Structure–property behaviour of hybrid materials incorporating tetraethoxysilane with multifunctional poly(tetramethylene oxide)

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Polytetramethylene oxide based polyurethane oligomers with multiple triethoxysilane groups have been successfully incorporated into a TEOS based silicate network. It is observed that the incorporation of these oligomeric compounds was enhanced by the presence of additional functional groups along their backbone. The materials produced showed significant improvement in both tensile modulus and strength over previous organic–inorganic hybrid systems. As the number of functional groups per molecule increased, the stiffness of the material increased and the oligomeric T_g shifted to higher temperatures. Also, the SAXS correlation distance decreased systematically. A schematic model suggested previously can still be used to interpret these results. Other effects of TEOS content and ageing are also reported and discussed.

(Keywords: sol-gel; hybrid; PTMO; TEOS; SAXS; DMA)

INTRODUCTION

In the last two decades, the sol–gel reaction has been extensively studied as an alternative to the conventional fusion method of making glasses[1–4]. Although this new approach does have the drawback of high cost, the advantages of relatively low processing temperature and high purity of the final products have attracted considerable interest. In particular, the possibility of making homogeneous, multicomponent glasses that are difficult to make conventionally has resulted in considerable effort being devoted to the sol–gel approach.

Basically, the sol–gel reaction can be viewed as a two-step network-forming process as shown by the following scheme:

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH$$

$$M(OH)_n \rightarrow MO_{n/2} + n/2H_2O$$

where M is a metal such as Si, Ti, or Al, and R is an organic group such as methyl, ethyl, etc..

To further elaborate the reaction scheme, one can see that the first step is the hydrolysis reaction of the metal alkoxide and the second step is a polycondensation reaction. This process is usually catalysed by either acid or base and the final structure of the inorganic glasses greatly depends on type of catalyst used. For making multicomponent glasses, more than one type of metal alkoxide can be employed and, with some modification of the reaction procedure, an amorphous, homogeneous product can be obtained with almost any composition. This network-forming process, or sol-to-gel transition, is usually carried out under ambient conditions. The resulting cured gel is clear and brittle and often fractures if the monolith is reasonably thick (about 1 mm). These gel materials will then undergo a sintering process (e.g., around 900°C for silicates) to form glasses which possess properties similar to those made by the conventional fusion method. Due to the high temperature of this gel-to-glass transition, any modification using completely organic based compounds has been considered unfeasible by most researchers.

By examining the reaction scheme and considering the polymerization nature of the sol–gel process, it seems possible to incorporate functionalized organic compounds with inorganic metal alkoxides if co-condensation of the two species can take place and if the problem of incompatibility can be minimized during reaction. If one takes the dried gel as the final product and never goes through the sintering procedure, the limitation of organic modifications can then be disregarded. Although these organic modified gels will not be considered as conventional sol–gel glasses, they do represent a new group of hybrid materials. They should show some characteristics of the inorganic glassy network and also some properties of the organic species. In particular, the cracking problem usually observed in the pure inorganic sol–gel systems may be solved due to the decrease in crosslinking density by the addition of some non-hydrolysable groups. Furthermore, it may also be possible that materials with special properties can be produced by choosing appropriate organic species. Indeed, a few studies have been carried out and the results are encouraging as will be discussed below.

Schmidt and coworkers[5,6] have reported several types

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of organic modifications to the sol–gel process. It has been shown that by incorporating hydroxyl groups into the gel, the hydrophobic nature of the silicate network can be considerably reduced[5]. Also, by incorporating methyl methacrylates into the network, the toughness of the final materials can be improved[6]. In addition, the work by Schmidt, Parkhurst *et al.*[7] also reported success in producing siloxane modified silica–titanium gel systems.

In the last few years, the authors have been developing some new hybrid materials based on sol–gel chemistry. The emphasis has been on the understanding of the structure–property relationships of these new materials and how the reaction variables such as acid, water, and composition affect the final products. Success has been achieved and the results have been reported in several previous publications[8–11]. The first group of hybrid systems prepared was based on tetraethoxysilane (TEOS) and oligomeric poly(dimethyl siloxane) (PDMS) with silanol terminal groups. Although the final materials were always amorphous and transparent, some microphase separation was observed. Also, the mechanical strength of those materials was not impressive. Nevertheless, the success of making those materials did provoke the development of additional hybrid systems.

The second group of materials prepared was also based on TEOS, however, the organic component was changed to several different molecular weights of oligomeric, triethoxysilane (tri-EOS) end-capped poly(tetramethylene oxide) (PTMO). Due to higher functionality (i.e., 3 in tri-EOS vs. 1 in silanol) and the nature of the PTMO oligomers, the mechanical strength of these materials improved considerably compared to the TEOS–PDMS systems. Also, almost no pure PTMO phase was observed. One important trend that has been observed in the previous TEOS–PTMO systems was that the tensile strength increased with the PTMO molecular weight (in the range of 650–2900 g/mol). This observation provoked the idea of investigating some higher molecular weight species as well as possibly higher functionality.

For the present study, PTMO based polyurethane oligomers with a number average molecular weight of 5800 were prepared. Unlike the previous systems in which PTMO was endcapped with triethoxysilanes, these higher molecular weight oligomers possessed various numbers of triethoxysilane groups along the backbone of the chain. The ideal structures for these oligomers are schematically shown in *Figure 1*. The additional functional groups were expected to help the incorporation of these organic species into orthosilicate network and assist compatibility during the sol–gel reaction. Also, it was expected that these additional linkages between PTMO and the silicate network would cause the final structure and properties of the resulting solids to change. Most importantly, if this approach of multiple functional groups was successful, other higher molecular weight species could be considered in the future. This would significantly raise the versatility of this organic modified sol–gel route.

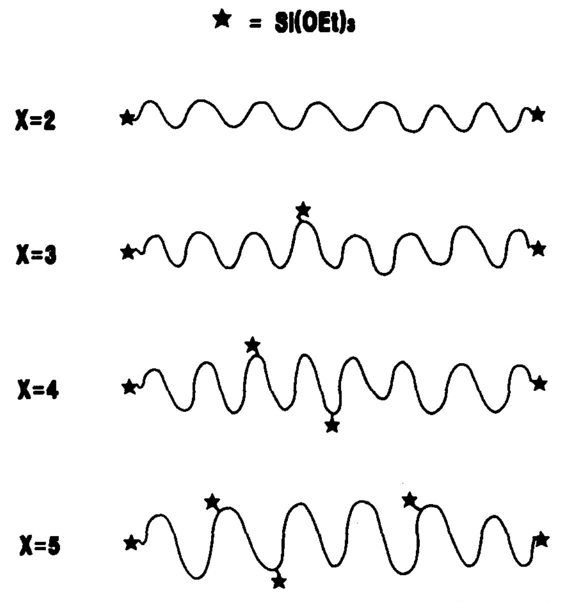


Figure 1 Schematic structure of PTMO with various numbers of triethoxysilane groups (for linear oligomers only)

In this paper, the effects of the number of tri-EOS groups along the backbone, the initial loading of TEOS, and the water content will be discussed. The mechanical and dynamic mechanical properties of these hybrid materials will be reported, and the structural information obtained from small angle X-ray scattering (SAXS) analysis will be provided.

EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS) of 99% purity from Petrarch Systems Inc. was used in this study as the inorganic silicate component. Four different types of tri-EOS functionalized PTMO based polyurethane oligomers were prepared for testing. These were made through the reaction of isocyanatopropyl triethoxysilane with polyurethane oligomers with free hydroxyl functionality. These hydroxyl functionalized poly urethanes were prepared in turn from polytetramethylene oxide diol (PTMO, 1000 molecular weight), butanediol, trimethylolpropane, and isophorone diisocyanate using stoichiometry calculated to give constant number average molecular weight, constant weight percent PTMO, and levels of excess hydroxyl functionality such that a molecule would have an average of 2, 3, 4 or 5 free hydroxyl groups. An example procedure for preparing a PTMO based polyurethane oligomer with five tri-EOS groups is as follows.

