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Structure property behavior of polydimethylsiloxane and poly(tetramethylene oxide) modified TEOS based sol-gel materials
V. Effect of titaniumisopropoxide incorporation

Raymond H. Glaser and Garth L. Wilkes*

Department of Chemical Engineering, Polymer Materials Interfaces Laboratory,
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-6496, USA

SUMMARY

Titanium has been successfully incorporated into polydimethylsiloxane and poly(tetramethylene oxide) modified TEOS based materials using sol-gel chemistry. Incorporation of titanium into the oligomer modified TEOS based materials altered the physical properties, however, the gross structural features remained the same.

INTRODUCTION

Sol-gel chemistry and processes have been known for at least twenty years (1-4). A metal alkoxide (usually a silicon alkoxide) is hydrolyzed then condensed to form a gel which can then be subsequently vitrified at ambient or elevated temperatures to form a hard glassy material. Unlike the traditional high temperature fusion process for making glasses, the sol-gel process allows for controlled composition and mixing of the glass precursors and also utilizes lower temperatures to achieve vitrification.

Within the last two years it has been demonstrated that PDMS (polydimethylsiloxane) oligomers/polymers can be successfully incorporated into a TEOS (tetraethoxysilane or tetraethylorthosilicate) based network via the sol-gel process (5-7). More recently, appropriately functionalized PTMO (poly(tetramethylene oxide)) based oligomers/polymers have also been successfully incorporated into a TEOS based glass system producing materials with unique physical properties (8-10). In addition to different oligomer/polymer modifiers, variations of the inorganic component have also been examined as a means of producing materials with specialized properties (high refractive index for example). While incorporation of metal atoms into silicate networks via the sol-gel process is not new (1-4), incorporation of metal atoms into organically modified TEOS based glasses is (11,10). Only recently, Parkhurst et al first reported the thermal properties of PDMS/TEOS based materials incorporating titaniumethoxide and titaniumbutoxide (11). The structure-property effects of titanium incorporation into organically modified sol-gel glasses will be reported here. In particular, the incorporation of titaniumisopropoxide into PDMS/TEOS and PTMO/TEOS systems will be examined.

MATERIALS

High purity (99%) TEOS was purchased from two sources, Fluka AG and Petrarch Systems Inc.. Petrarch Systems Inc. was also the source for the silanol terminated 1700 Mw PDMS oligomer used. Reagent grade titanium(IV)isopropoxide was obtained from the Aldrich Chemical Company Inc. while the triethoxysilane endcapped PTMO oligomers used were generously supplied by Dr. James G. Carlson of the 3M Company.

EXPERIMENTAL

The incorporation of titaniumisopropoxide into the TEOS based glass network posed one major experimental problem. Unlike the silicon alkoxides such as TMOS (tetramethoxysilane) or TEOS (tetraethoxysilane) which readily form an oxide network (SiO_2) the titanium alkoxides react rapidly with water to form a "molecular" or non-network oxide: titaniumdioxide (TiO_2). As a consequence, the previously used procedure for

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* To whom correspondence should be addressed

making PDMS/TEOS and PTMO/TEOS hybrid materials (5-9) caused added titaniumisopropoxide to precipitate out of the reaction mixture before it could react into the TEOS network being formed. Hence, a procedure had to be found that gently hydrolyzed the titaniumisopropoxide and would allow it to connect into the TEOS based glass network.

A Chemically Controlled Condensation (CCC) method similar to that proposed by Schmidt (12) was developed to incorporate titaniumisopropoxide into PDMS/TEOS and PTMO/TEOS systems. These systems were prepared in the following manner. Appropriate amounts of TEOS and PDMS or PTMO were added to a reaction vessel at ambient temperature. The solution was then diluted to 40 vol% reactants with a 4/1 mixture of isopropanol/THF. Glacial acetic acid was added in the molar proportion acid/TEOS of 2/1 and the solution was allowed to react overnight in a nitrogen atmosphere under constant stirring. After 24 hours the desired amount of titaniumisopropoxide was added and the reaction mixture was gently refluxed for an additional 1/2 - 2 hours. Generally, the deep yellow color of the reaction mixture caused by the addition of titaniumisopropoxide faded after approximately 1/2 hour of gentle refluxing. After the reaction mixture either faded in color or refluxed for 2 hours, the mixture was cast into covered Teflon-coated Petri dishes and allowed to gel under ambient conditions for at least one week prior to testing (gelation usually occured within 24 hours). All samples were stored in closed polystyrene Petri dishes under ambient conditions after gelation was completed.

