Structure–Property Behavior of New Hybrid Materials Incorporating Oligomeric Species into Sol-Gel Glasses. 3. Effect of Acid Content, Tetraethoxysilane Content, and Molecular Weight of Poly(dimethylsiloxane)

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ABSTRACT: A new type of hybrid material incorporating poly(dimethylsiloxane) (PDMS) with tetraethoxysilane (TEOS) has been successfully produced by using a sol-gel process. This material showed good optical transparency and very different mechanical behavior relative to pure sol-gel glasses. Systematic experiments were carried out to study the effect of the acid content, the content of TEOS, and the molecular weight of PDMS on the structure of such materials. Results from dynamic mechanical and SAXS studies indicate that these variables systematically change the dispersion of PDMS in the glass network and, consequently, the properties of the final product.

I. Introduction

In recent years, sol-gel reactions have been extensively studied to improve or modify the process of making inorganic glasses. The high-temperature (>1400 °C) fusion procedure used in traditional processing can be avoided by heating a sol-gel product to a much lower temperature (around 900 °C). Consequently, considerable energy is saved. Another important advantage for this new approach is that some multicomponent systems, which cannot be made by the conventional high-temperature processes due to crystallization upon cooling, can now be prepared by the sol-gel route. However, cracking caused by large stresses during the drying procedure makes the production of monolithic glasses difficult. This pitfall has seriously limited the application of the sol-gel process to principally the production of coatings.

Basically, sol-gel reactions can be viewed as a two-step network-forming polymerization process. Most commonly, metal alkoxides are hydrolyzed to generate intermediate species of metal hydroxides. These species then undergo a stepwise polycondensation reaction to form a three-dimensional network. This network structure imposes restrictions on the molecular movement, thereby making it possible to obtain a multicomponent system without crystallization. Essentially all studies on such systems have concentrated on a mixture of inorganic components, and the final products are usually hard and brittle.

In light of the success of making multicomponent sol-gel glasses, it appeared to the authors that new hybrid materials could be made through the incorporation of some organic-based oligomeric species that have appropriate functional groups to undergo the co-condensation reaction with inorganic-based alkoxides. If this attempt was successful, it could provide a new way of bridging organic and inorganic materials. In addition, the material obtained should show some properties of the inorganic glassy matrix as well as possibly some characteristics of the incorporated oligomeric components. Therefore, materials with new or special application might be made by choosing appropriate reacting components for this new sol-gel process. Furthermore, this type of material could be potentially used as a precursor of making ceramics, realizing that the organic species would be lost or altered in a high-temperature treatment.

For the first attempt, tetraethoxysilane (TEOS) was used as the basic inorganic component. This was mainly due to its controllable hydrolysis reaction rate,[1] which could assist the possibility of incorporating oligomeric species into the system. Silanol-terminated poly(dimethylsiloxane) (PDMS) was chosen to be the oligomeric component because of the similarity of its backbone structure (–SiO–) with the sol-gel glass matrix of TEOS sol-gel and also due to its good thermal stability. Successful production of these hybrids was reported in earlier publications[2,3] and a photograph of some samples is shown in Figure 1. All the samples produced are transparent and free of the usual cracking problem. Although brittleness may still be present depending upon the oligomeric level, the flexibility is much improved over the pure TEOS sol-gel glasses. These observations in conjunction with the mechanical data shown later indicate that oligomeric incorporation has been successful, and it is worthwhile pursuing this new and exciting area.

In the sol-gel process of making inorganic glasses, the acidity of the environment and the water content of the system have been proven to display a critical effect on the structure of the final products.[4,5] This is because each influences the rate of hydrolysis and the chemical equilibrium of the system, and they should still influence the present reaction scheme. However, some additional factors become important due to the addition of the oligomeric component, for example, the amount of the oligomer added, oligomeric molecular weight, the difference between the solubility parameters of the oligomer and the glassy component as well as the solvent(s) used, and the reaction temperature employed. All of these variables may affect the miscibility of the system during reaction and, therefore, the structure and properties of the final products.

In this paper, the effects of acid content, TEOS content, and the oligomeric molecular weight are discussed. Complete definition of the detailed structure of these new mateials is not our goal for the present stage but will be the topic of a future publication. However, an effort is made to provide sound rationale to all data obtained from the experimental work described and to show that a basic understanding of this system has been achieved.

II. Experimental Section

Reaction Scheme. A highly schematic mechanism for the synthesis of the hybrid material is shown in Scheme I. Several points should be noted for this oversimplified scheme:

(1) It is not likely that all ethoxy groups may be converted to hydroxyl groups. The extent of this conversion depends on the amount of water added and conditions under which the reaction is carried out. The residual ethoxy groups may later undergo

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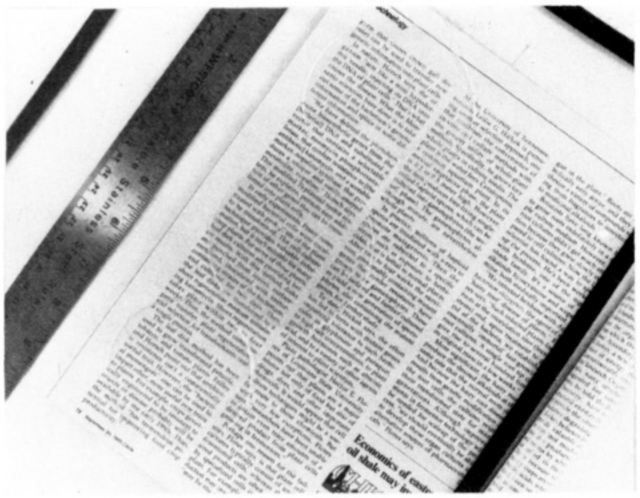
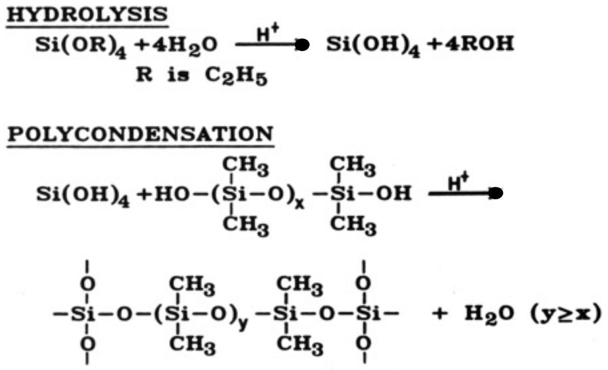


Figure 1. Hybrid materials made with 48 wt % TEOS (PDMS MW = 1700).

Scheme I



HYDROLYSIS

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

$$\mathrm{R\ is\ C_2H_5}$$

POLYCONDENSATION

$$\mathrm{Si(OH)_4 + HO{-}(\overset{CH_3}{\underset{CH_3}{Si}}{-}O)_x{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}OH \xrightarrow{H^+}}$$

$$\mathrm{{-}\overset{|}{\underset{|}{\overset{O}{\underset{O}{Si}}}}{-}O{-}(\overset{CH_3}{\underset{CH_3}{Si}}{-}O)_y{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{|}{\underset{|}{\overset{O}{\underset{O}{Si}}}}{-} \quad + H_2O \quad (y \geq x)}$$

further reaction and stiffen the system by introducing more cross-links.

