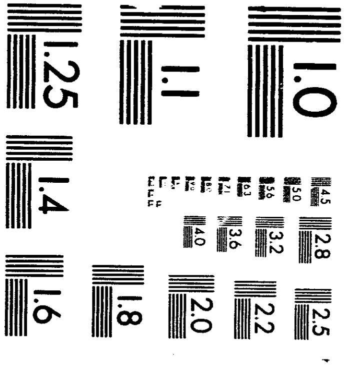
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# Sol-Gel Derived Silica/Siloxane Composite Materials: The Effect of Loading Level and Catalyst Activity on Silica Domain Formation

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## Introduction

Currently, the production of *in situ* reinforcement in polymeric systems by sol-gel methods is undergoing rapid development.[1-12] However, despite this activity, a detailed understanding of synthesis/structure/property relationships is still lacking. In order to produce sol-gel derived composite materials with sufficient mechanical properties for commercial applications, this deficit of information must be addressed. We have completed a detailed investigation of *in situ* silica growth in polydimethylsiloxane (PDMS)/tetraethylorthosilicate (TEOS) systems. Factors which affect the domain growth, such as catalyst activity and silica loading, have been examined by solid state $^{29}$Si NMR, SEM, mechanical testing and Small Angle Neutron Scattering (SANS).

## Experimental

Hydroxyl terminated polydimethylsiloxane was obtained from Dow Corning Corporation. TEOS (Reagent Grade) was obtained from Fischer Scientific and was used without further purification. Tin octoate (TO), $[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2Sn$, and dibutyltin dilaurate (DBTDL), $[CH_3(CH_2)_{10}CO_2]_2Sn[(CH_2)_3CH_3]_2$, were obtained from Hüls as 50% and 25% solutions in polydimethylsiloxane, respectively.

The $^{29}$Si NMR spectra were recorded at 39.6 MHz on a Chemagnetics console interfaced to a General Electric 1280 data station and pulse programmer. The samples were spun about the magic angle at 2.5 kHz. A direct polarization sequence was used with pulse delay times of 120s (a factor of 4 times the longest observed $T_1$) so the resonance areas are expected to be quantitative. Neutron scattering was performed at the High Flux Isotope Reactor at Oak Ridge National Laboratory. Data from different q ranges were matched by an arbitrary vertical shift factor. Scanning Electron Micrographs (SEM) were obtained on Au/Pd coated samples using a JEOL 6400 scanning microscope.

## General Procedure

TEOS and a tin catalyst (TO or DBTDL) were added to the hydroxyl terminated polydimethylsiloxane in amounts sufficient to both cross-link and fill the matrix with silica to the mole percent desired. The solution was stirred until it became homogeneous. The mixture was then poured into a glass petri dish which was previously treated with a mold release agent. The sample was degassed, placed into a humidity cabinet and cured at 60% relative humidity ($R_H$) for 1 week.

## Results and Discussion

In order to investigate the effect of loading and catalyst activity, two series of silica/siloxane composite materials were synthesized. The first series of samples were made using tin octoate (TO), which is a highly reactive tin(II) catalyst. The second series used dibutyltin dilaurate (DBTDL), which is a tin(IV) catalyst of moderate activity. With each catalyst, a series of samples were made at different calculated silica loading levels (5, 10, 20 and 40 mol% in the final product).

Small Angle Neutron Scattering (SANS) was used to study the small-scale silica domain growth within these materials while the large scale structure was investigated using SEM. All of the DBTDL catalyzed samples are featureless by SEM, while the TO catalyzed samples at higher loading levels contain domains a few microns in size. In addition, an increase in the number of particles is observed when going from 20% to 40% loading in the TO samples. In general, SANS indicates that in both the DBTDL and TO catalyzed samples small-scale domains are produced at higher loading levels (Figures 1 and 2). For both catalysts, increased loading leads to greater signal intensity, indicating greater phase separation. However, while DBTDL does not demonstrate a change in the correlation length with loading, TO does. For TO, the data follows a monotonic trend with the correlation length moving to larger length scales as the loading increases. In addition, DBTDL catalysis leads to smaller domains than TO. The differences in the SANS data illustrate the marked difference in the phase separation characteristics for the two catalyst systems.

