels with improved physical, mechanical, chemical and electrochemical performances.

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References