To a 1 litre flask were added 121.25 g hydroxyl terminated poly(tetramethylene oxide) (DuPont Terathane 1000, 0.247 equivalents), 8.75 g 1,4-butanediol (0.194 equivalents), 17.50 g trimethylolpropane (0.389 equivalents), and 503 g dry tetrahydrofuran. This mixture was stirred under nitrogen to dissolve all components whereupon 68.25 g isophorone diisocyanate (0.614 equivalents) and 0.04 g dibutyltin dilaturate were added. The mixture was heated at reflux for 4 h at which time an i.r. spectrum of the material showed no isocyanate remaining unreacted. Gel permeation chromatography (g.p.c.) showed the following results (polystyrene standards): $M_n = 5763$; $M_w = 16453$; $M_z = 35082$ and $M_w/M_n = 2.85$. The material prepared above was immediately combined with 55.6 g isocyanatopropyl triethoxysilane (97% pure, 0.218 equivalents) and the mixture was held at 60°C for 10 h. An i.r. spectrum of the product showed no unreacted isocyanate.

The other analogues were prepared by the same procedure and the details of the components used are

Table 1 Compositions of the reactions for preparing PTMO based polyurethane oligomers with various numbers of tri-EOS groups

Reactant	2 tri-EOS	3 tri-EOS	4 tri-EOS
Terathane 1000	110.3 g (0.225 eq)	113.7 g (0.232 eq)	117.3 g (0.239 eq)
1,4-Butanediol	19.7 g (0.437 eq)	16.3 g (0.363 eq)	12.7 g (0.283 eq)
Trimethylol propane	0.0 g	5.0 g (0.112 eq)	11.3 g (0.250 eq)
Isophorone diisocyanate	64.8 g (0.584 eq)	65.0 g (0.585 eq)	67.2 g (0.605 eq)
Isocyanatopropyl triethoxysilane	20.1 g (0.076 eq)	31.1 g (0.122 eq)	43.0 g (0.169 eq)
G.p.c. results			
M_n	5 736	5 575	5 632
M_w	14 326	16 064	15 956
M_w/M_n	2.50	2.88	2.83
M_z	22 653	28 302	31 174

listed in *Table 1*. The g.p.c. results do not indicate significant branching at the higher levels of triol, though M_z results may suggest some did occur. For purposes of the current study, the average functionality per molecule is of primary importance, but g.p.c. suggests the other molecular weight parameters were reasonably well controlled.

Reaction scheme

A simplified reaction scheme for the organic modified sol–gel process under investigation is suggested by the following:

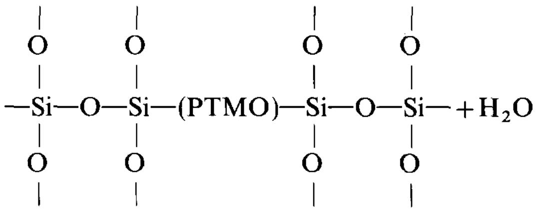
Hydrolysis

$$Si(OR)_4 + 4H_2O \xrightarrow{H^+} Si(OH)_4 + 4ROH$$

$$(RO)_3Si{-}(PTMO){-}Si(OR)_3 + 6H_2O \xrightarrow{H^+} (HO)_3Si{-}(PTMO){-}Si(OH)_3 + 6ROH$$

Polycondensation (not stoichiometrically balanced)

$$Si(OH)_4 + (HO)_3Si{-}(PTMO){-}Si(OH)_3 \xrightarrow{H^+}$$



$$\begin{array}{ccccccccc} & | & & | & & | & & | & \\ & O & & O & & O & & O & \\ & | & & | & & | & & | & \\ - & Si & -O- & Si & -(PTMO)- & Si & -O- & Si & - + H_2O \\ & | & & | & & | & & | & \\ & O & & O & & O & & O & \\ & | & & | & & | & & | & \end{array}$$

where R is the ethyl group in this case. Although only the terminal tri-EOS groups are shown, the reaction for those along the backbone should follow the same scheme. Basically, this is very similar to that shown in the previous scheme for the pure sol–gel systems except that two species are presented in the current systems for the hydrolysis reaction. Both of these species, organic and inorganic, can undergo hydrolysis and form hydroxides. Then, in the second step, these hydroxides can condense and form a network structure. From the results of previous studies, this scheme of random co-condensation of the hydroxides seems to be quite reasonable.

Example procedure

An amount (8.5 g) of a 30 wt% PTMO (5800) solution in THF was added to a mixture of 2.5 g of TEOS and 6 ml of isopropanol to form the base solution. This mixture was stirred thoroughly at ambient conditions until it appeared to be homogeneous. Then, a mixture prepared with a proper amount of deionized water and hydrochloric acid was added to the base solution under rapid mixing. After approximately 30 s, the clear solution was cast into several Teflon coated petri dishes and covered with perforated Parafilm. After 48 h, the Parafilm was removed and the gel was dried under ambient conditions for at least one week prior to testing.

In this particular procedure, a system with 50 wt% TEOS was produced. The reactants were mixed first to ensure homogeneity of the system. The water and the catalyst (HCl) were added later to initiate the sol–gel reaction. This procedure was used to prepare the series of samples to study the effect of the number of tri-EOS groups on PTMO. A Teflon coating was used to prevent the sample from adhering to the glass surface. In fact, due to the strong adhesion between the sample and the glass substrate, potential coating applications may be considered for such hybrid systems.

Nomenclature

The nomenclature that was developed for this project can be illustrated by the example shown below:

TEOS(60)–PTMO(58-4)–100

where TEOS(60) indicates the type of silicate used for the sol–gel reaction and its weight percent out of the total weight of TEOS and PTMO(5800) at the beginning of the reaction; PTMO(58-4) indicates the type of oligomer used is PTMO(5800) and the average number of tri-EOS groups on each oligomeric chain is four; 100 represents the percentage of stoichiometric amount of water added to the sol–gel reaction. A value of 100 indicates the amount of water is in exact stoichiometry of the hydrolysis reaction (i.e., molar ratio of H_2O:ethoxy = 1:1.)

Characterization

An Anton Parr Kratky camera system with a copper target X-ray tube was utilized for the small angle X-ray scattering (SAXS) experiment. The wavelength of the CuKα X-ray generated was 1.54 Å. A General Electric model XRD-6 X-ray generator was utilized. The operating voltage was 40 kV and the current was 20 mA. A position sensitive detector system (PSD) from M. Braun Inc. was used in conjunction with the Kratky camera.

An Instron model 1122 was utilized to measure the elongation at break, Young's modulus, and the ultimate strength of all the hybrid samples. Dogbone samples with a gauge length of 10 mm were used; the crosshead speed was fixed at 2 mm/min. All the measurements were carried out under ambient conditions.

A DDV-IIC Rheovibron dynamic viscoelastometer in conjunction with an automated system developed by Imass company was employed to measure dynamic mechanical behaviour. A frequency of 11 Hz was used. The measurement temperature ranged from −150°C to 200°C; the heating rate was controlled at 1–2°C/min. Nitrogen was used as the purge gas for all measurements.

Tetrahydrofuran was used for the swelling experiments. At least two samples from the same material were used, and the resulting weight uptake was the average value of all the samples. Equilibrium was usually reached within 2 h, however, the weight uptake was always measured after 24 h of immersion.

