

# Structure–property behaviour of sol–gel derived hybrid materials: effect of a polymeric acid catalyst

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Poly(styrene sulphonic acid) is used to prepare ceramers based upon poly(tetramethylene oxide) oligomers and tetraethyl orthosilicate. These hybrid network materials prepared by sol–gel processing demonstrate the successful use of a polymeric acid catalyst to prepare these previously described optically clear hybrid materials. The mechanical properties of the polymeric acid-catalysed ceramers are improved over systems of the same composition catalysed with HCl. The loss dispersion behaviour of these materials as well as general morphological features, evaluated by small-angle X-ray scattering, are quite similar to those of the ceramers catalysed with HCl. Some comparisons of their thermogravimetric behaviour are also made.

(Keywords: hybrid material; structure–property behaviour; sol–gel processing; catalyst)

## INTRODUCTION

The polymerization of liquid metal alkoxides to produce chemical glasses is commonly referred to as the sol–gel process<sup>1</sup>. More recently, however, the sol–gel process has been utilized successfully for the preparation of hybrid organic/inorganic networks<sup>2–4</sup>. The structure–property behaviour has been reported for a novel class of these sol–gel derived hybrid materials, commonly referred to as ‘ceramers’, prepared in our laboratories<sup>2,5–10</sup>. Initially tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS) was reacted under acidic conditions with silanol-terminated poly(dimethyl siloxane) oligomers (PDMS)<sup>2,5,6</sup>. The hybrid materials produced were monolithic and optically clear. The first generation of ceramers exhibited microphase separation and mechanical properties somewhat intermediate between those of a sol–gel glass and the polymeric phase. The next generation of ceramers were the product of a sol–gel reaction between triethoxysilane-terminated poly(tetramethylene oxide) oligomers (PTMO) and TEOS under acidic conditions<sup>7,8</sup>. The PTMO-based ceramers were also monolithic and optically clear. However, the mechanical properties of the PTMO/TEOS hybrids were improved significantly compared to the PDMS/TEOS ceramers. The increased functionality of the end-capped PTMO oligomers (six *versus* two for the PDMS) most likely improved the incorporation of both ends of the oligomer into the silicate network formed by the sol–gel process. The ceramers’ overall mechanical properties were improved by reducing the number of dangling chain ends. The higher modulus and tensile strength of the PTMO oligomers, compared with oligomers of PDMS, would also contribute to the improved properties of the PTMO/TEOS ceramers.

The mechanical and physical properties of ceramers are a function of their age and thermal history, as

reported by Huang *et al.*<sup>8</sup>. The Young’s modulus and stress at break increased along with a decrease in the elongation at break as a function of age for ceramers based upon TEOS and silane end-capped PTMO<sup>8</sup>. These same materials responded in a similar manner following post-curing at elevated temperatures with respect to the initial processing temperature. The changes in the mechanical properties were attributed to a ‘chemical ageing process’, for which a mechanism has not been determined, but is believed to be related to a higher extent of reaction of the silicon alkoxides. This would result in densification of the silicate structure by the elimination of alcohol and water as the by-products of the formation of a Si–O–Si linkage. (Note: The hydrolysis/condensation reaction products of TEOS will be referred to as ‘silicate structure’ in this text even though it is not completely accurate in describing the actual structure.) The elimination of the solvents, which would behave as plasticizers, would also contribute to the observed changes in the properties with time. The ageing effect was also reported, but to a lesser extent, for a hybrid composition incorporating titanium isopropoxide, which is considered a catalyst for the sol–gel reaction<sup>8,10,11</sup>.

One explanation of the time-dependent behaviour of the TEOS/PTMO systems, as well as other ceramers based upon poly(ether ketone) oligomers, is based upon the time–temperature transformation (TTT) model developed by Gilham for network-forming systems<sup>11</sup>. As the sol–gel process proceeds, the viscosity of the system continues to increase until at the gel point it goes to infinity. However, as the extent of conversion increases,  $T_g$  also increases until it reaches the reaction temperature, at which point the system vitrifies. Vitrification effectively stops the diffusion of the reacting species and thus stops the reaction. Time and thermal treatments at a temperature higher than the initial vitrification temperature will further the process (one will recognize that this must be below the degradation temperature of the oligomeric component). It is postulated that these

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changes with time in the ceramers are related to an increase in the connectivity of the network, which would support higher stresses, as has been demonstrated for numerous ceramers<sup>10,11</sup>. Another possible explanation for these time-dependent changes in the ceramers is diffusion of low-molecular-weight species out of the network. The low-molecular-weight species of concern would of course be the acid catalyst and the solvents used for dilution and compatibilization of reactants as well as those generated by the reaction.

The selection of an acid catalyst for these hybrid materials was prompted by the desire to produce well mixed systems on a molecular level. Brinker demonstrated that lightly branched linear-like silicate structures are formed for the acid-catalysed sol-gel conversion of TEOS<sup>12</sup>. Basic catalysts, on the other hand, tend to promote the formation of highly branched, dense silicate particles from TEOS. The acid-catalysed gels also develop a higher density than base-catalysed systems. Thus, acid-catalysed gels have a more continuous silicate structure that should promote mixing with the oligomers, assuming of course that the thermodynamics of mixing are favourable. HCl and glacial acetic acid are two catalysts that have been used effectively to produce ceramers based upon PDMS and TEOS as well as the PTMO/TEOS forms.