(2) Besides the co-condensation shown by this scheme, reactants can also undergo self-condensation. The relative rate of this self-condensation with respect to the co-condensation is crucial in determining the final bulk structure and thus the properties of the final materials. If co-condensation is the dominant reaction and the entire system maintains homogeneous during the process, it should lead to a more uniform structure. On the other hand, domination of the self-condensation will most likely produce a system displaying either macro- or microphase separation of the oligomer from the TEOS based species.

(3) Water is consumed in the hydrolysis reaction but is generated by the condensation reaction. Controversy exists in the sol-gel literature in defining the stoichiometric amount of water needed for this process. For consistency, the amount of water added in this work is always expressed as the percentage of water needed to complete the hydrolysis reaction (i.e., TEOS:water = 1:4).

Materials. High-purity tetraethoxysilane was obtained from the Fluka Co. Silanol-terminated poly(dimethylsiloxane) with two different molecular weights—1700 and 550—was obtained from Petrarch Scientific Inc. Data for GPC indicate that considerable amount of cyclics exist in the lower molecular weight PDMS (550). Tetrahydrofuran and 2-propanol were used as the cosolvents for the present system.

Example Procedure. An appropriate amount of distilled water and hydrochloric acid was first added to a 100-mL round-bottom flask with 8 mL of 2-propanol and 2 mL of THF, and the solution as mixed thoroughly. Then, the measured amounts of TEOS and PDMS (MW = 1700 or 550) were simultaneously poured into the solution. The flask was placed in a water bath at 80 °C, and the reaction took place under reflux with fast agitation for 20 min. Then the solution was poured into a Teflon-coated Petri dish and covered with Parafilm to allow the system to gel. After 24 h at ambient temperature, all of the samples gelled and the Parafilm was removed to continue the drying process for at least another 48 h before any test was carried out.

Table I
Description of Nomenclature: Example of TEOS(48)-PDMS(1700)-50-0.045-80C

item	description
TEOS(48)	silane used (wt %)
PDMS(1700)	oligomer (MW)
50	% stoichi amt water added
0.045	molar ratio of acid/silane
80C	reactn temp

Table II
Conversion Table for the TEOS/PDMS System

	molar ratio TEOS/PDMS		
wt % TEOS	MW = 1700	MW = 550	wt % SiO_2 in final product[a]
48	7.5	2.4	21.0
60	12.3	4.0	30.2
70	19.1	6.2	40.2

[a] Assuming reaction is complete.

Table III
Description of Materials Reacted at 80 °C

sample	wt % TEOS	MW PDMS	% stoichi. H_2O added	molar ratio HCl/TEOS
1	48	1700	50	0.022
2	48	1700	50	0.045
3	48	1700	50	0.067
4	48	1700	50	0.090
5	48	1700	50	0.111
6	60	1700	50	0.022
7	60	1700	50	0.045
8	60	1700	50	0.067
9	60	1700	50	0.090
10	60	1700	50	0.111
11	70	1700	50	0.045
12	60	550	50	0.022
13	60	550	50	0.045
14	60	550	50	0.067
15	60	550	50	0.090
16	60	550	50	0.111

Nomenclature. This is illustrated in Table I. The loading of the glassy component (TEOS) is expressed in the percentage of the total weight of glassy and oligomeric components used. However, two other quantities may be useful in specifying the system: (i) the molar ratio of TEOS to PDMS and (ii) the weight percent of the glassy matrix in the final product if the reactions are assumed to be complete (i.e., no ethoxy groups left in the system). Table II lists the conversion between these quantities.

A somewhat related hybrid system has been studied by Mark et al.[6] They have utilized an in situ precipitation technique to simultaneously cure and fill a PDMS rubber with TEOS. The reaction was carried out in a weak acidic environment and, in most cases, the TEOS loading was lower than 30% by weight. The molecular weights of the PDMS used were 8000 and 21 000, and the structure generated was a PDMS rubbery matrix with dispersed SiO_2 particles with the size of about 200 Å. Therefore, despite the similarity of the raw materials used, the objective of their work is apparently different from the present study.

Characterization Methods. Stress–strain experiments were carried out with an Instron 1122 Model. Dogbone-shaped samples of 10 mm in length were used, and the initial strain rate was 2 mm/min. Dynamic mechanical data were obtained by utilizing a DDV-IIC Rheovibron dynamic viscoelastometer. Most samples were tested within the temperature range of −140 to +300 °C with a heating rate of 2–3 °C/min. A frequency of 110 Hz was selected for all the dynamic mechanical experiments.

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

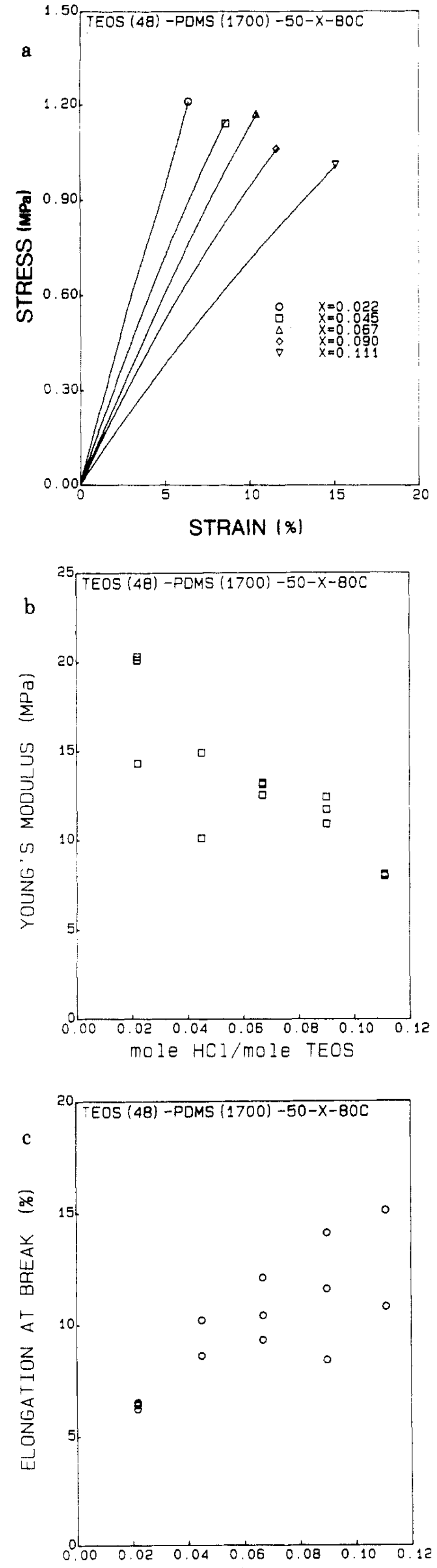


Figure 2. Effect of acid content on the (a) stress–strain behavior, (b) Young's modulus, and (c) elongation at break of samples made with 48 wt % TEOS (PDMS MW = 1700).

