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STRUCTURE-PROPERTY RELATIONSHIPS IN SILICA-SILOXANE  
NANOCOMPOSITE MATERIALS

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## Abstract

The simultaneous formation of a filler phase and a polymer matrix via *in situ* sol-gel techniques provides silica-siloxane nanocomposite materials of high strength. This study concentrates on investigating the effects of temperature and relative humidity ( $R_H$ ) on a trimodal polymer system in an attempt to accelerate the reaction process as well as evaluate subtle process-structure-property relationships. It was found that successful process acceleration is only viable for high humidity systems when using the tin(IV) catalyst dibutyltin dilaurate (DBTDL). Processes involving low humidity were found to be very temperature and time dependent.

Bimodal systems were investigated and demonstrated that the presence of a short-chain component led to enhanced material strength. This part of the study also revealed a link between the particle size and population density and the optimization of material properties.

## Introduction

In general, the key motivation for our research program is to completely understand process-structure-property relationships in *in situ* generated composite materials, since it is only through this understanding that commercial applications can be realized. We and others have previously demonstrated the usefulness of *in situ* sol-gel techniques for producing nanocomposite materials with unique and superior properties.<sup>1-5</sup> This paper explores our research efforts with one polymer system to accelerate the reaction process, through changes in temperature and relative humidity ( $R_H$ ), into a regime which would be industrially viable. In addition, the nature of the polymer matrix has been investigated.

Previous work with unfilled silicone elastomers has shown that bimodal polymer distributions lead to greatly enhanced material strength.<sup>6</sup> However, this concept of short-chain toughening has not been completely investigated for *in situ* reinforced silica-siloxane systems. To this end, we have examined a number of bimodal polymer systems at two different reinforcement levels at a set temperature and  $R_H$ .

## Experimental Details

## Materials and Instrumentation

Hydroxyl terminated polydimethylsiloxane (PDMS) with number average molecular weights (MW) ( $\times 10^3$ ) of 2.78, 19.8, 37.9, and 58.8 were obtained from Dow Corning Corporation and of 41.0, 52.0 and 60.0 were obtained from Gelest. Polydiethoxysilane (partially hydrolyzed tetraethoxysilane, TEOS-PH, MW=611 g/mol) was obtained from United Chemical Technologies (UCT). Dibutyltin dilaurate (DBTDL) from UCT was obtained as a 25% solution in cyclic dimethylsiloxanes. All materials were used as received without further purification. Relative humidity ( $R_H$ ) and temperature were maintained by a VWR Scientific model 9000 humidity cabinet. Room temperature  $R_H$  was also maintained in chambers containing saturated  $\text{CaCl}_2/\text{H}_2\text{O}$  baths.

Ultimate tensile strength and elongation were obtained using an Instron Model 1122 Tester. Die-cut samples 0.21 inch wide by 1 inch long were pulled to rupture at a speed of 20 inches/minute using the procedure defined by ASTM Standard D412-87. Values reported are the average of five tensile samples.

Hardness values were obtained on a Type A Durometer according to ASTM Standard D2290. Sample pieces were stacked to a thickness of about 1 cm and hardness measurements were done at three different positions on each side of the sample. The reported values are the averages of the six numbers.

SEM data were obtained on Au/Pd coated samples using a JEOL 6400 scanning electron microscope.

## General Procedure

To prepare the cured and filled elastomer samples, TEOS-PH was mixed ca. 1 minute with the appropriate mixture of silanol end-capped PDMS (trimodal formulation of weighted average MW=39.6 for temperature/ $R_H$  study and bimodal systems for all other work). The amount of TEOS-PH used allowed for the samples to be cross-linked and filled with silica to either a 10 wt% or 20 wt% loading level. After this initial mixing, the DBTDL catalyst was added at 0.2 wt% relative to the amount of PDMS and TEOS-PH and the mixture was stirred until homogeneous, ca. 1 minute. After the final mixing, the uncured material

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was cast to 2-3 mm thicknesses in glass petri dishes which were previously treated with a mold release agent. The samples were degassed for 3 minutes, placed into a humidity cabinet and cured. Trimodal samples were cured at 25% or 65%  $R_H$  at 27°C, 40°C, 50°C or 60°C for 2-7 days and bimodal samples were cured at room temperature and 65%  $R_H$  for 7 days.