RESULTS AND DISCUSSION

All the materials prepared using the multifunctional PTMO oligomers were transparent. Also, the strength seemed to be much higher than those materials made with endcapped, lower molecular weight PTMO reported earlier[10,11]. For purposes of later quantitative comparison, the stress–strain, dynamic mechanical behaviour, and SAXS profile of one of the earlier materials made with 50 wt% TEOS and triethoxysilane endcapped PTMO(2000) oligomer are shown in *Figures 2a–c*, respectively, and the mechanical properties of this material are listed in *Table 2*. As shown in *Figure 2a*, the stress–strain behaviour of this earlier material is quite linear in the beginning. The elongation at break is in the range of 70–80%, and the tensile strength is close to 15 MPa. Compared to the silanol capped PDMS containing systems[8,9], the mechanical properties of the PTMO systems are significantly improved. Regarding the dynamic mechanical behaviour in *Figure 2b*, a tan δ maximum is observed near 0°C. This temperature is much higher than the T_g for pure PTMO(2000) oligomers, which is *c.* −75°C. A weak maximum is also observed

Table 2 Mechanical properties of materials prepared with 50 wt% TEOS, 100% water content and PTMO with various average numbers of tri-EOS groups, i.e., the series TEOS(50)–PTMO(58-X)-100

Functional groups	Elongation at break (%)	Ultimate strength (MPa)	Young's modulus (MPa)
2(2000)	81	10	15
	73	11	14
2	225	35	209
	257	52	230
3	147	45	366
	158	43	393
4	82	43	602
5	48	39	718

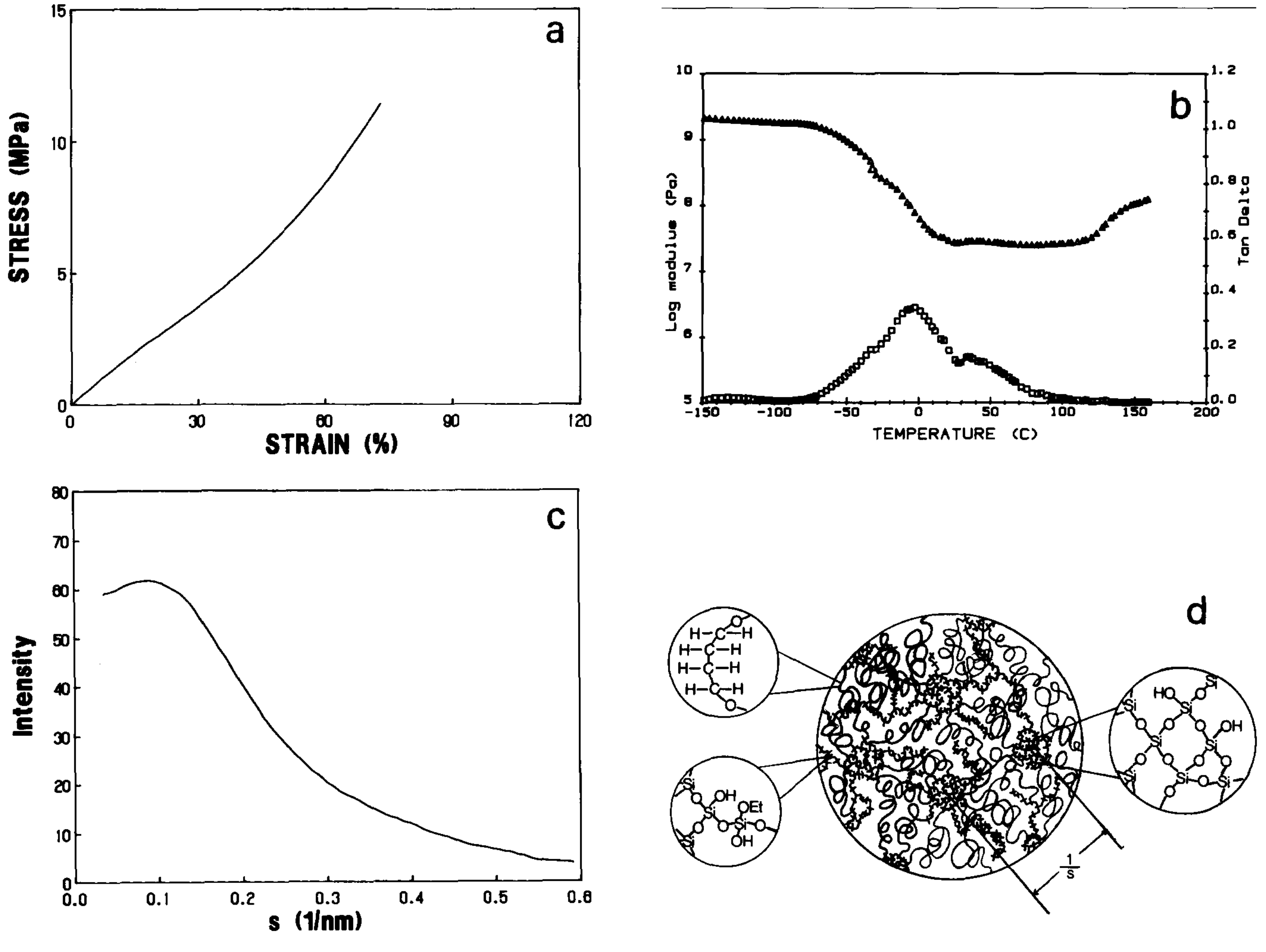


Figure 2 Results for a material prepared with 50 wt% TEOS and endcapped PTMO(2000) (a) stress-strain behaviour; (b) dynamic mechanical spectra; □, tan delta; △, storage modulus; (c) SAXS profile; (d) earlier suggested cluster model[10]

near −125°C, which has been attributed to methylene rotation within the PTMO segments. Besides that, no maximum in tan δ is observed at low temperatures which suggests the absence of a pure PTMO phase. In addition, the wide temperature spread of the transition (from −70°C to 90°C) implies a highly restricted environment of the PTMO chains. Another distinct feature of these PTMO systems is the existence of a maximum in the SAXS profile (*Figure 2c*). This maximum indicates that a correlation distance exists in the sample and, as reported earlier, this distance increases with the PTMO molecular weight and TEOS content[11].

With these and other supporting data, a schematic model was suggested to represent the structure of these hybrid systems. It is shown in *Figure 2d*. In this simplified model, it is postulated that all the endcapping tri-EOS groups of PTMO are connected to clusters formed by highly condensed TEOS species. Therefore, the distance between these clusters will be reasonably periodic and is believed to be related to the end-to-end distance of the PTMO oligomers. This model not only explains the existence of a SAXS correlation distance, but also is consistent with the fact that this SAXS correlation distance increases with the PTMO molecular weight (i.e., an increase of the PTMO end-to-end distance) and the TEOS content (i.e., an increase of the cluster size). In fact, by extrapolating to 0% TEOS the SAXS correlation distance agrees reasonably well with the calculated end-to-end distance of the PTMO(2000)[11]. All available results indicate that the model represents the actual structure rather well and in this paper, this model will be utilized to assist in interpreting the experimental results of the multi-functionalized PTMO systems.

Effect of number of reactive groups in PTMO(5800)

To investigate this variable, a series of samples made with 50 wt% TEOS and PTMO(58-X) were prepared. The average number of tri-EOS groups per PTMO oligomer (i.e., X) ranged from 2 to 5, and all the other reaction variables were kept constant. Warping and cracking problems became more noticeable as the average number of tri-EOS groups per molecule increased, indicating that the system became more densely connected. This point will be verified by other data given later in this section. It was readily apparent that the stiffness and brittleness increased with the average number of tri-EOS groups.

Stress–strain experiments were first carried out on these materials, and some examples of this series are shown in *Figure 3*. The range of elongation at break is considerably higher than those shown by the endcapped PTMO(2000) materials (recall *Figure 2a*), which seems reasonable because the molecular weight is higher in this case. The elongation at break decreases as the average number of tri-EOS groups decreases. The tensile strength is also much higher for these materials than for the PTMO(2000) systems. In fact, it reaches 50 MPa for the sample with only two tri-EOS groups (i.e., tri-EOS terminated). This relatively high strength along with high strain at break makes these materials attractive in terms of practical non-high temperature applications. The initial modulus of these materials increases with the number of tri-EOS groups on PTMO, and most importantly as the average number of tri-EOS groups increases to four and higher, a yield point is clearly shown and the yield stress increases with the number of tri-EOS groups. This observation of a yield point and increasing modulus strongly suggests that the material has become more glass-like as the tri-EOS group concentration increases. It should be mentioned that all the mechanical properties presented were measured three months after the gelation. Details of the ageing effect on mechanical properties will be discussed later.