The SANS data at small q indicates the presence of large-scale domains which also differ for the two catalyst systems. For DBTDL (Figure 1), the scattering due to the large scale domains is pushed to very small q values, indicating either very few large-scale domains exist or they are extremely large compared to the TO system. The strength of the tail from the large-scale domains in the TO system (Figure 2) suggests that either a large number of these domains are present or they are of smaller size than those produced with DBTDL. Two explanations exist for the SANS large scale structure data. However, in view of the presence of SEM-observable domains only in the TO system, the SANS data is best interpreted as indicating few large-scale domains for DBTDL and many large-scale domains for TO. Since the development of ceramics by sol-gel chemistry depends on the relative rates of hydrolysis and condensation within the system, the catalyst activity should have a profound effect on the silica domain growth. Hence, the differences in these growth patterns may be due to the differences in catalyst activity.

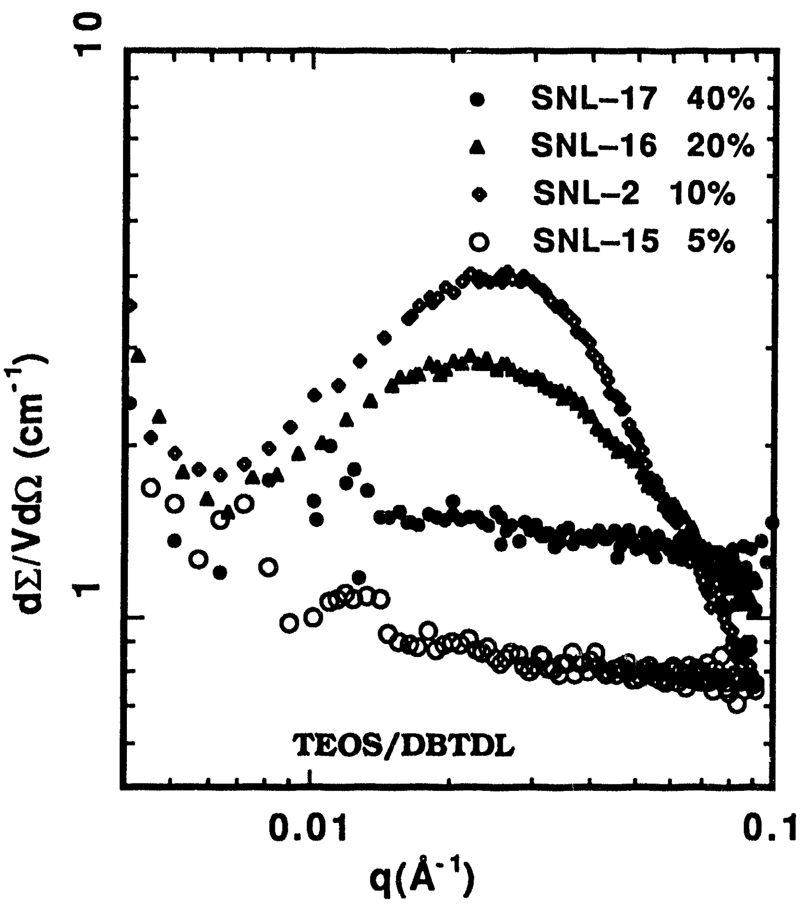

Figure 1. SANS data for 5-40% loaded TEOS/DBTDL samples.

As expected, the mechanical properties show that the tensile (stress at 50% and 100%) and durometer measurements generally increase with higher loading, while the elongation decreases (Table 1). These trends are attributed both to an averaging of the properties of the two phases as well as to increased cross-link density in the base polymer. It is difficult to separate the importance of these two effects on the domain growth since they are coupled. An increase in the crosslink density leads to greater incompatiblity of the two phases and, therefore, to more distinct domains. Again, this enhanced phase separation with loading is supported by the aforementioned increase in intensity of the SANS data and the increased growth of large domains as indicated by SEM.

A further comparison of the two catalyst systems is provided by $^{29}$Si NMR. For example, while the phase separation is markedly different in the 20% loaded samples, the extent of reaction and Q distribution are the same (Table 2). This similarity indicates that the differences are not due to changes on the molecular level, but are due to changes in the overall growth or connectivity on a macromolecular level.