## Results and Discussion

### *Effect of Temperature and Relative Humidity*

In order to determine whether the *in situ* process could be accelerated, we examined 20% silica loaded samples under four distinct temperature (T)/relative humidity ( $R_H$ ) environments, namely, low T/low  $R_H$ , high T/low  $R_H$ , low T/high  $R_H$  and high T/high  $R_H$ . To monitor the effectiveness of the acceleration the samples were tested after 2 to 7 days of cure time.

Examining the low  $R_H$  system, we discovered that curing at low temperature leads to samples with properties which are very time dependent (Table 1), showing increasingly favorable properties with increasing time. This dependence is seen predominantly in the tensile strength and durometer values. While raising the temperature (at low humidity) lessens the time dependence for achieving maximum properties (Table 2), it is clear that in low  $R_H$  environments a DBTDL-catalyzed system of this type can not be accelerated.

In contrast to the low  $R_H$  system, the high  $R_H$  system is only somewhat time dependent at low temperature, needing 5 days to reach ultimate properties vs 7 days at low  $R_H$  (Table 3). Of greatest interest is the high temperature analog, which is time independent after 2 days (Table 4). While this is only a moderate process acceleration, it does show promise for more active catalyst systems, such as tin(II) based catalysts.

The differences in the low and high humidity systems is also seen in the micron-level phase separation shown by SEM. For both temperatures at low  $R_H$ , there is a particle size increase from 2 to 5 days. In contrast, the high  $R_H$  system shows no apparent change in the particle size after 2 days.

In order to further study the effects of temperature and humidity on these silica-siloxane systems, we have also looked in more detail at the effect of temperature at a constant humidity and cure time (7 days). For low humidity, there is a definite increase in tensile strength and durometer with increasing temperature (Figure 1). The property increase is accompanied by a decrease in the average particle size (from 7.1  $\mu\text{m}$  to 5.8  $\mu\text{m}$ ) with no

trend in the particle population. As will be discussed later, this increase in strength is thought to be a manifestation of generating a more optimal particle size for reinforcement (see discussion on bimodal systems). The high humidity system, in contrast, has properties which are insensitive to changes in temperature. Accordingly, the SEM data indicates that there are no trends with regards to particle size or population with increasing temperature.

### *Effect of Molecular Weight in Bimodal Systems*

To investigate whether or not short-chain toughening was effective for *in situ* reinforced silica-siloxane materials, a number of bimodal systems were synthesized, both at 10% and 20% silica loading. Both the short-chain/long-chain ratio and the molecular weights of the systems were varied. The molecular weight of the short-chain was either 2.78 or 19.8 ( $\times 10^3$ ) g/mol. Materials involving lower molecular weight short-chain moieties were attempted, but were too brittle and property data could not be reliably obtained. The molecular weight of the long-chain ranged from 37.9 to 60.0 ( $\times 10^3$ ) g/mol.

Looking at the durometer data (Figure 2), we can see that the hardness of the sample is predominately driven by the identity of the low molecular weight fraction. The durometer increases with decreasing short-chain molecular weight and is not significantly different for the two loading levels investigated. The amount (wt%) of the high molecular weight component does not dramatically change the durometer value until very high weight fractions are reached.

Elongation and tensile strength are also dominated by the molecular weight of the short-chain component (Figures 3 and 4), leading to similar properties for a given system regardless of the long-chain component. Close examination reveals the benefits of short-chain toughening with the lower molecular weight (2.78) series. Unlike the durometer values which do not overlap, the 2.78-based system can achieve elongation values comparable to the 19.8-based system, while optimizing tensile strength. This ability to improve both elongation and tensile strength is the key factor to be noted regarding the benefits of a bimodal system.

In order to understand the structural changes which are associated with this property optimization, bimodal samples were examined by SEM. Generally, as the loading increases, the particle size increases and the relative population (number of particles per area) decreases. However, closer inspection indicates that the loading level alone does not define the particle size. Monomodal samples (0 and 100% high MW samples) show increasing particle size with increasing molecular weight. This link between the elasticity of the network and the particle size has been demonstrated previously for angstrom-level phase

separation by Small Angle Neutron Scattering (SANS) techniques.<sup>7</sup> Clearly, multiple factors are leading to the ultimate phase separation characteristics.