CHARACTERIZATION

Stress-strain experiments were carried out on an Instron Model 1122 tensile testing machine. Dumbbell samples 10mm in length were tested at an initial strain rate of 2mm/min. Dynamic-mechanical spectra were obtained using a DDV-IIC Rheovibron Dynamic Viscoelastometer. Samples were tested at 11 Hz in the temperature range of -150°C to 220°C at a heating rate of 2-3°C/min. Small-angle x-ray scattering (SAXS) profiles were obtained using a Siemens Kratky camera system with an M. Braun position sensitive detector from Innovative Technology Inc..

RESULTS AND DISCUSSION

Tensile Properties:

The films cast were all transparent though the addition of titanium did impart a yellowish-orange color to the samples. Primarily, three different compositions of Ti-isop (titaniumisopropoxide)/TEOS/oligomer (PDMS or PTMO) were prepared to observe the effects of titanium incorporation on the final materials. These compositions were (in terms of starting weight percentages): (6% Ti-isop)/(44% TEOS)/(50% oligomer), (15% Ti-isop)/(35% TEOS)/(50% oligomer) and (30% Ti-isop)/(20% TEOS)/(50% oligomer). Hereafter, the various compositions will be referred to in terms of the starting weight percentage of Ti-isop and the specific oligomer used to make the material.

The pure PDMS/TEOS materials reported earlier (5-7) showed relatively poor physical-mechanical properties. For example, under ambient conditions using a draw rate of 2mm/min a 48% TEOS 52% 1700 Mw PDMS sample made using 0.045 moles of HCl catalyst had an initial modulus of ca. 12 MPa, a stress at break, of approximately 1 MPa and a 9% elongation at break (7). The incorporation of titanium, it was hoped, would increase the observed stress at break and initial modulus of the PDMS modified materials by strengthening the TEOS based network. The titaniumisopropoxide, it was thought, might catalyze the condensation reaction driving the TEOS based network to a higher degree of completion than attainable for the pure siliconalkoxide TEOS. Comparable materials made with 6, 15 and 30 wt% Ti-isop proved to be stiffer but very brittle, though, and could not be tested; tensile test specimens were impossible to obtain. However, the stiffness observed in the titanium containing samples was certainly interpreted as an indication of an increased modulus. Therefore, the effect of titanium incorporation on the final materials is suspected to be caused by a higher degree of network formation of the TEOS based system (as was expected) resulting in an increased initial modulus and a

Table 1. Tensile Properties of Ti Containing PTMO Systems

wt % Ti-isop	Elongation at break (%)	Ultimate strength (MPa)	Young's Modulus (MPa)
0	104	1	7
15	136	11	22
30	57	11	67
30†	61	12	71

† Opaque samples (different reaction batch)

decreased elongation at break.

Unlike the PDMS materials, materials containing PTMO were quite flexible and specimens for all mechanical tests were easily obtained. Table 1 lists the average values of the stress-strain data for four PTMO modified materials having three levels of Ti-isop content. As was qualitatively observed for the PDMS materials, the incorporation of titanium into the PTMO materials increased the modulus and decreased the elongation at break. The addition of 15% Ti-isop increased the ultimate stress tenfold and the Young's modulus three-to-fourfold and also increased the elongation at break as compared to either 0% Ti-isop material. Increasing the amount of Ti-isop from 15% to 30% results in a lowering of the observed elongation at break (from ca 136% to 60%) and a tripling of the Young's modulus (from ca 22 to 70 MPa).

Dynamic Mechanical Properties:

Though "dumbbell" tensile test specimens could not be easily obtained from the titanium containing PDMS/TEOS materials, specimens for dynamic-mechanical analysis were able to be prepared. The sample films had sufficient flexibility so that narrow strips could be cut (using a razor blade) and mounted in the Rheovibron. This flexibility indicates that this material may have useful coating applications.