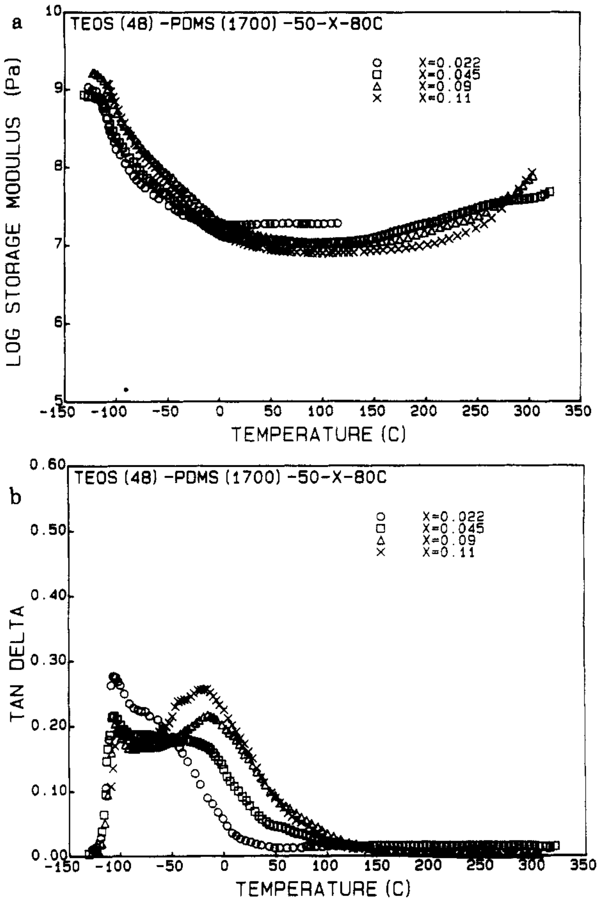


Figure 3. Effect of acid content on the (a) storage modulus and (b) tan δ behavior of samples made with 48 wt % TEOS (PDMS MW = 1700).

Philips table-top X-ray generator.

III. Results and Discussion

All the samples being studied are listed in Table III. The experimental results illustrating the effect of acid content are presented and discussed in the first part of this section. Then data and interpretation of the change of structure due to different TEOS contents are given. Finally, the effect of the oligomeric molecular weight on the structure–property behavior is shown and some related interpretation is offered.

A. Effect of Acid Content. For pure sol-gel systems, it has been reported that the acidity has a significant influence on the structure of the final product.[4] Hence, it is expected that the amount of acid used will also influence the bulk structure of the hybrid materials in this work. A systematic study therefore was carried out to determine how the acid content would alter the structure–property behavior. Five different acid contents were employed as indicated in Table III (samples 1–5). All samples were transparent and therefore did not display any sign of incompatability between components. As expected, the sample with higher acid content tends to gel faster than the one with lower acid content. Although all samples were relatively flexible, the flexibility tends to increase with acid content.

Mechanical tests were first carried out on this series to denote any differences in macroscopic properties. Results of the stress–strain experiments are shown in Figure 2. In spite of some scatter, the data show a clear trend of decreasing modulus and increasing elongation at break with increasing acid content. The dynamic mechanical results are illustrated in Figure 3. At very low temperatures, all samples show a plateau in modulus with a magnitude of ca. 10^9 Pa, which is typical for glassy polymers. As the temperature increases, each sample initially goes through a broad transition region showing a gradually decreasing modulus and finally reaches another plateau which has the magnitude of about 10^7 Pa, the modulus of a stiff elas-

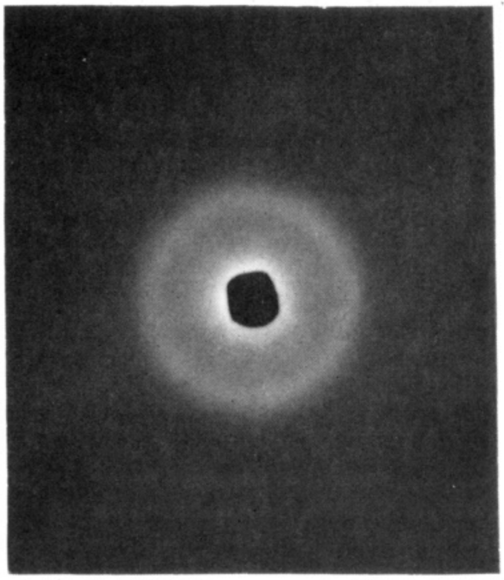


Figure 4. Typical WAXD pattern of a TEOS–PDMS hybrid sample.

tomer. This low-modulus plateau extends over a range of almost 200 °C before the modulus begins to increase at high temperature. Inspection of the tan δ behavior in Figure 3b shows that a peak is observed near −106 °C for all materials and its magnitude decreases with increasing acid content. Another peak, which is near −10 °C, develops and intensifies when more acid is used. This trend is very important in the later discussion of results.

Wide-angle X-ray diffraction (WAXD) was employed to investigate the potential of any crystalline structure within these hybrid materials. All samples displayed a similar pattern with a single amorphous halo, which indicates a disordered structure for the system (see Figure 4).

As an oligomer is incorporated into the network, two types of restrictions may be imposed on this moiety: (1) that caused by coupling of its ends through chemical bonding (these bonds may connect to a TEOS species or another oligomer through the silanol functionality); (2) that caused by the local dense structure of the three-dimensional network developed through the self-condensation of the hydrolyzed TEOS. Therefore, the thermal energy needed to mobilize a oligomeric chain would be higher than that needed for an unconstrained oligomeric chain. This would result in an increase of the glass transition temperature of the oligomeric chain. If PDMS were to undergo self-condensation, a rich or pure phase of siloxane would be expected to develop on the basis of thermodynamic incompatibility of the species increasing in molecular weight. If this did occur, such phase-separated PDMS should display a T_g near that for the pure oligomer (about −120 °C). However, if the PDMS is better incorporated into the TEOS network in the form of relatively short chains, i.e., it did not chain-extend by reacting with other oligomers, its T_g would be shifted to a higher temperature if its motion is also restricted by the presence of the TEOS network components. Therefore, the low-temperature peak (near −106 °C) shown in the tan δ data is speculated to be attributed to a rich PDMS phase, while the high-temperature peak (near −10 °C) is believed to arise from better dispersed PDMS oligomers in the midst of TEOS network regions.