While all of the factors which control the particle size in a bimodal system are not understood, it is apparent that there is a relationship between the particle size and population and the ultimate tensile strength (Table 5 and Figures 5 and 6). Samples with the lowest strength typically had particles in the 6-11  $\mu\text{m}$  range, showing that these particles may be too large to provide optimal reinforcement, and instead act as defect sites. Samples with higher strength either had particles around 1  $\mu\text{m}$  or in the 4-5  $\mu\text{m}$  range. However, closer examination reveals that in the case of 1  $\mu\text{m}$  particles, a higher population density must be achieved to allow for maximum properties.

### Conclusion

In this study of *in situ* reinforced silica-siloxane materials, it has been shown that low humidity reaction conditions are not suitable for minimizing temperature and time effects. Using DBTDL as the catalyst system restricts the processing conditions to high humidities if reaction acceleration is desired.

The bimodal system studies demonstrate that the concept of short-chain toughening is effective for *in situ* sol-gel techniques. In addition, this work reveals that there is a link between the particle size and population and the optimization of tensile strength. Particles above a threshold value lead to decreased strength and if particles are below the optimal size, then a sufficient population density must be achieved to obtain maximum properties.

### Acknowledgments

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### References

1. Due to the high activity in this area in recent years, a few key reviews follow and all dominant researchers are not represented individually.
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**Table 1.** Mechanical properties for low temperature (27°C) and low RH (25%) versus cure time.

Cure Time (days)	Tensile Strength (psi)	Elongation (%)	Durometer (Shore A)
2	103 $\pm$ 28	220 $\pm$ 35	13 $\pm$ 3
5	529 $\pm$ 65	318 $\pm$ 42	44 $\pm$ 3
7	682 $\pm$ 53	294 $\pm$ 32	49 $\pm$ 3
7	666 $\pm$ 31	279 $\pm$ 18	46 $\pm$ 4

**Table 2.** Mechanical properties for high temperature (60°C) and low RH (25%) versus cure time.

Cure Time (days)	Tensile Strength (psi)	Elongation (%)	Durometer (Shore A)
2	871 $\pm$ 40	278 $\pm$ 17	57 $\pm$ 1
2	873 $\pm$ 37	235 $\pm$ 34	60 $\pm$ 1
2	904 $\pm$ 40	277 $\pm$ 12	53 $\pm$ 0
4	965 $\pm$ 45	225 $\pm$ 18	66 $\pm$ 2
5	1023 $\pm$ 25	235 $\pm$ 28	71 $\pm$ 2
5	995 $\pm$ 59	265 $\pm$ 49	71 $\pm$ 1
7	1083 $\pm$ 40	236 $\pm$ 29	70 $\pm$ 1
7	1036 $\pm$ 96	255 $\pm$ 57	64 $\pm$ 1

**Table 3.** Mechanical properties for low temperature (27°C) and high RH (65%) versus cure time.

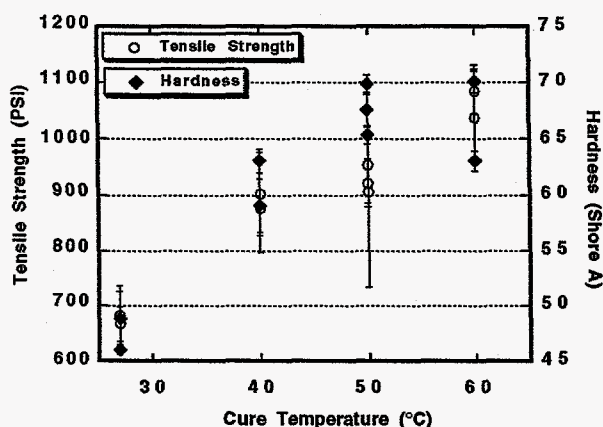
Cure Time (days)	Tensile Strength (psi)	Elongation (%)	Durometer (Shore A)
2	627 $\pm$ 40	360 $\pm$ 29	35 $\pm$ 1
5	899 $\pm$ 88	351 $\pm$ 37	63 $\pm$ 2
7	920 $\pm$ 24	304 $\pm$ 15	62 $\pm$ 1
7	874 $\pm$ 13	308 $\pm$ 12	65 $\pm$ 4