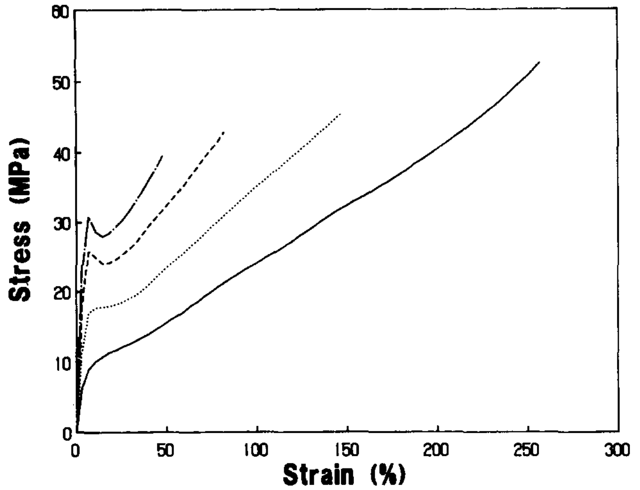


Figure 3 Stress–strain behaviour of materials prepared with 50 wt% TEOS, 100% water content, and PTMO with various numbers of tri-EOS groups: TEOS(50)–PTMO(58-X)–100. X = : ——, 2; ....., 3; – – –, 4; – . — . –, 5

To further understand the effect of the number of reactive groups on the mechanical properties, repetitive experiments were performed and the results are shown in *Table 2* where data on a TEOS–PTMO(2000) system is also included for comparison. Again, the high modulus and tensile strength for this group of hybrid materials are clearly shown. In particular, the modulus of the material made with the highest level of tri-EOS groups is approaching the value of 10^9 Pa, which is that of a typical glassy polymer. This again indicates the glass-like nature of this particular material.

As shown by the stress–strain results, the modulus of these multifunctional PTMO containing materials is always close to that of a glassy polymer. In other words, these PTMO chains must be under significant constraint so that their T_g has been shifted to considerably higher temperatures. To verify this speculation, dynamic mechanical experiments were performed. The results are shown in *Figures 4a* and *b*. The general behaviour of the storage modulus is similar for all materials. A very long plateau region with a magnitude of approximately 10^9 Pa is observed ranging from −150°C to near 0°C. The temperature at which the modulus begins to decrease depends on the number of tri-EOS groups. The greater this number, the higher is the transition temperature. After this glassy region, the modulus decreases gradually until reaching a minimum with a magnitude of the order of 10^7 Pa. The more tri-EOS groups the oligomer possesses, the higher is the modulus value of this minimum. After reaching this minimum, the modulus begins to increase with the temperature until the end of the experiment. This behaviour is similar to that shown in *Figure 2b*. The fact that the glassy plateau region shows no significant decrease in magnitude at subambient temperatures indicates the absence of a pure oligomer region, i.e., the T_g of the oligomers has clearly been shifted upward. Also, the trend of modulus with various numbers

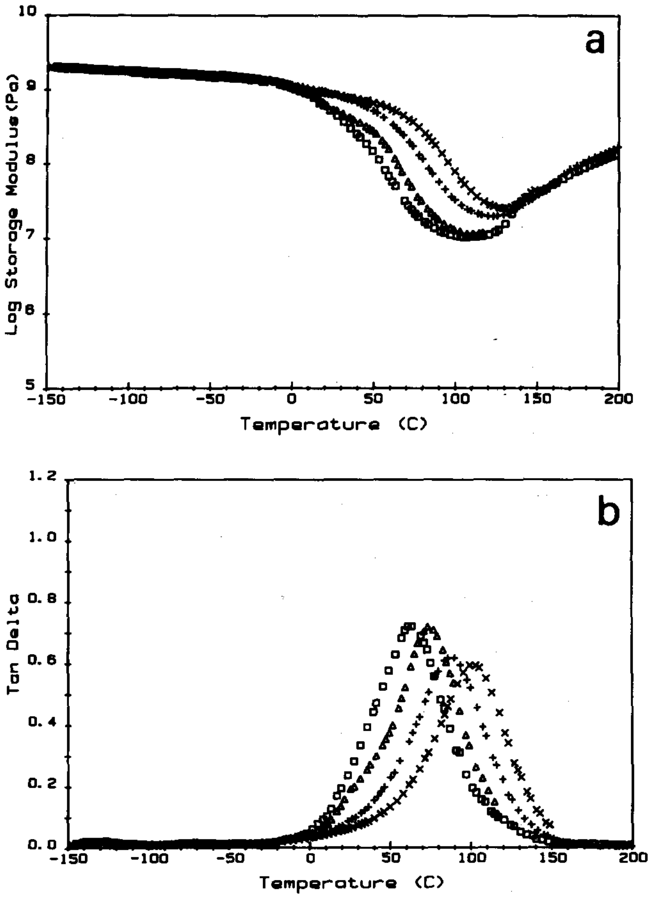


Figure 4 Dynamic mechanical behaviour of materials prepared with 50 wt% TEOS, 100% water content, and PTMO with various numbers of tri-EOS groups: TEOS(50)-PTMO(58-X)-100. (a) Storage modulus; (b) tan δ. X= : □, 2; △, 3; +, 4; ×, 5

of tri-EOS groups is consistent with what was shown in the earlier stress–strain experiments. The increasing trend at very high temperatures has also been observed in most of the previous hybrid systems and it has been attributed to further curing of the materials[9–11].

To further understand the physico-chemical environment of the oligomers in these hybrid materials, one can examine the tan δ spectra shown in *Figure 4b*. First, a low maximum is observed near −125°C for all materials. As reported in a previous paper[11], this is attributed to the rotation of the methylene groups of the PTMO. Secondly, a very low maximum is observed at −70°C. As shown in the previous chapter on the endcapped PTMO containing materials, this can probably be attributed to a nearly pure PTMO phase. However, because the intensity of this maximum is very low, it is reasonable to conclude that very little pure PTMO exists as a separated phase in the present systems. Finally, a high intensity maximum is observed at higher temperatures. This major transition temperature increases from 63°C to 102°C as the average number of tri-EOS groups increases from 2 to 5, which clearly indicates that the restrictions on the oligomers change with the number of tri-EOS groups.

As discussed in several previous publications[9–11], the restrictions being imposed on the oligomers have a direct effect on the mobility of these incorporated chains and, consequently, on the glass transition temperature of these oligomers. For the endcapped PTMO(2000) species, restrictions are caused by both the endlinking of these oligomeric chains and the interaction between them and the partially condensed TEOS (recall *Figure 2d*). However, in the present systems, two more factors will have to be taken into account. First, the restrictions caused by linking the additional tri-EOS groups with the condensed TEOS. For molecules with the same molecular weight, this type of restriction might be expected to increase with the number of tri-EOS groups along the backbone. This point is strongly supported by the fact that the T_g observed in the tan δ spectra increases with the average number of tri-EOS groups. Secondly, the mobility of the chain may also be reduced by the aggregation of the hard segments. As mentioned earlier, the structure of these multifunctional PTMO is somewhat similar to that of a segmented polyurethane. The soft segments consist of the PTMO(1000) and the hard segments are formed by isophorone diisocyanate and butanediol. Due to the presence of these hard segments, the mobility of the PTMO chain should also be reduced.