At the beginning stages of the reaction, most of the silanol groups are from the PDMS and some self-condensation of these species will likely take place, particularly if given sufficient time. As the hydrolysis reaction of TEOS occurs, silanol groups from the TEOS are generated. Therefore, the dominant type of reaction will shift from self-condensation to co-condensation and, eventually, to the self-condensation of the silanol groups from TEOS—due to the exhaustion of silanol functionalities of the oligomers. The relative length of these three reaction periods clearly plays a crucial role in determining the structure of the final product. If the first period is relatively short, it suggests that less PDMS will be phase-separated and more will be dispersed in the network regions of self-condensed hydrolyzed TEOS. The reverse will be true if the first period is relatively long.

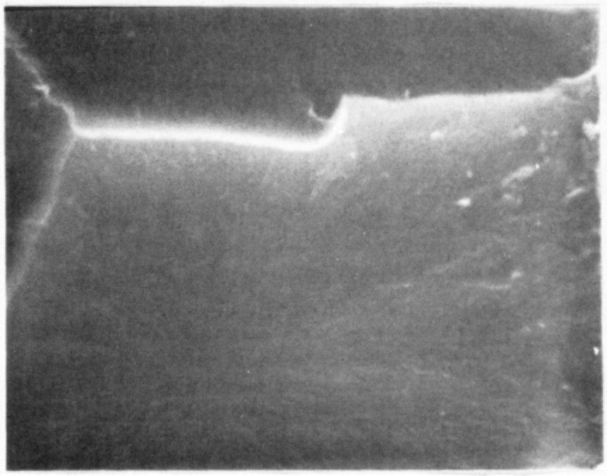


Figure 5. SEM micrograph of a hybrid sample with 48 wt % TEOS (PDMS MW = 1700). (Magnification ×1000).

According to the reaction scheme suggested earlier, acid is the catalyst for the present system. As the acid content increases, the rate of the hydrolysis reaction is increased and the first period (mainly self-condensation of PDMS) will be shortened. The oligomer should, therefore, be more dispersed according to the rationale given above. This should result in a decrease of the low-temperature tan δ peak and an increase of the high-temperature one, which is exactly the case observed from the experimental data.

Another remark should be noted for the dynamic mechanical data. In Figure 3a, the modulus shows a slight increase between 50 and 200 °C. This may be, at least partially, attributed to the rubber elasticity behavior of the PDMS that has been incorporated into the network. Above 200 °C, the increasing tendency becomes much steeper and the sample becomes more brittle and stiffer. This indicates that further curing of the system occurs to cause an increase in the cross-linking density arising from the further condensation of hydrolyzed TEOS. This curing process is currently under investigation and results will be reported in a future publication.[7] It is important to add, however, that reproducibility of the dynamic mechanical response has been demonstrated for a given reaction scheme. In addition, identical spectra are obtained even after thermal cycling a sample to 100 °C. This latter point is crucial for it demonstrates that the thermal transition observed during the first heating cycle is not a result of a loss of volatiles or other major changes in composition.

To provide further evidence for the presence or lack of phase separation of the PDMS component, scanning electron microscopy was employed to study the fracture surfaces of various hybrid materials. In this series as well as the others discussed in this paper, scanning electron microscopy provided no signs of phase separation within the limits of the instrument resolution. An example of a typical fracture surface is shown in Figure 5, where the

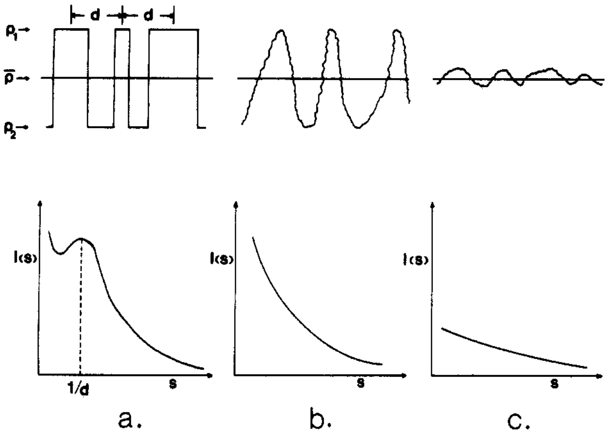


Figure 6. Schematic models for the electron density profile and corresponding SAXS curves: (a) periodic fluctuation with correlation length "*d*"; (b) random electron density fluctuations; (c) random fluctuations with smaller magnitude than for (b).

reader will observe no distinct signs of domain structure that may have arisen from the presence of a pure or rich siloxane phase. This data clearly provides additional support to the earlier hypothesis for good dispersion of the siloxane oligomeric components within the three-dimensional TEOS self-condensation network, although it certainly does not rule out the possibility of some smaller scale microphase formation.

To further substantiate the development of greater homogeneity (dispersion) of the PDMS material with increasing acid catalyst content, the method of small-angle x-ray scattering (SAXS) was applied. The purpose of utilizing this technique was to provide two modes of structural characterization. The first was to detect if any periodicity or "interdomain spacing" might be detected should the siloxane phase develop a "correlated structure" such as is common in phase-separated block and segmented copolymers.[8] Specifically, in some of these latter mentioned materials, it is difficult to denote phase separation directly by electron microscopy techniques. However, if a sufficient electron density contrast exists between the two components and if there is a correlation (regularity) in the general interdomain spacing, this can often be detected by the utilization of small-angle X-ray scattering if this correlation length is within the range 2–100 nm. As shown in Figure 6a, a hypothetical electron density profile, which has a correlation distance d between periodic electron density fluctuations, is illustrated along with the general sketch of how the corresponding SAXS intensity $I(s)$ might behave with respect to s. The variable s is defined as $s = 2(\sin\theta)/\lambda$, where θ is half of the radial scattering angle and λ is the wavelength of the X-ray beam used. The parameters ρ_1 and ρ_2 are the electron densities of the two components, and $\bar{\rho}$ is the average electron density of the system. Without detail, s is inversely related to the distance over which autocorrelations in electron density fluctuations occur, i.e., the correlation length d as indicated above. Hence, if strong distance correlations exist, that is some regularity in structure occurs, a shoulder or peak can be detected in $I(s)$. If high regularity exists, higher order scattering peaks will be observed.[9] As shown in Figure 6a, the electron density profile illustrating regularity in structure would indeed provide a maximum where the peak is correlated to the value $1/d$. However, if a slit collimation system is used, as in our measurements, a correction for the smearing effect would have to be made.[10]

The second utilization of the SAXS technique was to provide an index of homogeneity within a given series of materials through comparison of the calculated SAXS invariant, Q, which is dependent upon the mean-square fluctuation in electron density $\overline{(\Delta\rho)^2}$. In the case where no regular correlations in fluctuations exist, as illustrated in Figure 6b, the scattered intensity will be more monotonic in behavior with s. Furthermore, if the fluctuations are much smaller, i.e., the system is more homogeneous, the general scattering profile will be further decreased in intensity as illustrated in Figure 6c. Hence, the mean-square fluctuation in electron density provides an index of the average magnitude of the electron density fluctuations and therefore is an index of homogeneity in a given system with other factors being constant. For the case at hand, if the siloxane components are well dispersed within the network structure of the TEOS, a more homogeneous structure is expected and a lower mean-square electron density fluctuation should be evident from a smaller value of the invariant, Q, which is defined as