**Table 4.** Mechanical properties for high temperature (60°C) and high R<sub>H</sub> (65%) versus cure time.

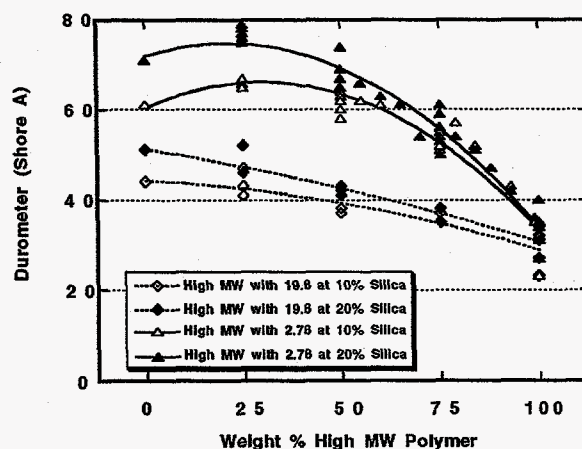
Cure Time (days)	Tensile Strength (psi)	Elongation (%)	Durometer (Shore A)
2	753 ± 56	263 ± 40	64 ± 1
2	887 ± 27	281 ± 35	56 ± 4
4	836 ± 40	269 ± 21	64 ± 1
4	857 ± 46	255 ± 22	67 ± 1
6	897 ± 42	288 ± 38	73 ± 2
7	810 ± 55	244 ± 58	67 ± 2

**Table 5.** Mechanical properties and SEM analysis for 60.0/2.78 MW bimodal system.

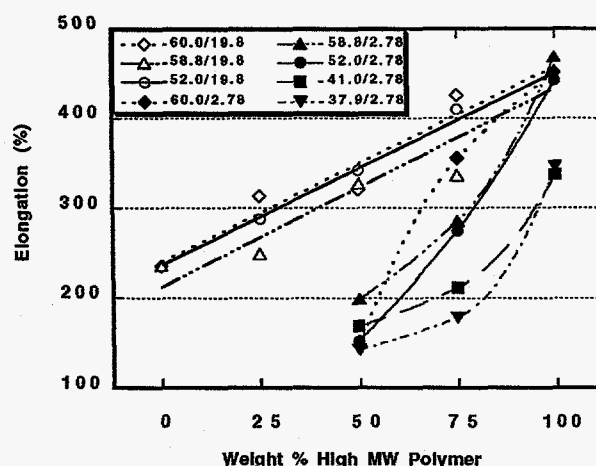
SiO <sub>2</sub> Level & MW Ratio	Relative Population & Ave. Particle Size	Ave. Elongation (%)	Ave. Tensile Strength (psi)
10% 1:1	5.5 4.5 μm	152	805
20% 1:1	1.0 11 μm	78	465
10% 3:1	12 1.0 μm	275	747
20% 3:1	5 5.0 μm	307	764



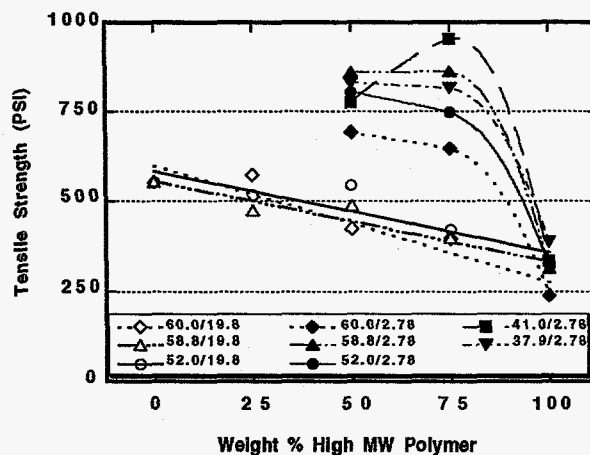
**Figure 1.** Tensile strength and hardness vs cure temperature for low R<sub>H</sub> cured system at 20% SiO<sub>2</sub> loading level.