Since both HCl and glacial acetic acid would be prone to diffusion, a polymeric catalyst was suggested by one of the authors (G.L.W.). A polymeric catalyst might reduce the observed chemical ageing of the ceramers compared to low-molecular-weight mineral or organic acids. In view of Sakka's work in which fibres were drawn from sols composed of silicon-based metal alkoxides<sup>13</sup>, a high-molecular-weight catalyst might be useful as a rheological modifier to enhance spinnability. The ability to draw fibres from sols is quite sensitive to the viscosity. At low extents of reaction the viscosity is too low in contrast to the viscosity of a gel, which is not suitable for fibre spinning. Thus, it would be desirable for these applications to increase the sol viscosity.

The purpose of this paper is to report the successful application of poly(styrene sulphonic acid) (PSS) as a catalyst for preparation of these novel inorganic/organic hybrids based upon TEOS and the silane end-capped oligomers of PTMO. Poly(styrene sulphonic acid) is readily available in various molecular weights and degrees of sulphonation, so it was selected for this study. The mechanical and morphological features of ceramers produced with PSS will be compared with equivalent compositions catalysed with HCl. In addition, the thermogravimetric behaviour will be discussed in terms of retained solvent effects and general degradation behaviour of the ceramers.

## EXPERIMENTAL

### Materials

The nomenclature that was developed for these systems is shown in Table 1<sup>6</sup>. The number in the parentheses immediately following TEOS refers to the initial weight fraction of TEOS with respect to the oligomer. The value in the parentheses following PTMO, in this case 2 K for 2000 g mol<sup>-1</sup>, is the number-average molecular weight of the uncapped oligomer. The value 100 refers to the water added, which will hydrolyse 100% of the alkoxide groups in the solution. The final value, 0.014, refers to

**Table 1** Nomenclature describing the composition of ceramers

Item	Description
TEOS(50)	Tetraethyl orthosilicate (wt% fraction with respect to oligomer)
PTMO(2K)	Functionalized oligomer ( <i>MW</i> )
100	Ratio water to alkoxide (mol%)
0.014	Ratio acid to alkoxide (%eqs)
(IPA/THF)	Solvents for compatibility

the acid-to-alkoxide ratio in equivalents. The specific acid catalyst will be designated in this paper as either PSS or HCl. The TEOS was obtained from Fluka Co. and used as received. The synthesis of the triethoxysilane end-capped poly(tetramethylene oxide) (PTMO) oligomers has been described elsewhere<sup>5</sup>. The PSS (70 000 g mol<sup>-1</sup>) was supplied as a 30 wt% solution (Polysciences Inc.; Cat. No. 8770). This was used as received without further purification. There were 0.0026 equivalents/gram of the PSS solution as determined by titration with standardized NaOH. The density of the PSS solution was determined to be 1.2 g ml<sup>-1</sup>.

### Example procedures

Six millilitres of isopropanol (IPA) and four millilitres of tetrahydrofuran (THF) are mixed in a 50 ml flask at ambient conditions. A 5 g portion of TEOS and 5 g of the silane end-capped oligomer are weighed into the IPA/THF solvent and stirred for approximately 10 to 15 min. The distilled-deionized water is then added volumetrically with stirring. One millilitre of the PSS solution (~0.9 g of PSS) is then added dropwise to the solution with vigorous stirring. Upon addition of the PSS solution, the viscosity appears to increase significantly, as indicated by a reduction of the magnetic stir bar speed. The mixture (sol) is stirred for 1 to 2 min after addition of the acid and then cast into a Teflon-coated Petri dish and covered to reduce evaporation. The high viscosity of the solution necessitated extra care in casting to remove bubbles generated by the stirring. This is not required for a system catalysed with an equivalent amount of HCl. The sol is then allowed to gel undisturbed at ambient conditions for approximately 4 days and then opened to the air to remove excess solvent. The age of a gel is designated as the elapsed time from the date of preparation of the sol.

### Characterization methods

The dynamic mechanical data were obtained using an automated Toyo Rheovibron Dynamic Viscoelastometer model DDV-IIC. Most samples were analysed between -150 and 100°C at a rate of 1 to 3°C min<sup>-1</sup>. All spectra represent data obtained at 11 Hz.

The mechanical properties were measured with an Instron model 1122 using an initial strain rate of 2 mm min<sup>-1</sup> at ambient conditions. The dogbone specimens ranged in thickness from 10 to 35 mils (0.25–0.90 mm) with a 10 mm initial length. The reported values represent an average of at least four specimens.

A Siemens Kratky camera system was utilized for small-angle X-ray scattering (SAXS) measurements in conjunction with a M. Braun position-sensitive detector from Innovative Technology Inc.