To understand the effect of the hard segments, one can compare the sample with only terminal tri-EOS groups (i.e., $x=2$) to those made with endcapped PTMO(2000) (i.e., comparing *Figure 2b* with *Figure 4b*). As shown in an earlier publication on materials prepared with various molecular weights of endcapped PTMO (ranged from 650–2900 g/mol)[11], the T_g of PTMO decreases as the molecular weight increases. For the material made with PTMO(2000), the T_g is near 0°C. Therefore, one would expect the T_g to be lower for a PTMO oligomer with a molecular weight of 5800. However, as shown in *Figure 4b*, the T_g of this particular material ($x=2$) is 63°C. This difference (63 vs. 0°C) indicates the influence of the hard segments.

Regarding the yield behaviour observed in the stress–strain results, two possible causes should be considered. First is that the condensed TEOS species might become continuous in these systems. If this was the case, as the deformation is applied, some of these linkages may be broken and result in a maximum stress. The second case is that due to the high T_g of these materials, they will promote glassy behaviour at ambient temperature. Therefore, a yield point which is typical for a ductile glassy polymer is observed[12]. To further investigate this point, a sample which showed yield behaviour was deformed past the yield point and released in the first run. After three days, the same sample was deformed again and a yield point was again observed. This excludes the possibility of covalent bond cleavage mentioned above and, hence, the second interpretation is adapted.

As the number of tri-EOS groups increases, the oligomers are connected into the network through more sites and, therefore, the crosslinks per unit volume should increase. This increase in the crosslinking density should not only result in an enhanced modulus but also in a decrease of the equilibrium swelling of the material. To verify this point, all the materials were swollen with THF. The results are shown in *Figure 5*. As the average number of tri-EOS groups increase, the swelling ratio of the final material systematically decreases, which is in line with all the experimental results. To actually calculate the molecular weight between crosslinks (i.e., M_c) of these systems would be difficult due to the complex nature of the inorganic phase.

To provide further information on the structure of these hybrid materials, SAXS experiments were per-

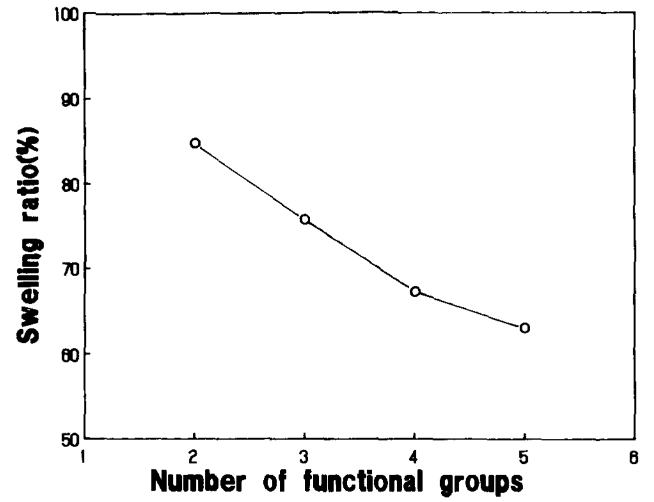


Figure 5 Swelling ratio of materials prepared with 50 wt% TEOS, 100% water content, and PTMO with various numbers of tri-EOS groups

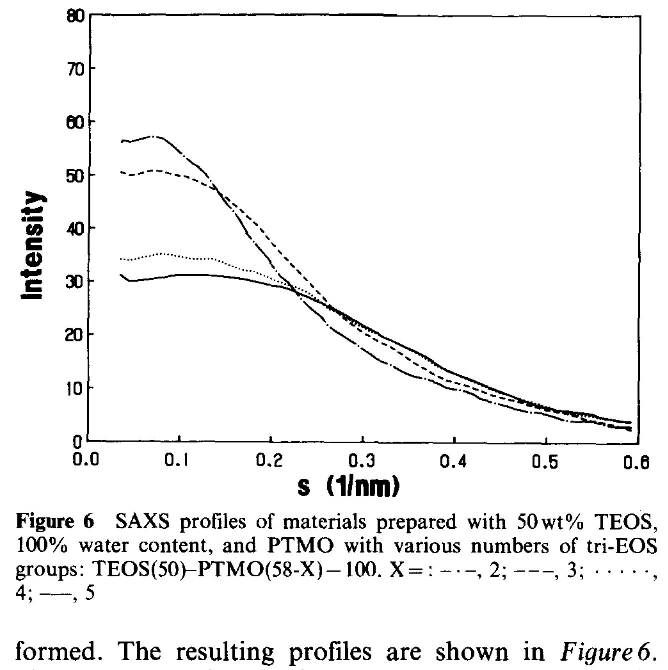


Figure 6 SAXS profiles of materials prepared with 50 wt% TEOS, 100% water content, and PTMO with various numbers of tri-EOS groups: TEOS(50)–PTMO(58-X)–100. X= : —·—, 2; – – –, 3; · · · · ·, 4; ——, 5

formed. The resulting profiles are shown in *Figure 6*. Similar to all the previous SAXS results on hybrid systems that contain PTMO oligomers, a broad maximum is observed. This indicates that a correlation distance exists in the investigated system, and its magnitude can be estimated by 1/s where s is the value of the scattering vector at which the maximum is observed. Since the s value at the maximum increases with the average number of tri-EOS groups, the correlation distance becomes shorter as the average number of tri-EOS groups increases.

For the hybrid systems prepared with endcapped PTMO oligomers, a schematic model was suggested earlier to explain the SAXS behaviour (see *Figure 2d*). As suggested by the model, part of the TEOS may become highly condensed and form a cluster-like structure. Due to the high functionality of the oligomer end groups, both ends of the oligomers will probably be connected to these clusters. However, for the present systems, not only the terminal groups, but the additional tri-EOS groups along the backbone should also connect to the highly condensed TEOS clusters. From the high T_g observed in dynamic mechanical experiments, these tri-EOS groups must have been linked to the glassy phase (i.e., the clusters). Therefore, the distance between clusters should probably decrease as tri-EOS groups increases, which should result in a decrease in the SAXS correlation distance. This line of argument is consistent with the trend shown by the SAXS results.

Generally speaking, the SAXS results confirm that the tri-EOS groups along the backbone offer additional linkages for the oligomers to be incorporated into the silicate network. Most of these tri-EOS groups should be connected to the silicate clusters suggested in the previous model, and these additional crosslinks cause the oligomeric chains to be more restrained and the stiffness of the final material to become higher.

Effect of TEOS content

To study the effect of system composition, a series of materials with various TEOS content were prepared using the PTMO oligomer with an average number of four tri-EOS groups (i.e., $x=4$). The initial TEOS content ranged from 0 to 70 wt%, while other variables were kept constant. The gelation time tended to increase with TEOS content, and this trend was similar to that observed in using endcapped PTMO oligomers[11]. This trend is reasonable when considering the relatively high functionality of the tri-EOS containing PTMO. The system made with 0% TEOS (i.e., 100% tri-EOS containing PTMO) was soft and flexible. As TEOS content increased, the material became stiff and tough and the cracking problem also tended to be more significant. Nevertheless, fairly large films were still obtainable even for the 70 wt% TEOS content material.