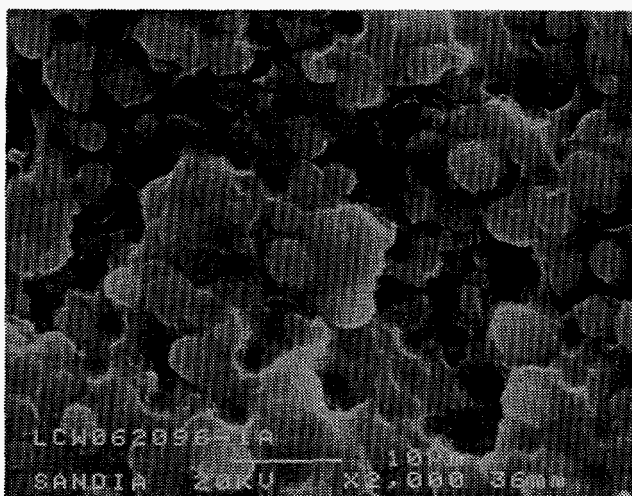
**Figure 2.** Hardness vs weight percent of high molecular weight polymer (MW x10<sup>3</sup>) for 10% and 20% SiO<sub>2</sub> loadings.



**Figure 3.** Percent elongation vs weight percent of high molecular weight polymer (MW x10<sup>3</sup>) for 10% loaded SiO<sub>2</sub> system.



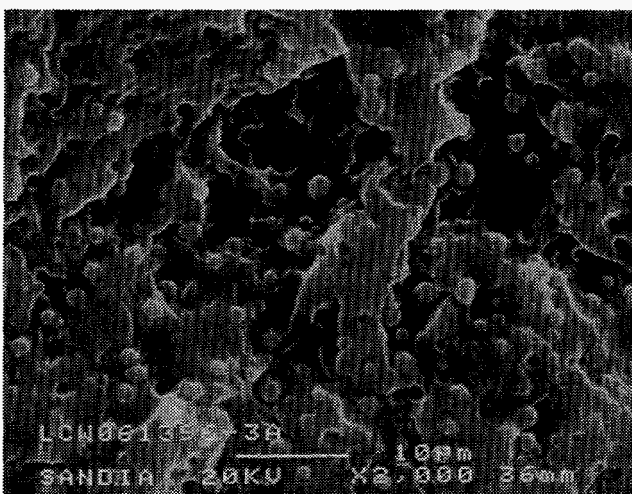
**Figure 4.** Tensile strength vs weight percent of high molecular weight polymer (MW x10<sup>3</sup>) for 10% loaded SiO<sub>2</sub> system.



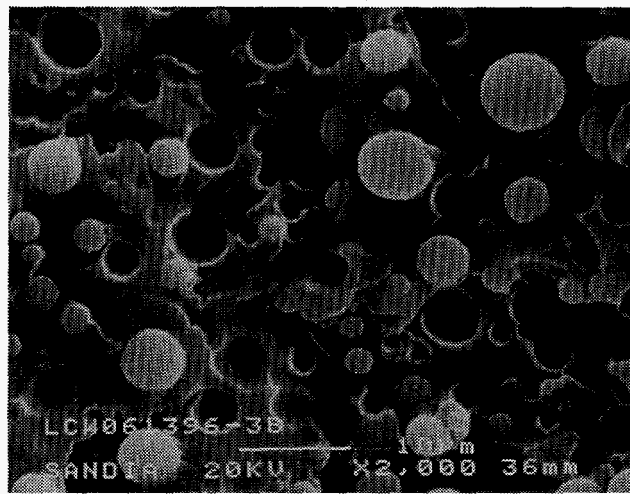
a.



a.



b.



b.

**Figure 5.** Scanning electron micrographs of 10% SiO<sub>2</sub> loaded bimodal samples. a) with 1:1 ratio of 52.0 MW to 2.78 MW polymer with average particle size of 5 $\mu$ m b) with 1:3 ratio of 52.0 MW to 2.78 MW polymer with average particle size of 1 $\mu$ m.

**Figure 6.** Scanning electron micrographs of 20% SiO<sub>2</sub> loaded bimodal samples. a) with 1:1 ratio of 52.0 MW to 2.78 MW polymer with average particle size of 11 $\mu$ m b) with 1:3 ratio of 52.0 MW to 2.78 MW polymer with average particle size of 5 $\mu$ m.

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