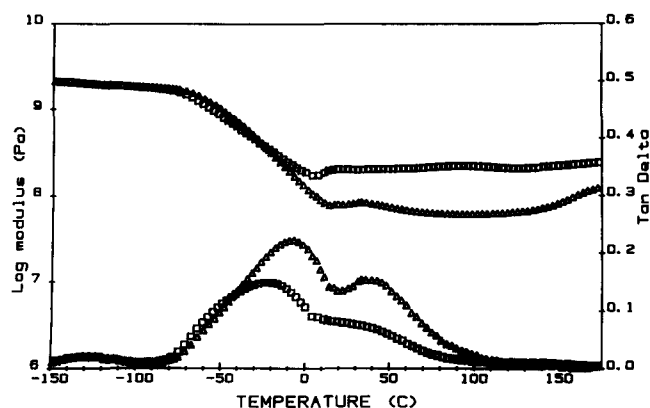
Thermogravimetric analysis was performed on a Seiko TG/DTA200 Simultaneous Thermo-Gravimetric/Differential Thermal Analyzer attached to a Seiko SSC5000 Series TA Disk Station. The samples, weighing approximately 10 to 15 mg, were evaluated at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . The atmosphere was either air or nitrogen at a flow rate of  $100 \mu\text{l min}^{-1}$ .

## RESULTS AND DISCUSSION

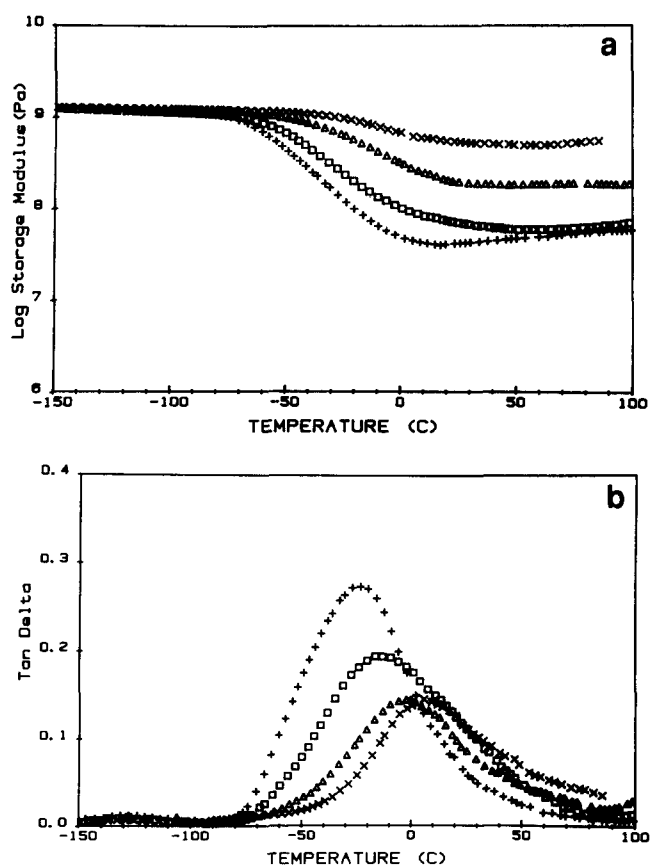
### Dynamic mechanical behaviour

The storage moduli,  $E'$ , and  $\tan \delta$  behaviour are represented in *Figure 1* for two TEOS(50)-PTMO(2K)-100-0.014 ceramers aged for 120 days. One sample was catalysed with HCl and the other with PSS. The storage modulus in the glassy state is similar for the two systems. Indeed, the storage moduli behaviour below  $-100^{\circ}\text{C}$  is what one would expect for a glassy polymer, *ca.* 1 GPa. The onset of  $T_g$  occurs at nearly the same temperature, approximately  $-70^{\circ}\text{C}$ , for both the HCl- and PSS-catalysed ceramers, as indicated by the drop in the storage modulus. However, the rubbery plateau above  $T_g$  is distinctly higher for the PSS-catalysed ceramer than for the HCl-catalysed ceramer. The observed difference is believed to be related to a higher extent of reaction for the PSS system, which will be discussed later.

The loss behaviour of these two materials provides more information as to the nature of the structural differences that account for the higher storage modulus of the PSS-catalysed ceramer in the rubbery region. The broadness of the loss dispersion peak is representative of the distribution of relaxation times of the PTMO segments associated with the different environments. The bimodal nature of the loss behaviour in *Figure 2b* is most likely related to some partial microphase separation. The broad  $\tan \delta$  peak indicates by its maximum that the  $T_g$  ( $-15^{\circ}\text{C}$ ) of the PSS ceramer is slightly lower than the  $T_g$  ( $0^{\circ}\text{C}$ ) of the HCl-catalysed ceramer. This is contrary to the expected  $\tan \delta$  behaviour for a network-forming system where  $T_g$  increases with higher conversions of the functional species. A model, proposed for a related system by one of the authors of this paper, describes two types of segmental restrictions imposed on the PTMO oligomers that influence the  $\tan \delta$   $T_g$  peak<sup>6</sup>. A type 1 restriction, according to this model, is due to the PTMO segments that are reacted at both ends into the silicate network. This type 1 restriction of the PTMO segments limits backbone mobility and thus increases the thermal