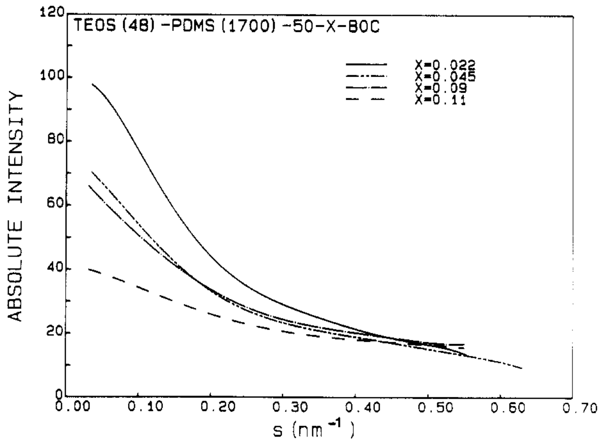


Figure 7. Effect of acid content on the SAXS behavior of samples made with 48 wt % TEOS (PDMS MW = 1700).

$$Q = \int_0^\infty s\tilde{I}(s)\,\mathrm{d}s \tag{1}$$

The variable $\tilde{I}(s)$ represents the smeared scattered intensity at a given value of s. (It might be noted that if desmeared intensities are utilized for calculating the invariant, a somewhat different equation must be applied.[10])

With this background, the respective scattered intensity plots obtained of the previously discussed acid-catalyzed series are shown in Figure 7. It is clear that there is a systematic decrease in the overal scattering behavior for these materials with increasing acid content. Following correction for background scattering whereby the method of Bonart was utilized,[11] the invariant for each material was calculated through use of a computer program of Vonk that incorporates eq 1. The results of this analysis are given in Figure 8, which plots $\overline{(\Delta\rho)^2}$ (as determined from the invariant calculation) vs. the acid/TEOS ratio. It is obvious that for the four samples investigated $\overline{(\Delta\rho)^2}$ systematically decreases and hence the homogeneity increases as the acid-catalyzed reaction is enhanced. This is in direct support of the earlier interpretation of the dynamic mechanical data. Similar to the dynamic mechanical data, the values of the invariant and $\overline{(\Delta\rho)^2}$ were reproducible and not altered by thermal cycling even up to ca. 150 °C.

From the earlier stress–strain data, the behavior can be explained by the oversimplified schematic model shown in Figure 9. The system of Figure 9a is an extreme case for PDMS phase separation, while Figure 9b is for high dispersion of PDMS within the TEOS network. As the former system is stretched, the probability of stretching

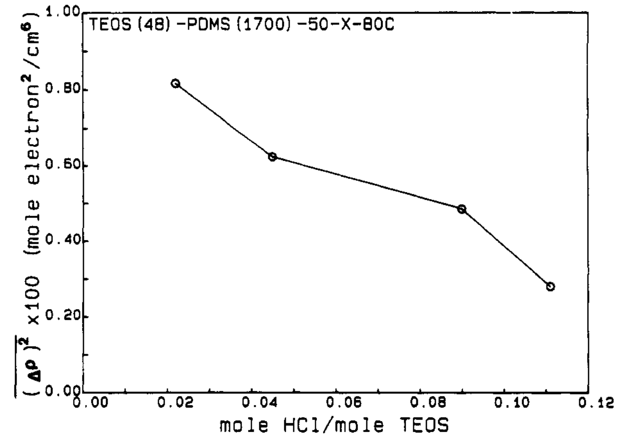


Figure 8. Effect of acid content on the mean-square electron density fluctuation of samples made with 48 wt % TEOS (PDMS MW = 1700).

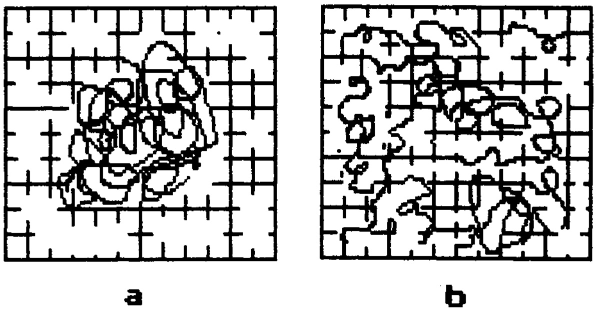


Figure 9. Simplified schematic models for the hybrid system: (a) phase-separated organic; (b) better dispersed organic.

a Si–O–Si linkage from the TEOS should be higher than that of the latter system. A second important point is that in the case of higher phase separation the dispersed regions of pure PDMS may serve as stress concentrators and thereby have a negative effect on obtaining high elongation. Both of these two factors lead to a result of higher modulus and lower elongation at break for the system with more phase separation. Clearly, these results and their interpretation are in parallel with the dynamic mechanical and SAXS data.

In summary of the effect of acid content, it has a prominent influence on the final structure and therefore the properties of the hybrid material produced. An increase in acid content shortens the period for self-condensation of PDMS and results in a material with more dispersed oligomers. Consequently, the homogeneity and flexibility of the sample can be improved.

B. Effect of TEOS Content. According to the rationale given above, the relative length of the three periods—self-condensation of PDMS, co-condensation, and self-condensation of TEOS—can determine the final structure of the hybrid material. The points of transition should be influenced by changing either the rate of TEOS hydrolysis and its self condensation or the relative amount of reactants. While the former has been done by using different acid contents, the latter is now varied by changing the composition ratio of TEOS to that of PDMS.

Three different TEOS contents—48, 60, and 70 wt %—were employed to investigate the effect of this component on the structure of the final product where acid content was also systematically varied in each case. Figure 10 shows the dynamic mechanical results for an acid series with 60 wt % TEOS. For lower acid content, the general behavior of the modulus curve is similar to that shown previously except the midrange plateau is in the magnitude of 10^8 Pa, as is to be expected. As acid content increases further, the plateau region is no longer observed. Instead, the modulus continues to drop until 150 °C and then starts to increase. The tan δ curve shows three peaks (although broad in nature) for higher acid content materials: near −90, 0, and +90 °C, respectively. The low-temperature peak tends to decrease while the other two peaks increase with increasing acid content. However, their magnitudes are lower than that of the 48 wt % series. Results from mechanical tests for this series are shown in Figure 11. Despite some scatter of the data, the trend is similar to that of the 48 wt % series. Regarding to the stress–strain behavior shown in Figure 11a, one important point should be noted: as the acid content increases to 0.067 the shape of the curve changes from an almost linear behavior to one that is close to a yield behavior. Interestingly, this is also the acid content where the tan δ peak near 90 °C begins to develop.