Figures 1a&b compares the dynamic mechanical spectra of a 48% TEOS 52% PDMS 0.045 moles HCl material (7) mentioned previously with that of materials containing 6 and 30 wt% Ti-isop.. Comparing the storage modulus curves first (Fig. 1a) one immediately notes that the PDMS/TEOS material exhibits a decrease of 1.5 orders of magnitude in the storage modulus after the very broad glass transition whereas the titanium containing materials all exhibit a decrease in the storage modulus of only one order of magnitude. Furthermore, the magnitude of the storage modulus of the titanium containing materials is essentially the same for all three compositions (only data for 6 & 30 wt% Ti-isop are

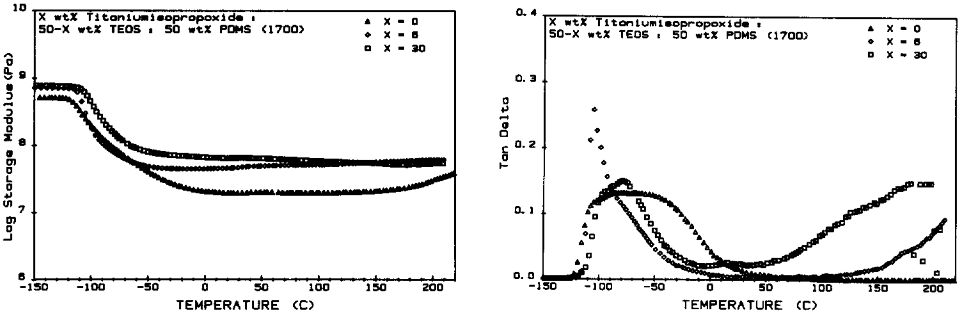

Figure 1 Dynamic mechanical spectra of PDMS modified TEOS based materials as a function of titanium content (a) storage modulus (b) tan δ.

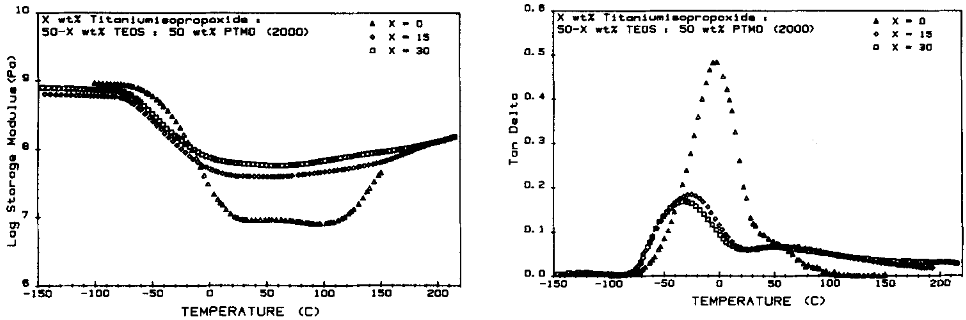

Figure 2 Dynamic mechanical spectra of PTMO modified TEOS based materials as a function of titanium content (a) storage modulus (b) tan δ.

shown). This data gives credence to the hypothesis that the incorporation of titanium drives the TEOS based network to a higher degree of completion due to a "catalytic-like" effect of the titanium on the condensation reaction. The corresponding tan δ curves, also given in Fig. 1b, show differences between the samples incorporating 6 & 30 wt% Ti-isop and one with 0 wt% Ti-isop. The material with only PDMS i. e., no titanium (0% Ti-isop), displays a broad bimodal tan δ behavior with peaks at approximately -100°C and -50°C. The tan δ transition for this material eventually decreases to near zero after 70°C. The 6% Ti-isop material is quite different in that it displays one sharp tan δ transition at -110°C but then slowly decreases to near zero at 0°C. The 15% and 30% Ti-isop materials exhibit tan δ curves that are qualitatively the same though only the 30 wt% Ti-isop curve is shown (Fig. 1b). Both curves contain broad bimodal behavior with the transitions being similar to that of the 0% Ti-isop material. However, unlike the 0% Ti-isop material, the tan δ transition for samples containing 15% and 30% Ti-isop does not decrease so greatly after 70°C but, rather, it increases giving rise to a second extremely broad transition between 50°C and 200°C.