**Figure 1** The storage modulus and  $\tan \delta$  behaviour for two ceramers of composition TEOS(50)-PTMO(2K)-100-0.014. Acid is either HCl ( $\Delta$ ) or PSS ( $\square$ )



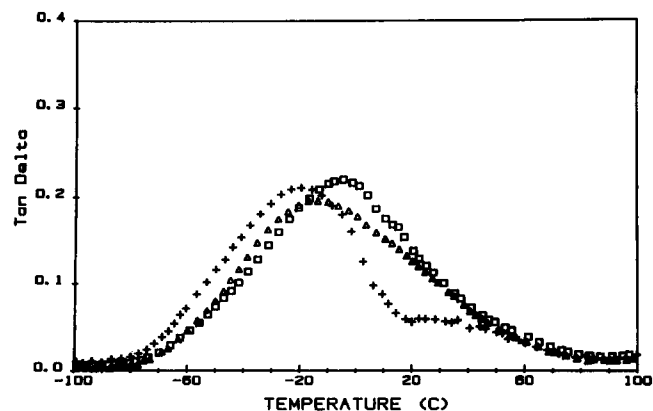
**Figure 2** The storage moduli as a function of increasing weight fraction of TEOS:  $\times$ , 70%;  $\Delta$ , 60%;  $\square$ , 50%;  $+$ , 40%. (b) The  $\tan \delta$  behaviour as a function of increasing weight fraction of TEOS. Symbols as in (a)

energy requirement necessary for long-range segmental motion associated with the glass transition. The second restriction, referred to as a type 2, occurs when the PTMO oligomer is partially 'encapsulated' by a partially condensed TEOS network. It has been reported that sol-gel derived silicate structures similar to those formed in the ceramers under acidic conditions are a combination of linear and cyclic polymers<sup>13,14</sup>. The formation of cyclic silicates could conceivably contribute to the loss dispersion curve in two different modes. One mode, as suggested by FTIR studies, is a ring bending and/or a bond rocking mode associated with the cyclic structures<sup>15</sup>. The other mode, in terms of loss dispersion, is the restriction of the chain segments passing through the cyclic structures. It was reported by Mauritz that the relative concentration of the cyclic silicate structures with respect to linear silicates formed by the condensation of TEOS within Nafion membranes decreased with time<sup>15</sup>. Thus, it is conceivable that, in the early stages of gel formation in the ceramers, PTMO segments could become encapsulated by these cyclic silicate structures. The density and thus rigidity of these silicate structures, as well as restrictions on the PTMO segments encapsulated within them, increase as the condensation of the reactive species proceeds. The structural changes associated with the higher extent of reaction lead to a decrease in the magnitude of the  $\tan \delta$  peak towards the higher temperature range of the broad dispersion and thus cause an apparent shift of the  $\tan \delta$  maxima to a lower temperature. This, in conjunction with the higher rubbery modulus, is indirect evidence that the PSS-

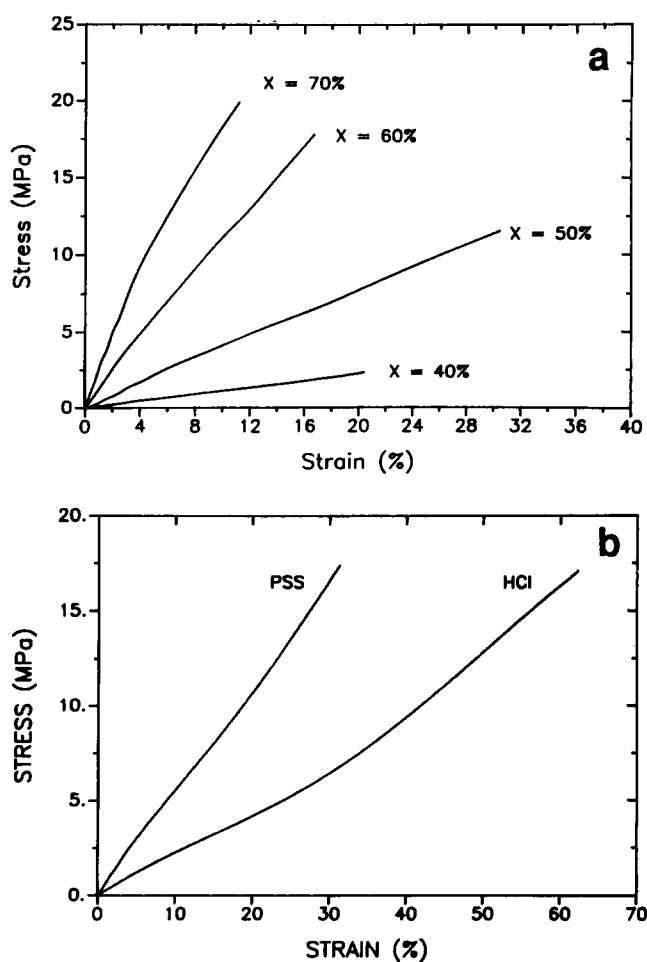
catysed ceramers convert a higher percentage of TEOS for an equivalent composition catalysed with the same concentration of HCl.