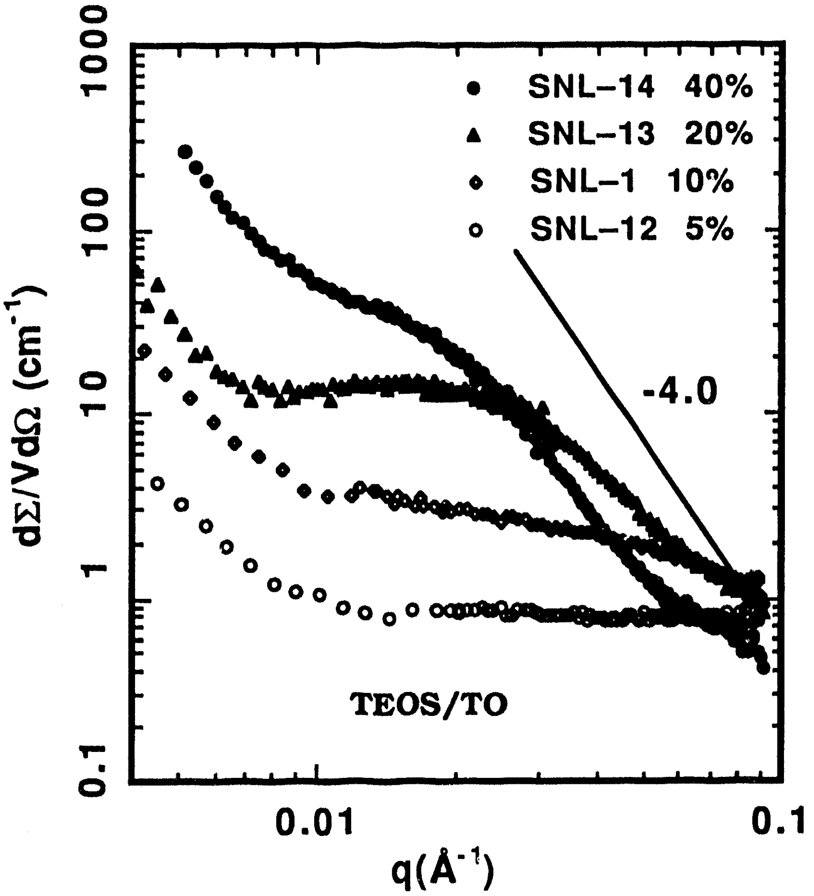

**Figure 2.** SANS data for 5-40% loaded TEOS/TO samples.

## Acknowledgments

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**Table 1.** Mechanical measurements for TEOS/DBTDL and TEOS/TO samples as a function of loading.[a]

| Sample/Cat. | Loading | Duro. | Elong | Tensile[b] | Stress 50% (100%) |
|---|---|---|---|---|---|
| 1/TO | 5% | 34 | 204 | 648 | 53 (165) |
| 2/TO | 10% | 45 | 106 | 529 | 255 (527) |
| 3/TO | 20% | 51 | ----[c] | ---- | -------- |
| 4/TO | 40% | 43 | ---- | ---- | -------- |
| 5/DBTDL | 5% | 34 | 194 | 647 | 51 (133) |
| 6/DBTDL | 10% | 42 | 174 | 925 | 74 (306) |
| 7/DBTDL | 20% | 47 | 92 | 677 | 259 (574) |
| 8/DBTDL | 40% | 55 | ---- | ---- | -------- |

[a] Durometer (Type A), Elongation (%), Tensile and Stress (psi).

[b] Poor correlation between loading and tensile strength exists with these samples because of the flaw-dependent nature of this measurement.

[c] Due to poor mechanical properties of the higher loaded samples, mechanical measurements were not obtained.

**Table 2.** $^{29}$Si NMR of Q distribution and extent of reaction for 20% loaded TEOS/DBTDL and TEOS/TO

| Sample/Cat. | $Q^2$ | $Q^3$ | $Q^4$ | %Q | Extent of Reaction |
|---|---|---|---|---|---|
| 3/TO | 12.1 | 44.1 | 43.8 | 22.0 | 0.83 |
| 7/DBTDL | 11.3 | 45.3 | 43.1 | 20.8 | 0.83 |

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