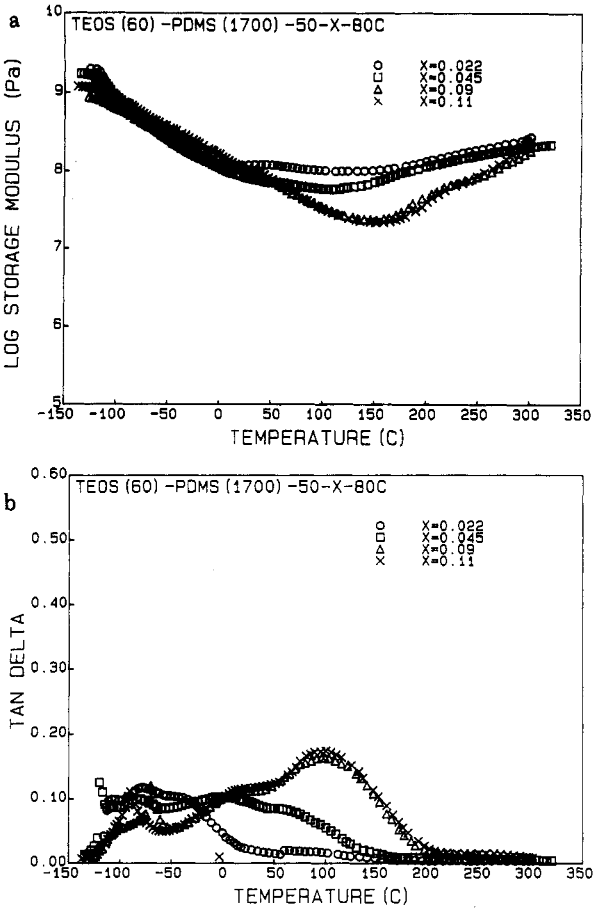


Figure 10. Effect of acid content on the (a) storage modulus and (b) tan δ behavior of samples made with 60 wt % TEOS (PDMS MW = 1700).

Figure 12 provides a comparison of the dynamic mechanical data between three different TEOS contents at the same acid level. Within the testing temperature range, it is clearly shown that the modulus increases as the TEOS content increases and is expected. Moreover, the high-temperature peak of tan δ tends to shift to higher temperatures as the TEOS content increases from 50 to 70%. The stress–strain data was not obtainable for the 70 wt % series due to the brittleness of the samples. This is likely caused by the higher connectivity of the rigid TEOS network and, if so, would be expected to provide some yield behavior in the stress–strain response at a strain level where the TEOS network is disrupted.

From the first acid content series (with 48% TEOS), it was concluded that the increase of acid concentration can

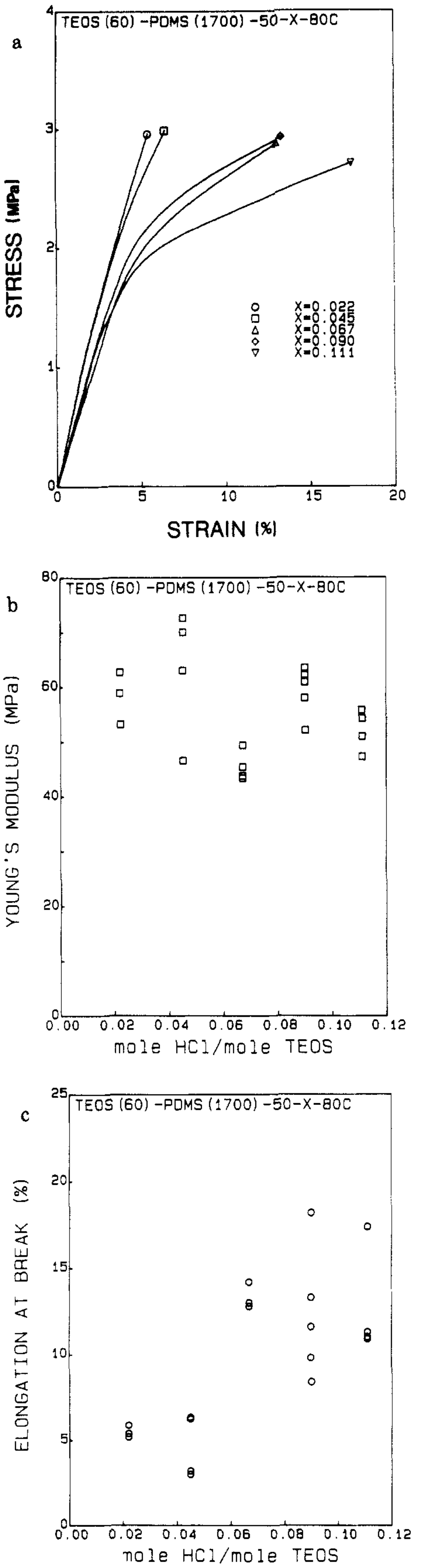


Figure 11. Effect of acid content on the (a) stress–strain behavior, (b) Young's modulus, and (c) elongation at break of samples made with 60 wt % TEOS (PDMS MW = 1700).

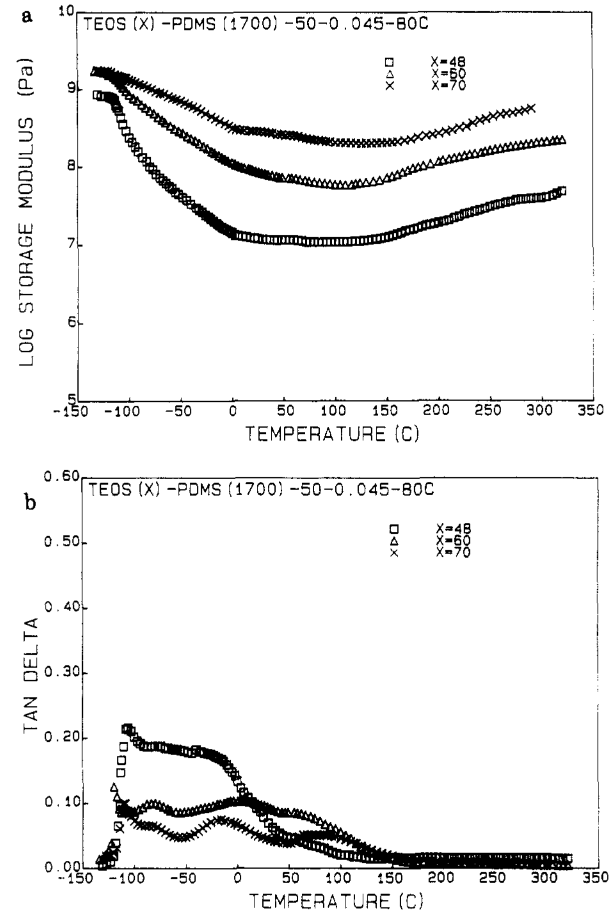


Figure 12. Effect of TEOS content on the (a) storage modulus and (b) tan δ behavior (PDMS MW = 1700).