The molecular environments that give rise to the conjectured type 1 and type 2 restrictions should depend upon the volume fraction and compatibility of TEOS and PTMO for a given set of reaction conditions. The influence of the silicate phase on the dynamic mechanical behaviour is demonstrated in *Figure 2*. The storage moduli are plotted in *Figure 2a* for a series of PSS-catalysed ceramers, TEOS(*X*)-PTMO(2K)-100-0.014, where the initial weight fraction of TEOS was varied from 40% to 70%. At temperatures below  $-100^{\circ}\text{C}$  all four of the ceramers behave as a glassy polymer in terms of the storage moduli as seen for the two in *Figure 2*. The storage moduli (*Figure 2a*) in the rubbery region increases from *ca.*  $10^7$  to  $10^8$  Pa as the weight fraction of TEOS is raised from 40 to 70 wt%, respectively.

The loss dispersion peaks show both a temperature shift to a higher range and a decrease in the area with higher volume fraction of TEOS (*Figure 2b*). All the  $\tan \delta$  peaks appear to begin near  $-80^{\circ}\text{C}$ , then broaden significantly as the TEOS level is increased. The  $\tan \delta$  maxima (0.3) peak for the ceramer containing 40% TEOS is nearly twice the maxima (0.16) of the  $\tan \delta$  peak of the 70% TEOS hybrid. This reduction in the loss dispersion is attributed to the entrapment of PTMO segments within the silicate network, which limits their contribution to the molecular motions that give rise to the peak. The decrease in the magnitude of the  $\tan \delta$  along with the shift of the peak maxima to a higher temperature for this series is similar to reported trends for previous studies in this laboratory on formulations catalysed with HCl<sup>6,8,10</sup>. Additional insight into the influence of these two types of environments on the damping behaviour of the ceramers can be provided by *Figure 3*. Three different levels of water, 50%, 100% and 200%, were evaluated in a ceramer based upon the same  $2000 \text{ g mol}^{-1}$  silane end-capped PTMO oligomer. Each ceramer contains 50% TEOS and 0.014 equivalents of PSS catalyst. Note that the bimodal nature of the damping curve diminishes as the level of water is increased. This trend correlates well with previous reports in the literature, which indicate that the sol-gel reaction proceeds further as the mole ratio of water to alkoxide is increased. It is interesting to note that the change to higher levels of water shifts the overall maxima of each peak to a higher temperature,



**Figure 3** The  $\tan \delta$  behaviour for one particular ceramer composition (TEOS(50)-PTMO(2K)-*X*-0.014 PSS) as a function of stoichiometric water for alkoxide hydrolysis. +, 50%;  $\Delta$ , 100%;  $\square$ , 200%



**Figure 4** (a) Stress-strain response for PSS catalysed ceramers (TEOS(*x*)-PTMO(2K)-100-0.014) as a function of TEOS initial weight %. (b) Stress-strain response of two ceramers (TEOS(*x*)-PTMO(2K)-100-0.014) catalysed with different acids (PSS versus HCl). Initial strain rate in (a) and (b) is  $2 \text{ mm min}^{-1}$

but the range of the overall loss dispersion does not change significantly. The interpretation might be that at this level of TEOS, i.e. 50%, type 1 restrictions predominate the environment of the PTMO chains; however, there is no direct evidence for this.

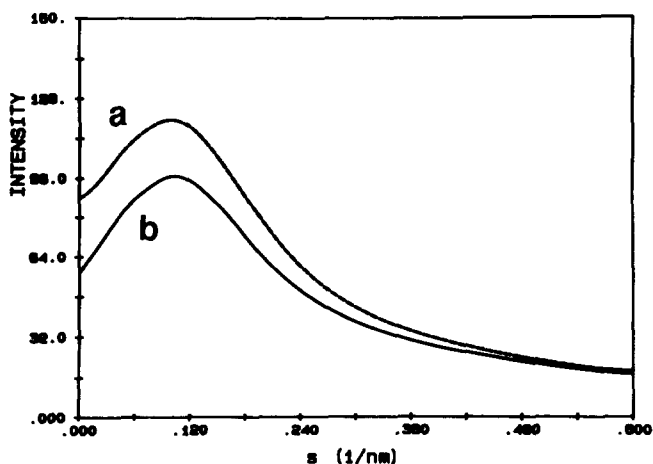
The corresponding stress-strain behaviour of this series of PSS-catalysed ceramers as a function of TEOS levels (*Figure 4a*) clearly demonstrates an increase in the modulus at  $25^{\circ}\text{C}$  with an increase in the level of TEOS. The modulus for the 40 wt% TEOS ceramer is 25 MPa compared to 250 MPa for the modulus of the 70 wt% TEOS sample. These values, measured 10 days after casting, compare to equivalent compositions of the HCl ceramers which were tested 30 days after casting<sup>15</sup>. There is no evidence of yield behaviour in any of the compositions presented in *Figure 4a* and in fact most show nearly 100% recovery at elongations of less than 50% of the strain at break. The sharp increase of Young's modulus with increasing TEOS in the PSS-catalysed ceramer can also be interpreted in terms of the type 1 and type 2 restrictions. The lower modulus of the 40% TEOS ceramer reflects an environment in which there is sufficient freedom from restrictions for PTMO chains to alter conformations in response to the strain applied during the experiment. Eventually the inorganic phase will become the continuous phase and support the bulk

of the applied load. Similar trends were observed for HCl-catalysed ceramers of equivalent compositions<sup>8,15</sup>.