Figures 2a&b show the dynamic mechanical spectra of PTMO modified TEOS based materials as a function of Ti-isop content. As was the case for the PDMS systems (Fig. 1a), Ti-isop incorporation into PTMO modified systems reduces the change in the storage modulus above the glass transition from two to one order of magnitude (Fig. 2a). Unlike the PDMS systems, the PTMO systems all show a distinct, partially reversible increase in the storage modulus at temperatures above 100°C (9,10). However, the titanium containing materials exhibit a smaller increase than do the pure PTMO/TEOS materials (Fig. 2a). The rise in the storage modulus at high temperatures can be partially attributed to a continuation or "thermal curing" of the sol-gel reaction (specifically, condensation) (7-10). However, the higher modulus above T_g and smaller rise in modulus at high temperatures is strong evidence that the titanium containing materials have reached a higher extent of reaction as compared to 0% Ti-isop PTMO modified materials.

Comparison of the tan δ curves (Fig. 2b) also brings out differences between the 0% Ti-isop PTMO materials and those containing Ti-isop. The 0% Ti-isop material displays a prominent PTMO transition centered at 0°C with a shoulder at ca 50°C. Both the 15 & 30wt% Ti-isop materials display a "weaker" PTMO transition centered at -30°C with a second broad transition centered at 50°C continuing beyond 100°C. As is suspected for the PDMS materials, a bimodal tan δ curve suggests that the oligomer chains are contained in two different physical-chemical environments.

A complete explaination is not yet available but the tan δ transitions observed in the PDMS and PTMO modified materials are believed to be due to the oligomers undergoing the glass transition temperature, T_g. The shifting to higher temperatures and broadening of the glass transitions relative to that of the pure PDMS oligomers (ca -120°C) or the pure PTMO oligomers (ca -80°C) are the result of the physical-chemical environment of the oligomer chains in the glass network as has been accounted for elsewhere (10). This shifting of the T_g strongly indicates that the oligomers are well, but not necessarily uniformly, dispersed throughout the material "matrix" (5-10). The two distinct transitions observed in the titanium containing tan δ curves for both the PDMS & PTMO systems indicate that at least two types of physical-chemical environments exist for the oligomer chains in these materials.

The incorporation of titanium into the PDMS/TEOS & PTMO/TEOS materials results in an apparent *"shifting"* of the oligomer T_g to lower temperatures accompanied by an increase in a second higher temperature (50°C or greater) oligomer transition. In terms of a "two environment" model, the higher PDMS or PTMO transition would correlate to an area in which the oligomer chains are sterically hindered or "encapsulated" by the inorganic glass based network whereas the lower transition (closer to the T_g of pure oligomer) would correlate to a less hindered "oligomer-rich" area (10). If such were the case, titanium incorporation would increase the level of steric hindrance or "encapsulation" by driving the overall system to a higher degree of reaction. This would explain the tan δ curves in that the PDMS or PTMO chains undergoing their glass transition at ca -50°C (PDMS) or 0°C (PTMO) in the 0% Ti-isop material would undergo their glass transition at higher temperatures in the titanium containing materials (see Figs. 1b & 2b). Further, the "unencapsulated" chains with T_g at ca. -50°C (PDMS) or 0°C (PTMO) would be missing in the titanium containing materials thus causing the apparent *"shift"* in the first tan δ peak to lower temperatures.

Structural Data - Small Angle X-ray Scattering:

SAXS profiles of PTMO modified TEOS based sol-gel materials display a broad peak in the plot of smeared intensity vs the scattering vector, s ($s = 2 \sin \theta/\lambda$ where λ is the wavelength and θ is 1/2 the radial scattering angle) (9). Unlike the PDMS systems which showed no SAXS peaks (7), the SAXS peaks exhibited by the PTMO systems indicated features of some degree of microphase separation (9). Furthermore, the estimated "d spacing" or "correlation length" between the two phases - approximated by taking the inverse of the scattering vector s at which the SAXS peaks were centered - was on the order of 10nm.