Examples of the stress–strain curves for each TEOS content are shown in *Figure 7*. For the materials with low TEOS contents (i.e., 0 and 20 wt%), the stress increases steadily with the strain. The initial modulus is low and the elongation at break is relatively high, which implies the rubbery nature of these materials. As the TEOS content increases to 40 wt%, a 'bending' of the curve is observed. Although the onset of this non-linearity may not be directly viewed as a yield point, rather it provides a first indication of the relatively glassy nature of the material. The initial modulus of this 40 wt% TEOS sample is considerably higher than the two samples with

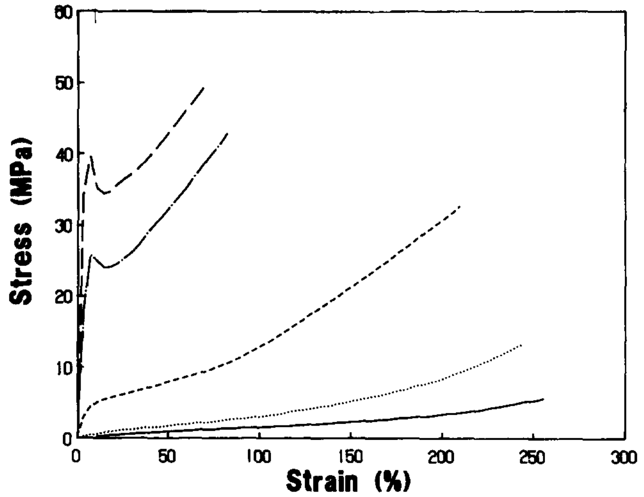


Figure 7 Stress–strain behaviours of materials prepared with various TEOS contents and PTMO with four tri-EOS groups: TEOS(X)–PTMO(58-4)–100.X= : ——, 0; · · · · ·, 20; – –, 40; —·—·–50; — — —, 60

lower TEOS content (i.e., 0 and 20 wt% TEOS). As the TEOS content increases further to 50 wt%, a yield point is observed. Meanwhile, the initial modulus shows a drastic increase while the elongation at break decreases to less than half of the 40 wt% TEOS material. Finally, for the case of 60 wt% TEOS, the yield point is also observed and the yield stress is higher than the 50 wt% sample. This development and enhancement of a yield point suggests that these materials have shifted from rubbery to glass-like in nature.

Collective data of the mechanical properties are shown in *Table 3*. Both the modulus and tensile strength increase systematically with the TEOS content and seem to reach a plateau at 60 wt%. The values of the elongation at break for the three lower TEOS content samples are approximately in the same range. However, it decreases significantly as the TEOS content increases to 60 wt%. As the TEOS content increases to 70 wt%, the elongation at break again decreases drastically from *c.* 70 to 9%. This large drop indicates that there may be a phase inversion taking place, after which the glassy component (i.e., condensed TEOS) may become the continuous phase. This type of phase inversion was also shown in the systems prepared with TEOS and endcapped PTMO(2000) oligomers.

To better understand how the TEOS content influences the environment of PTMO chains, dynamic mechanical experiments were carried out. The results of the storage modulus spectra are shown in *Figure 8a*. The general behaviour of these materials is similar to other hybrid systems prepared previously. A glassy plateau region at low temperatures is followed by a transition region in which the modulus decreases with increasing temperature. Then, a 'rubber' plateau region is observed before the modulus begins to increase again at high temperatures. Several important observations should be noted. First, the rubbery plateau modulus increases with the initial TEOS content. This trend is in line with what was observed in the results of stress–strain experiments. Secondly, the temperature at which the modulus begins to decrease (i.e., the temperature at which the transition region starts) increases with TEOS content. In fact, for the sample prepared with 40 wt% TEOS, the glassy plateau region extends almost to ambient temperature. As the TEOS content increases further to 60%, the glassy plateau region extends beyond the ambient temperature. This is also the sample that shows a yield point. Finally, there is almost no loss in modulus at temperatures lower than −30°C for all systems. Also, there is no sign of PTMO crystallization even for the 0% TEOS system. This is not true for the system made with 100% endcapped PTMO(2000), in which a significant drop in modulus was observed at low temperature (*c.* −75°C) followed by crystallization of PTMO oligomers^{10}. This difference of these two systems strongly suggests that the existence of additional tri-EOS groups and hard segments along the backbone contribute significantly to the structural response of these materials and, in fact, limits crystallization of the PTMO at lower temperatures.

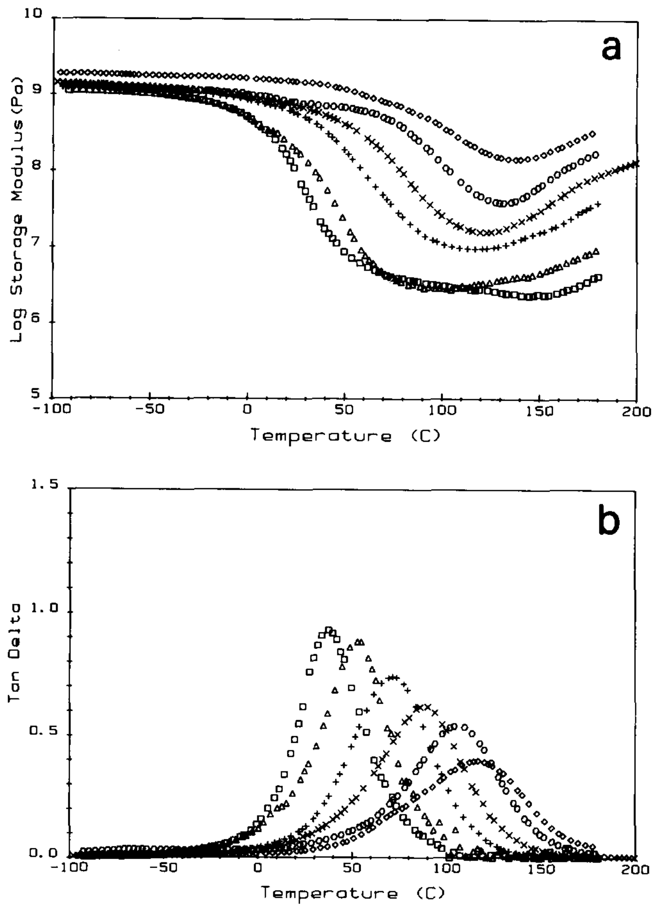


Figure 8 Dynamic mechanical behaviour of materials prepared with various TEOS contents and PTMO with four tri-EOS groups: TEOS(X)–PTMO(58-4)–100. (a) Storage modulus; (b) tan δ. X = : □, 0; △, 20; +, 40; ×, 50; ○, 60; ◇, 70

Table 3 Mechanical properties of materials prepared with various TEOS contents and PTMO with four tri-EOS groups, i.e., the series TEOS(X)–PTMO(58-4)-100

TEOS content	Elongation at break (%)	Ultimate strength (MPa)	Young's modulus (MPa)
0	255	6	3
20	244	13	12
	200	9	11
40	209	33	92
	208	29	84
60	70	50	1030
	75	50	1060
70	9	32	940

To obtain further insight on the transition behaviour of these materials, the tan δ spectra were examined (*Figure 8b*). Similar to those shown in *Figure 4b*, a single maximum is observed in every case. The temperature at which the maximum is shown increases from 30°C to 110°C as the initial TEOS content increases from 0 to 70 wt%. In particular, for the sample with 0% TEOS, the onset of the maximum is near −30°C. This is about 50°C higher than the T_g of the pure PTMO species. Again, such a large shift in T_g must be accounted for by the linking of the tri-EOS groups and the existence of the hard segments. For samples of 0 and 20 wt% TEOS, a large portion of the tan δ maximum is below ambient temperature. However, as the TEOS content increases to 40 wt% or higher, almost the entire maximum is observed above ambient. This is closely related to the observation of the yield point. Another important point to note is that the overall intensity of the tan δ maximum decreases with increasing TEOS content which is similar to what was observed in the series made with PTMO(2000)[10].

For the hybrid systems under investigation, the condensed TEOS species will be relatively rigid and, therefore, an increase of this component is likely to increase the stiffness of the final materials. This has been shown by the modulus from both the stress–strain and the dynamic mechanical experiments. As the content of the stiff component increases, the restrictions imposed on the flexible PTMO chains are also expected to increase if some mixing occurs. This explains the systematic increase of the T_g of the PTMO species observed in the tan δ spectra (see *Figure 8b*). Regarding the decrease in the overall tan δ intensity, because most of the mechanical loss should be caused by the flexible PTMO chains, it is thus reasonable to see a decrease as the amount of PTMO present in the systems decreases. As for the increase of modulus at high temperatures, it is believed to be caused by further curing.