A direct comparison of the stress-strain behaviour for two ceramers (TEOS(50)-PTMO(2K)-100-0.014), one catalysed with PSS and the other HCl, are presented in *Figure 4b*. Note that the ultimate strain is lower (35% versus 60%) and the Young's modulus is higher (55 MPa versus 36 MPa) for the PSS-catalysed ceramer compared with the HCl-catalysed hybrid. The higher Young's modulus supports the earlier statement that the PSS-catalysed network is more completely reacted than one prepared with HCl as the catalyst. This was verified by swelling experiments on samples prepared at the same time which were previously extracted in a Soxhlet apparatus for 48 h using THF as the solvent. Both the PSS- and HCl-catalysed ceramers (TEOS(50)-PTMO(2K)-100-0.014) contained less than 1% extractables by this method, which indicates that the networks contained an insignificant sol fraction. The equilibrium volume increase for the PSS-catalysed ceramer was 33% after swelling for 24 h in THF compared to 46% for the HCl ceramer. This behaviour, in conjunction with the dynamic mechanical and stress-strain data, is strong evidence that the PSS-catalysed ceramer has a more fully crosslinked or interconnected network than the HCl-catalysed ceramers.

#### Small-angle X-ray scattering behaviour

The morphological features of these materials were investigated by small-angle X-ray scattering (SAXS) to gain further insight regarding the local structure. The results presented up to this point indicate that structural differences between the HCl-catalysed and PSS-catalysed ceramers are mainly related to the extent of condensation of the silicate component. The bimodal nature of the loss dispersion behaviour (*Figure 2*) indicates some microphase separation, which has been described in terms of type 1 and type 2 environments. The SAXS behaviour of the HCl-catalysed hybrid materials has been well characterized in this laboratory and supports this observation<sup>5-8,15</sup>. The SAXS profiles are presented in *Figure 5* for two ceramers (TEOS(50)-PTMO(2K)-100-0.014) as a plot of the scattering intensity versus  $s$ , an angular factor related to the scattering vector. The angular factor  $s$  is defined as  $(2 \sin \theta / \lambda)$  where  $\theta$  is one-half



**Figure 5** SAXS intensity as a function of angular factor  $s$  for two ceramers (TEOS(50)-PTMO(2K)-100-0.014) catalysed with different acids (PSS versus HCl). Curve a, PSS; curve b, HCl

the radial scattering angle and  $\lambda$  is the wavelength. The reciprocal of  $s$  can be used as an estimate of the correlation length, as discussed earlier, but is only an approximation due to the smearing effect<sup>2</sup>. The presence of a maximum in the profile is indicative of a characteristic length in the scattering source, which is due to microphase separation within the network. Recall that the HCl-catalysed ceramers are optically clear and thus there is no evidence of any macrophase separation capable of scattering in the visible range. The PSS-catalysed ceramers do scatter a small amount of light as a consequence of surface roughness (application of a silicone oil to the surface eliminates the scattering). The SAXS behaviour of a PSS ceramer in *Figure 5* illustrates the similarity in morphology with the same composition as a HCl-catalysed hybrid. The position of the maxima of the two scattering profiles implies the average spacing of domains. The somewhat higher scattering intensity for the PSS ceramer compared to the HCl-catalysed material is further support of a denser silicate phase in the PSS ceramer. A higher silicate density increases the average electron density fluctuation for the system and thus raises the scattering intensity. This is supported by other more complete studies from our laboratory on HCl-catalysed ceramers<sup>6</sup>.

A morphological model has been developed for these novel materials, which is based upon the structure-property behaviour of these novel hybrid materials<sup>5</sup>. This model (*Figure 6*) illustrates the relationship between the PTMO oligomers and the inorganic-rich regions. The correlation distance, expressed as the reciprocal of  $s$ , is represented as the spacing between the inorganic phases made up largely of the silicate structure. It also accounts for the encapsulation of the PTMO segments referred to throughout this discussion. It also attempts to demonstrate the mixing between the PTMO and the silicate structure, which is indicated by the cross-hatches. This model helps to explain the broad nature of both the loss dispersion behaviour of the dynamic mechanical studies and the diffuse SAXS profiles. The influence of varying the volume fraction of the silicate phase has been discussed and visually one can relate the observed changes in the dynamic mechanical behaviour with the model, i.e. increase the silicate phase and the modulus will increase. That is to say, as the silicate volume fraction is increased, with higher levels of TEOS, it would significantly inhibit the motion of a larger number of PTMO segments.