Figure 3 shows the SAXS profiles of the PTMO modified TEOS based sol-gel materials as a function of Ti-isop content. The increase in the scattering intensities observed as titanium is incorporated into the materials can be explained in terms of an increase in the relative electron density difference between the network "phase" and the polymer "phase". This is expected due to the inherent electron density difference between SiO_2 and TiO_2 and a higher degree of completion of the metal-oxide network in the Ti containing materials. The result, therefore, would be a greater difference in electron density between the Ti containing phase and the "PTMO rich" phase and hence higher scattering intensities. The most notable feature of Fig. 3 is that the SAXS peaks for all of the materials are centered at the same value of s, approximately $s = 0.11 nm^{-1}$. The SAXS peak at $s = 0.11 nm^{-1}$ implies a correlation length of 9.1nm between phases of the same electron density in the sample (9,10). The fact that all of the materials in Fig. 3 show SAXS peaks at nearly this same value, $s = 0.11 nm^{-1}$, indicates that the general character of the microphase separation is the same in all of the materials, i.e., titanium incorporation does not appear to change the gross structural features of the sol-gel material. Additionally, the HCl catalyzed procedure produces a structurally similar material to that made by the CCC procedure provided Ti-isop is added

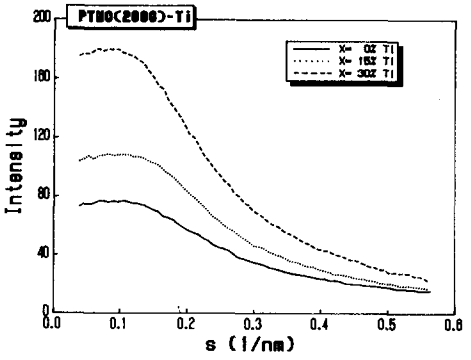

Figure 3 SAXS profiles of PTMO modified TEOS based materials as a function of titanium content.

- note: 0% Ti-isop made by the CCC method takes a much longer time to gel and shows a SAXS peak at s = $0.9nm^{-1}$ (10).

Aging:

PDMS/TEOS sol-gel materials have demonstrated long time stability under ambient conditions (7). However, unlike the PDMS/TEOS materials, the PTMO/TEOS materials are effected by aging under ambient conditions (data presented here for comparison are for samples of similar age). Aging the PTMO modified materials under ambient conditions can result in an increase in the observed initial modulus and stress at break of as much as 700% and 100% respectively with a corresponding tenfold decrease in the observed elongation at break (9,10). Furthermore, the aging phenomenon is more dramatic in materials without titanium as opposed to those with titanium incorporated into the TEOS based network (10). The aging phenomenon is, no doubt, merely a slow completion of the sol-gel process (10); additional studies are currently underway to fully assess the chemical and/or structural changes involved in aging.

CONCLUSIONS

The incorporation of titanium into a TEOS based oligomer modified system via the sol-gel process significantly alters the physical properties of the final material. Mechanical data collected for PDMS and PTMO modified systems demonstrate increases in initial modulus and stress at break on the incorporation of titanium. Also, the elongation at break for titanium containing materials is much lower than that of comparable materials containing no titanium. Finally, the storage modulus in titanium containing materials, as measured by dynamic mechanical experiments, decreases only one order of magnitude after T_g whereas in non-titanium containing materials the storage modulus exhibits a greater decrease. These findings all support the hypothesis that titanium incorporation drives the TEOS based network to a higher degree of completion - possibly through a catalytic effect on the condensation of silanol groups.

Small angle x-ray scattering profiles do not indicate "major" structural differences between PTMO materials with and without titanium incorporated in the network. Though the scattering intensities of titanium containing materials is much higher than materials containing no titanium, the correlation lengths observed in the SAXS profiles are qualitatively the same. This leads to the conclusion that the systems containing titanium are structurally the same but have reacted to a higher degree of completion as compared to systems without titanium. The fact that titanium containing PTMO/TEOS materials demonstrate smaller aging effects on mechanical properties than do pure PTMO/TEOS materials further supports this hypothesis (10).

Additional structural studies, including Raman spectroscopy and solid state ^{29}Si NMR, have been undertaken to further verify these conclusions by determining the degree of reaction and the "fine" structure of the oligomer modified TEOS based sol-gel materials. The results of these studies will be presented in a future publication.

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