One important point to note is that besides thermal treatment, long term ageing of these materials can also result in further curing of the system. In this case, a stiffening effect on the sample will be observed. An example of this ageing effect on the dynamic mechanical behaviour is shown in *Figure 9*. Also important to note on this result is the further shifting of the PTMO T_g for *c.* 10°C, indicating that higher restrictions have resulted by further curing of the system. Further discussion of the ageing effect will be provided later.

With the understanding of the T_g behaviour of these materials, the yield behaviour shown in the stress–strain curve can now be rationalized. In earlier discussions, the yield point observed in the stress–strain experiments was attributed to the glassy nature of these materials. This point has been further supported by this series of samples with various TEOS contents. As shown in *Figure 7*, the development of a yield point is closely related to the increase of the TEOS content. In fact, by examining *Figures 8a* and *b*, one can say that the environment or the physico-chemical state of the PTMO chains determine whether a yield point will be observed. For samples with the highest content of PTMO chains in the rubbery state at ambient temperature (i.e., sample with 0 and 20 wt% TEOS), no yield point will be observed. Conversely, if most of the T_g transition is above the ambient temperature (i.e., materials with 60 and 70 wt% TEOS), a yield behaviour will be noted. For the sample with 40 wt% TEOS, it is right on the edge of the T_g transition and, hence, a 'bending' behaviour is shown in the stress–strain response.

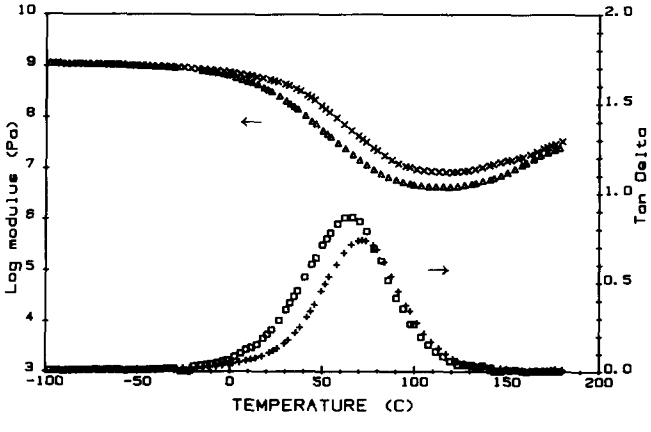


Figure 9 Ageing effect on the dynamic mechanical behaviour of materials prepared with 40 wt% TEOS and PTMO(5800) with four tri-EOS groups. Ageing times: △ and □, 21 days; × and +, 355 days

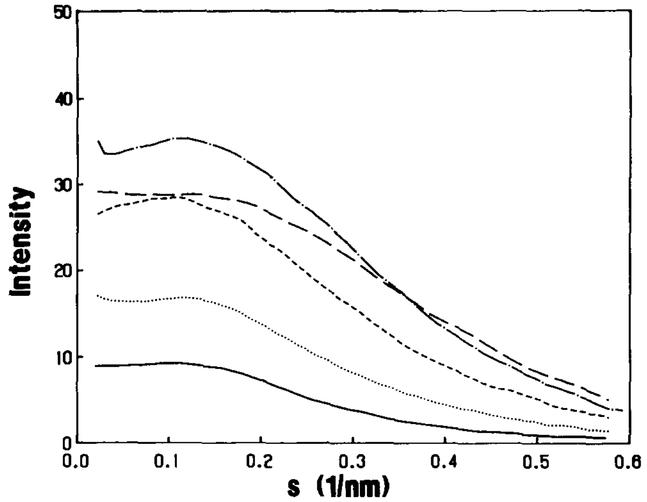


Figure 10 SAXS profiles of materials prepared with various TEOS contents and PTMO with four tri-EOS groups: TEOS(X)–PTMO(58-4)–100. X = : —, 0; · · · ·, 20; – – – –, 40; – · – ·, 50; ———, 60

Up to this point, it has been assumed that the general structure of these hybrid materials prepared with multifunctional PTMO(5800) can still be represented by the schematic model suggested previously (see *Figure 2d*). However, the highly condensed TEOS clusters may now be connected not only to the end groups, but also to the reactive groups along the backbone. For the systems prepared with endcapped PTMO oligomers, an increase of the TEOS content causes the cluster size to increase. As a result, the SAXS correlation distance also increases with TEOS content. For the present systems, the situation may be different. Because the average distance between tri-EOS groups is fixed by the structure of the oligomer and some of the clusters are connected with these tri-EOS groups, a change in TEOS content should not significantly change the distance between the clusters. Therefore, the SAXS correlation distance should always be of approximately the same magnitude. To confirm this speculation, SAXS experiments were performed on this TEOS series and the resulting profiles are shown in *Figure 10*. Clearly, the peak position does not show significant changes with TEOS content which again provides additional support for the suggested model.

Although the correlation distance does not change, the overall scattering intensity increases with the TEOS content. A similar trend was also observed for the TEOS series based on the endcapped PTMO(2000) oligomer[10]. This increasing tendency may be attributed to the formation of more highly condensed TEOS clusters which, in effect, increase the scattering power of the system. As a result, the overall scattering intensity increases as well. However, as the TEOS content increases to 60 wt%, the profile begins to change its shape and the scattering intensity in the tail region increases considerably. This change in SAXS profile was also observed in the series made with PTMO(2000)[13]. Although the exact cause is still not clear, it is presently postulated that this may be an indication of the onset for phase inversion. That is, the size of the TEOS clusters become so large that some of them may connect and form a somewhat continuous phase of the condensed TEOS component. Because the maximum observed by SAXS has been suggested to be caused by the cluster-to-cluster distances, this connecting of clusters should result in less 'regularity' in terms of the inter-cluster distance. Hence, the scattering intensity at lower angles should decrease. On the other hand, because the pure sol–gel glasses will mainly scatter at relatively high angles[14], this growing of continuous condensed TEOS phase should cause the tail region of SAXS profiles to intensify.

Effect of water content and ageing

For all the materials discussed so far, 100% stoichiometric amount of water for the hydrolysis of silane was always used in the reaction. To understand the effect of water content, a series of samples with 50 wt% TEOS, 50% stoichiometric amount of water content, and PTMO(5800) with various numbers of tri-EOS groups were prepared. All the other variables were kept constant so that a direct comparison between this series and the ones shown in *Figures 3* to *5* could be made. Also to be discussed in this section is the ageing effect on these hybrid materials. In fact, as the discussion continues, the reader will realize that these two effects are closely related.

The best example to illustrate the effect of water content is the dynamic mechanical behaviour shown in *Figure 11*. Three DMA spectra are shown in this figure: one with 50% water content but relatively fresh (four weeks after reaction), one with 100% water content and also fresh, and another one with 50% water but aged for several months. For the case of 50% water content and short ageing time, the behaviour of the storage modulus is rather peculiar. A glassy plateau region is observed at low temperatures, followed by a transition region where the modulus decreases. However, following the rubbery plateau, the modulus begins to increase again indicating that the material is somehow stiffening. This peculiar stiffening effect is reproducible, in fact, it is even observed on a sample which was heat treated at 80°C for 16 h (data not shown). Therefore, it should not be caused by any volatile species. After this stiffening effect reaches a maximum, the modulus begins to decrease again. This decreasing tendency continues until very high temperatures, at which time the modulus increases due to further curing of the system. The corresponding tan δ spectra of this material is shown in *Figure 11b*. A bimodal type of behaviour is observed. The first maximum is observed at a temperature right before the onset of the peculiar stiffening behaviour, whereas the second maximum is at the same temperature where the tan δ peak is observed for the 100% water content samples.