Another variable one can evaluate to test the model in terms of the scattering behaviour is the molecular weight of the oligomer separating the silicate regions. The expectation is that, as the molecular weight of the oligomer is decreased, the spacing between these regions would decrease. This should shift the maximum in the scattering profile to a higher  $s$  value. A corresponding decrease in the intensity will also occur since the volume fraction of the PTMO will decrease at a given level of TEOS as the molecular weight of the PTMO is decreased. This is clearly demonstrated in *Figure 7*, which is a comparison of the SAXS behaviour for three ceramers catalysed by PSS using silane end-capped PTMO oligomers of 650, 1000 and 2000 g mol<sup>-1</sup>. All three were formulated with 50% TEOS, 100% water and 0.014 equivalents of PSS. The maxima of the scattering profile is shifted to a higher  $s$  value with decreasing molecular weight of the oligomer, as predicted. As noted, the

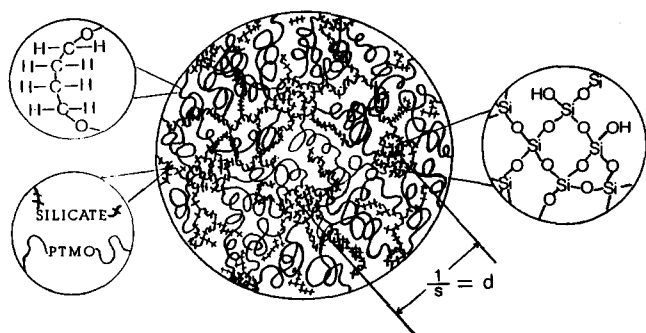


Figure 6 Morphological model for ceramers based upon PTMO/TEOS. The value  $d$  represents the correlation length, i.e.  $1/s$

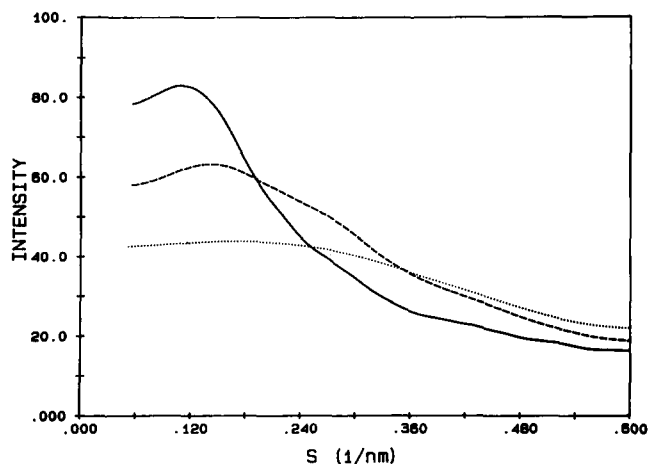


Figure 7 SAXS intensity as a function of angular factor  $s$  for PSS-catalysed ceramers (TEOS(50)-PTMO(X)-100-0.014 PSS) with oligomers of different molecular weight:  $\cdots$ , 650;  $---$ , 1000 and  $—$ , 2000  $\text{g mol}^{-1}$

maxima for the 650  $\text{g mol}^{-1}$  oligomer is very broad but a maximum value still exists. It is also evident that the intensity is higher at larger  $s$  values for the ceramer based upon the 650  $\text{g mol}^{-1}$  PTMO oligomer compared with the ceramers made with 1000 and 2000  $\text{g mol}^{-1}$ , which indicates more mixing. This trend also follows those observed for the HCl-catalysed materials and demonstrates the similarity in morphologies for these ceramers based upon PTMO and TEOS<sup>6,15</sup>.

#### Thermogravimetric behaviour

The main distinction between ceramers catalysed with PSS and HCl appears to be a small but significant difference in the extent of reaction. While the difference is small, it is reproducible and significant with respect to measured properties. It is reasonable that a higher extent of condensation should result in a higher residue on ignition, i.e. thermogravimetric analysis to 800°C, for the PSS-catalysed materials, which corresponds to lower weight loss due to ethanol or water by-products. As stated earlier, samples that were extracted and dried prior to swelling experiments demonstrated significantly more swelling for the HCl-catalysed ceramer than the PSS-catalysed ceramer, which supports other data indicating a higher conversion for the PSS ceramers. There is, as illustrated in Figure 8a, a slightly lower weight loss for the PSS ceramer compared to the HCl ceramer as measured between 30 and 800°C. The difference of 1 to 2% is reproducible. However, the initial weight loss

of nearly 16% in the PSS ceramer between 100 and 160°C does not occur with the HCl system.

Three possible explanations for this loss are: (1) some differences in degradation mechanism(s); (2) residual solvent within the pore structure; or (3) adsorbed species such as water. This weight loss is not highly sensitive to the purge gases of air and nitrogen as indicated by curves A and N, respectively in Figure 8b, which suggests that it is not due to oxidative degradation<sup>16</sup>. Residual solvents are considered unlikely since the boiling points of THF and IPA are 60°C and 74°C, respectively, and thus should have occurred at temperatures lower than 100°C. Also, there would be a corresponding decrease in the  $T_g$ , which was not observed. A third sample from the same PSS ceramer was treated isothermally at 60°C for 120 min (curve B, Figure 8b) to eliminate any possible entrapped or adsorbed solvents from the network. The temperature selected represents the upper end of the broad loss dispersion behaviour (Figure 1); thus the network chains should have increased mobility to enhance diffusion of solvent molecules through the pore structure. The weight loss of only 7% for the temperature range of 110 to 160°C after the isothermal treatment suggests some of the observed loss is due to entrapped solvents. However, it does not explain all of the weight loss observed for the PSS ceramer.