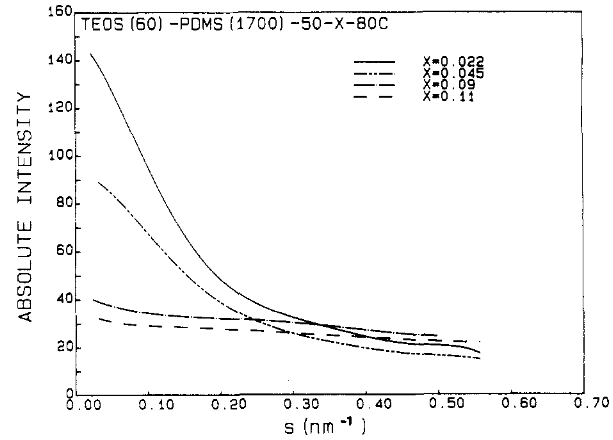


Figure 13. Effect of acid content on the SAXS behavior of samples made with 60 wt % TEOS (PDMS MW = 1700).

improve the homogeneity of the sample. This behavior is also observed for the current series (with 60% TEOS) by the intensification of the tan δ peak near 90 °C. However, the position of this increasing peak has shifted from −10 to +90 °C. This indicates that the "time distribution" of the three periods mentioned above may have been altered. By reviewing Table II, one notices that the molar ratio of TEOS to PDMS changes from 7.5 to 12.3 as the TEOS content increases from 48 to 60 wt %. For the same acid content, the rate of hydrolysis should be the same for both systems. Since the concentration of the silanol groups from PDMS is lower in the higher TEOS materials, less time is needed for the silica hydroxyl to reach the concentration that the transition from self-condensation to co-condensation can take place. Moreover, due to the decrease in PDMS concentration, the chance for the self-condensation of PDMS molecules would also decrease. Therefore, further dispersion of PDMS should

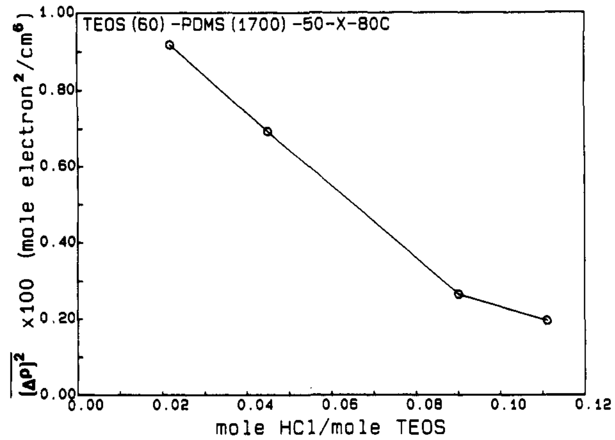


Figure 14. Effect of acid content on the mean-square density fluctuation of samples made with 60 wt % TEOS (PDMS MW = 1700).

result. This hypothesis is reinforced by inspecting the SAXS results from this second series (see Figure 13). It is noted that the scattered intensity again systematically decreases as acid content increases. Figure 14 provides a plot of the calculated mean-square fluctuation in electron density vs. acid–TEOS ratio and again it is clear that as acid content increases homogeneity increases as based on our earlier discussion.

It should be pointed out that a direct comparison of the scattered intensities from this series vs. the earlier series shown in Figure 7 is not proper due to the fact that there is also a change in the relative volume fractions of the two components (TEOS and PDMS) and hence the general scattering behavior may well be somewhat different. For example, it is well-known that in the case of a two-component system having sharp phase separation, the mean-square fluctuation in electron density scales as the product of the volume fractions of the two components and hence goes through a maxima when these two values are 0.5.[10] While indeed we do not have such sharp phase-separated components, the same argument can be utilized accordingly. Even so, the reader will note that the absolute values of the mean-square fluctuation in electron density are of the same order of magnitude as observed in the previous systems. Any difference in their absolute values, however, are of little utility in our discussion at this point since it is unknown what the relative extent of reaction is for the materials—this subject is presently being investigated through use of Raman spectroscopy and ^{29}Si NMR.

As the TEOS glass content increases, the network structure should become more highly cross-linked. This tighter structure should impose higher restrictions on the incorporated chains, and the consequence would be to shift the T_g even further to the right on the temperature scale. This may be the reason why the high-temperature peak is shifted form −10 to +90 °C as seen in the tan δ behavior as TEOS content increases. This point can be illustrated better by returning to Figure 12b, which shows a systematic shifting of the high-temperature peak with increasing TEOS content. Although it was suggested that higher homogeneity may cause the modulus to decrease (referring to the model in Figure 9), the glass content is also a major factor in determining the stiffness of the sample. By reviewing Table II, one realizes that the molar ratio of TEOS to PDMS increases considerably as the TEOS loading is raised. This would easily compensate for the effect of the increasing dispersion and results in an increase in modulus as shown earlier in Figure 12a. At the limit of pure TEOS, the modulus will reach the stiffness of a pure sol-gel glass.

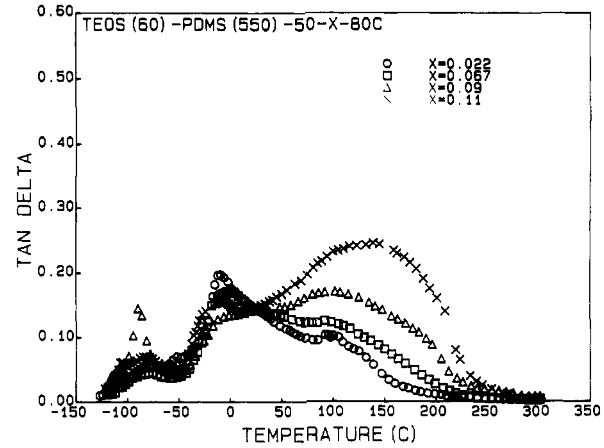


Figure 15. Effect of acid content on the tan δ behavior of samples made with 60 wt % TEOS (PDMS MW = 550).

According to the rationale given above, the appearance of the tan δ peak near 90 °C indicates a better dispersion of the PDMS chains in the sol-gel network. By returning to the schematic model in Figure 9b, one realizes that as the dispersion of PDMS becomes better, these coiled oligomeric chains might still maintain the mechanical integrity of the system when the glassy bonds are broken by stretching. This will result in a drop in stress when straining the sample to the point where the Si–O–Si linkage from TEOS starts to break. However, this transition point may not be as clearly defined as a yield point usually observed for hard plastic materials due to the wide distribution of the length of the dispersed PDMS chains and the imperfections of the TEOS network. These latter statements may help in explaining the change in the shape of the stress–strain curve when the acid content increases beyond 0.067.

Another remark before leaving this section is that as the TEOS content increases the samples become more brittle. Fracture and shrinkage problems also become significant. All of these factors would undoubtfully affect the processibility and applications of these materials.

C. Effect of Oligomeric Molecular Weight. Besides the 1700 molecular weight PDMS, a molecular weight of 550 was used to study the effect of the chain length of the oligomer. TEOS of 60 wt % was employed, and the molar ratio of TEOS to PDMS was fixed at 4.0.