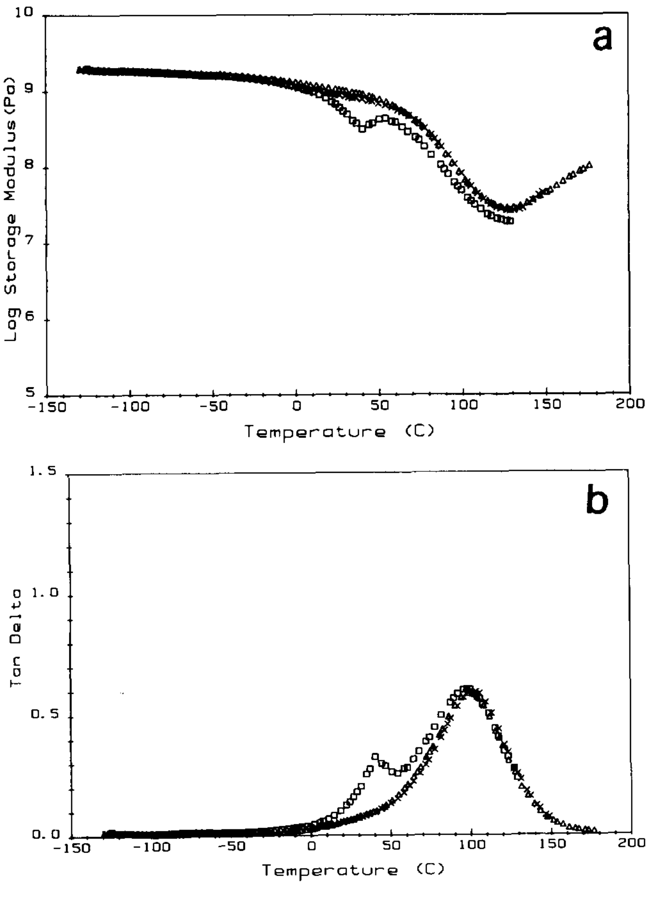


Figure 11 Dynamic mechanical behaviour of materials prepared with 50 wt% TEOS and PTMO with five tri-EOS groups: TEOS(50)–PTMO(58-5)–X. (a) Storage modulus; (b) tan δ. □, X = 50, aged 28 days; △, X = 50, aged 300 days; ×, X = 100, aged 28 days

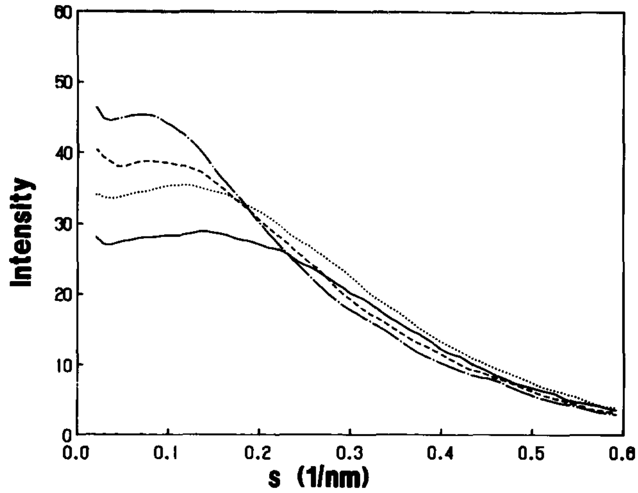


Figure 12 SAXS profiles of materials prepared with 50 wt% TEOS, 50% water content, and PTMO with various numbers of tri-EOS groups: TEOS(50)–PTMO(58-X)–50. X = : – · –, 2; – – – –, 3; · · · · ·, 4; —, 5

To account for the effect of water content on the dynamic mechanical results, two possible interpretations are postulated. First, due to the difference in water content, the final structure may be significantly changed, which results in the peculiar behaviour observed. The second possibility is that the general structure does not change with water content. However, due to the fact that there was insufficient water present for the reaction in the case of 50% water content, unreacted groups would still exist in the final materials. Therefore, the network structure was not as dense. Two other experiments were therefore carried out to determine which interpretation was closer to the actual case.

The first attempt was to obtain structural information using SAXS analysis, and the results for the series of samples with 50% water content are shown in *Figure 12*. Except for the slight differences in intensity, the general behaviour and trend are identical with those shown in *Figure 6*. This result strongly suggests that the basic structure (see model in *Figure 2d*) should be the same between samples made with these two different water contents. This result supports the second interpretation mentioned above. Another means of experimental

Table 4 Mechanical properties of materials prepared with 50 wt% TEOS, 50% water content, and PTMO with various average numbers of tri-EOS groups, i.e., the series TEOS(50)-PTMO(58-X)-50

Functional groups	Elongation at break (%)	Ultimate strength (MPa)	Young's modulus (MPa)	Ageing (days)
2	122	16	25	42
	123	20	42	42
	116	14	17	42
3	156	30	116	42
	168	37	89	42
	115	32	134	42
4	143	39	244	42
	127	38	267	42
5	64	42	612	42
	64	48	644	42
	75	48	612	42
2	89	36	203	686
	67	23	150	686
3	69	33	297	686
	69	30	331	686
4	83	46	680	686
	101	44	678	686
	71	36	641	686
5	51	39	712	686
	59	45	1046	686
	53	40	839	686

support may come from the dynamic mechanical behaviour on aged samples (see *Figure 11*). After a long term exposure to humidity, the possible unreacted groups should be considerably reduced and the effect of water content should not be so significant anymore. As shown in *Figure 11*, the results from DMA on samples aged for 300 days show almost identical behaviour with those made with 100% water content. Therefore, it was concluded that, for the range of water content under investigation, the general structure was not affected except that more unreacted groups existed in the lower water samples.

Finally, to understand the effect of water content and ageing on the mechanical properties, stress–strain results for the 50% water content series at different ageing times are listed in *Table 4*. Obviously, the ageing effect on this series of samples is significant, especially on Young's modulus and elongation at break. The stiffness of the materials increases while the elongation at break decreases with ageing time. However, the ultimate strength is approximately the same. Another point to note is that by comparing the mechanical properties of the aged samples to those shown in *Table 2*, one can see that the modulus is approximately the same. This further supports that the water content effect will be less significant for aged samples.

One important remark about the water content is that, although the final structure does not seem to be affected by the change of water content from 50 to 100%, any extrapolation of this result to either higher or lower water content is not warranted. Especially, as water content becomes very high, the compatibility between the oligomer and water may become important. Furthermore, as a considerably large amount of water is used, the system will be diluted and the formation of cyclics may be possible. Both of these factors will significantly change the structure and properties of the final hybrid materials.

CONCLUSIONS

The addition of pendant tri-EOS groups to PTMO based oligomers shows a significant effect on the organic–inorganic incorporating process. Due to the additional constraints caused by the tri-EOS groups along the backbone, the mobility of the oligomers decreases and T_g increases. This results in a more glassy final material and, therefore, higher modulus and lower elongation at break. Also, the tensile strength improves considerably as more tri-EOS groups are attached to the backbone of PTMO. Results from SAXS show that a correlation distance exists in each sample, and this distance decreases with an increasing amount of tri-EOS groups. This trend indicates that the cluster model suggested previously is probably still valid.

The initial TEOS content has also proven to be important to the mechanical properties and final structure. As the TEOS content increases, the T_g increases and the final material becomes stiff and glassy. The result is higher modulus, lower elongation at break, and higher tensile strength. However, as the final TEOS content increases beyond 60 wt%, a phase inversion may take place. Such an inversion may explain a decline in the tensile strength of the final materials. The SAXS results show that the correlation distance does not change significantly with the TEOS content, which is in line with that suggested by the cluster model.

The water content relates closely to the amount of unreacted groups and, therefore, the post-gelation curing behaviour of these hybrid materials. Material prepared with 50% water content shows a significant ageing effect but, eventually, becomes similar to that prepared with 100% water content.

One important improvement of these materials is in tensile strength, which reaches 50 MPa for some cases. This high strength may become crucial when considering practical applications for these hybrid materials. Furthermore, the success of preparing these systems also suggests the possibility of utilizing high molecular weight polymers for this modified sol–gel reaction.

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