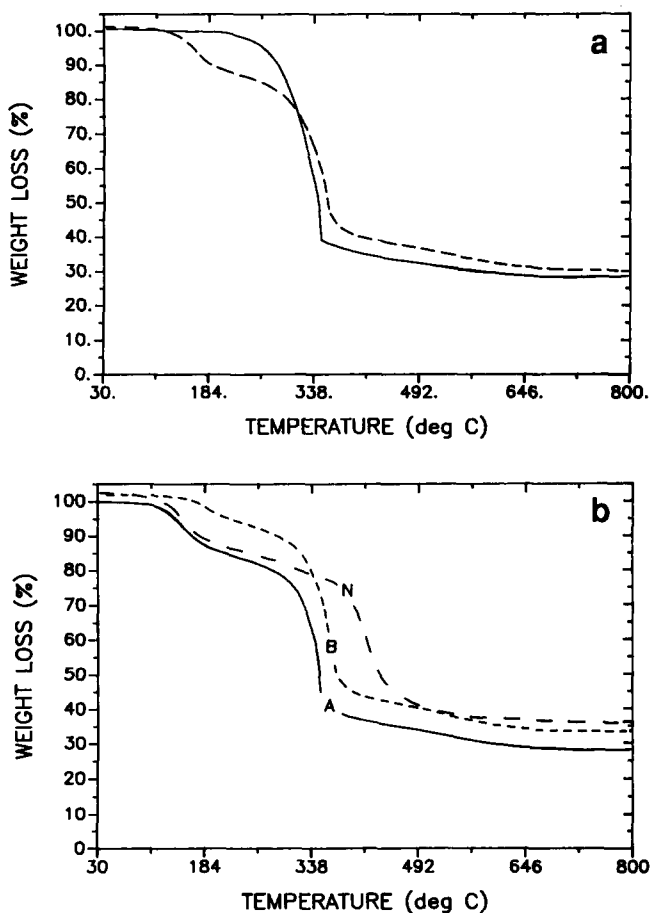


Figure 8 (a) Thermogravimetric behaviour of two ceramers (TEOS(50)-PTMO(2K)-100-0.014) catalysed with different acids.  $—$ , 0.014 HCl;  $---$ , 0.014 PSS. (b) Thermogravimetric behaviour of a TEOS(50)-PTMO(2K)-100-0.014 PSS ceramer after 20 days at ambient (curve A), same sample as in curve A but annealed for 120 min at 60°C (curve B), and same as curve A but under a nitrogen purge (curve N)

The final weight loss of all samples in both *Figures 8a* and *8b* occurring between 200 and 500°C is tentatively associated with oxidative degradation of the alkyl substituents of PTMO. This is supported by the fact that the onset of this weight loss between 200 and 500°C is delayed by the non-oxidative nitrogen purge gas. The chemical composition of the products generated by the pyrolysis of these ceramers is currently being investigated by t.g.a./mass spectroscopy.

## CONCLUSIONS

Poly(styrene sulphonic acid) has been shown to be an effective catalyst for the preparation of novel materials, referred to as ceramers. The use of the polymeric acid catalyst PSS promotes a higher level of condensation in gels prepared from PTMO/TEOS via the sol-gel process. The loss dispersion behaviour of these materials, which is quite broad, is attributed to molecular relaxations of PTMO segments constrained by the silicate structure derived from the hydrolysis and condensation reactions of the silicon alkoxide. There are two general classifications for these restrictions on the PTMO segments referred to as type 1 and type 2, which describe endgroup restrictions and segmental restrictions, respectively.

The magnitude of the loss dispersion behaviour of a PSS ceramer was lower than that of gel prepared with HCl as the catalyst. The elastic modulus at ambient conditions increased from 25 to 200 MPa as a function of an increasing level of TEOS from 40 to 70 wt%. The stress at break, also at ambient (12 MPa), and modulus (56 MPa) were higher for the PSS-catalysed ceramer compared to the HCl-catalysed material. The SAXS behaviour was similar for both systems, indicating similar morphological features. Overall, we have noted slight changes in the ultimate mechanical properties of those ceramers made using the PSS catalyst. There is an initial weight loss measured by t.g.a. between *ca.* 100 and 200°C for the PSS ceramer, which is not observed for HCl ceramer of the same composition. However, the overall residue on ignition (to 800°C) is higher for the PSS ceramer, which supports a higher extent of reaction in the PSS ceramer compared with an HCl ceramer. In summary, the poly(styrene sulphonic acid) is an effective catalyst for these novel hybrid materials, which suggests that it may apply equally as well for classical sol-gel

reactions. Observed changes in the sol viscosity upon addition of these catalysts indicate a possible method for modification of rheological behaviour of the sols.

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