The dynamic mechanical results are illustrated in Figure 15. Since the behavior of the storage modulus is somewhat similar to that shown in Figure 10a, only the tan δ spectrum is given. The magnitude of the low-temperature tan δ peak (near −90 °C) is very low, while the higher temperature loss behavior is much more significant, compared to the previous series. Furthermore, the tail of the high-temperature tan δ peak extends to almost 250 °C, which is much higher than previous cases. For the sample with the highest acid content, the high-temperature tan δ peak shifts upward to around 140 °C which is about 50 °C higher than the other samples discussed so far.

In this 550 MW PDMS series, the chain length is much shorter than previously used. Although self-condensation can still occur, the chance of forming a long chain to cause phase separation is much smaller. This results in a relatively small low-temperature tan δ peak. As the dispersion becomes better due to the increase of acid content, more oligomer would be incorporated into the network in the form of very short chains and a more uniform TEOS network environment. The chain may be so short that the first type of restriction—caused by bonding chain ends—becomes dominant, and the T_g could be shifted up con-

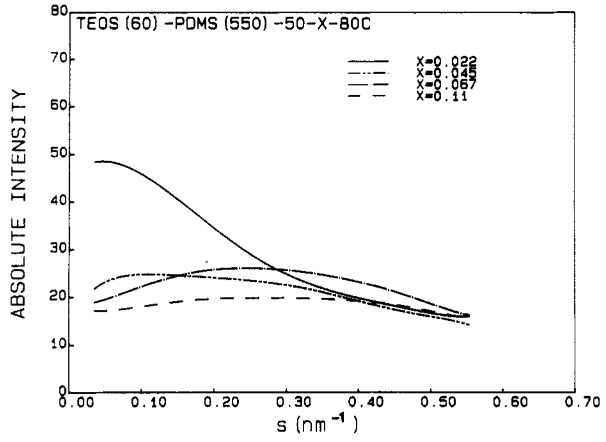


Figure 16. Effect of acid content on the SAXS behavior of samples made with 60 wt % TEOS (PDMS MW = 550).

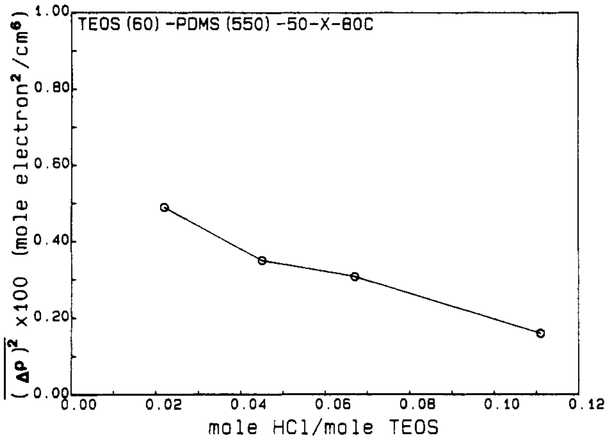


Figure 17. Effect of acid content on the mean-square electron density fluctuation of samples made with 60 wt % TEOS (PDMS MW = 550).

siderably. This suggested explanation is supported by the extension of the tail of the high-temperature tan δ peak. Figure 16 provides the corresponding SAXS data obtained on this series. Again, as acid content increases, the degree of scattering decreases and in fact leads to a smaller invariant and hence smaller mean-square electron density fluctuation (see Figure 17). Also of interest is the fact that there seems to be a rather broad diffuse maxima in the intensity as a function of s although there is some question as to the "realness" of this maximum since the scattered intensity for these samples of higher acid content was quite low and, hence, the signal-to-noise ratio of the PSD detector was lessened. The important feature here, however, are the resulting values of the mean-square fluctuation in electron density as given in Figure 17. These show again that the homogeneity increases as acid content increases. This of course is in line with the two previous series. Also, it is noted that the value of the electron density fluctuation is somewhat lower than the previous two series. This may result from the fact that there is even a better dispersion due to the lower molecular weight of this PDMS component and hence its solubility is higher, thereby leading to better dispersion and higher homogeneity.

This low molecular weight oligomer series provides very useful information. First, the material uniformity is much improved over the system with higher oligomeric molecular weight. Second, the phase separation problem becomes less pronounced. Preliminary data show that the cycles in the PDMS affect only the modulus and not the transition behavior. However, more detailed study is currently under way, and the results will be reported in a future publication.[7]

IV. Conclusions

A new hybrid material incorporating oligomeric PDMS with inorganic glasses (TEOS) by a sol-gel process has been successfully produced. This material shows high transparency and improved flexibility over pure sol-gel glasses, although certainly the stiffness is decreased as oligomer content is increased.

The acid content of the reacting system is crucial in determining the structure of the final product. As the acid content increases, PDMS is better molecularly dispersed into the system. As a result, the final product becomes more homogeneous and shows higher extensibility (for 48 and 60 wt %).

An increase of the TEOS content results in a more homogeneous system and a tighter network with higher modulus. However, cracking and shrinkage may cause problems in making thick monolithic materials as is the case for pure sol-gel glasses. With the use of oligomers with shorter chain lengths, phase separation becomes less pronounced and the uniformity is improved considerably.

Further work is being undertaken to investigate other variables such as water content, reaction temperature, and solvent used. In addition, other types of oligomers are being utilized to produce materials with different characteristics. We firmly believe that, by carefully choosing components, this process can become a useful way to produce new hybrid materials for new applications.

References and Notes

(1) Yoldas, B. E. *J. Non-Cryst. Solids* **1982**, *51*, 105.
(2) Wilkes, G. L.; Orler, B.; Huang, H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26*(2), 300.
(3) Huang, H.; Orler, B.; Wilkes, G. L. *Polym. Bull. (Berlin)* **1985**, *14*, 557.
(4) Zerda, T. W.; Artaki, I.; Jonas, J. *J. Non-Cryst. Solids* **1986**, *81*, 365.
(5) Strawbridge, I.; Craievich, A. F.; James, P. F. *J. Non-Cryst. Solids* **1985**, *72*, 139.
(6) Mark, J. E.; Jiang, C. Y.; Tang, M. Y. *Macromolecules* **1984**, *17*, 2613.
(7) Huang, H.; Wilkes, G. L., manuscript in preparation.
(8) Wilkes, G. L.; Samuels S. L. *Block and Graft Copolymer*; Syracuse University Press: Syracuse, NY, 1973; Chapter 12.
(9) Hashimoto, T.; Shibayama, M.; Fujimura, M.; Kawai, H. *Mem. Fac. Eng., Kyoto Univ.* **1981**, *43*.
(10) Alexander, L. E. *X-ray Diffraction Methods in Polymer Science*; Wiley: New York, 1969; Chapter 5.
(11) Bonart, R.; Muller E. H. *J. Macromol. Sci., Phys.* **1974**, B*10* 345.