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13. ABSTRACT (Maximum 200 words)
A task was undertaken to increase the powder fraction of the AS800 Si_3N_4 slurry in case a higher volume fraction slurry was needed to fill the shells produced by SRI with their solid freeform method with a special Si_3N_4 formulation that might require a different particle packing density relative to that used to form the shell, and thus avoid problems that might be encountered due to differential shrinkage either during densification. In addition, the slurries produced with the increased volume fraction reported here were also used to mold bar specimens via a colloidal iso-press forming method developed at UCSB. Prior to the demonstration that SRI could fill the shell with a slurry of the same volume fraction as used to form the shell, it was thought that the colloidal iso-press forming method would be useful for consolidation both the shell and the filled composition during in a single operation. This research was carried out by, Reto Joray, a Masters Degree student from the Technical University of Zürich for his diploma work. Mr. Joray spent approximately 6 months at UCSB and returned to Zürich at the end of May, 1999.

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Final Report

Beta Site Testing of the SRI Stereolithography Machine
UCSB Contribution to SRI/DARPA,
Solid Freeform Fabrication and Design

N00014-99-1-0989

I. Increasing the Solid Fraction in AlliedSignal AS800 Slurry

1. Goals

A task was undertaken to increase the powder fraction of the AS800 Si_3N_4 slurry in case a higher volume fraction slurry was needed to fill the shells produced by SRI with their solid freeform method with a special Si_3N_4 formulation that might require a different particle packing density relative to that used to form the shell, and thus avoid problems that might be encountered due to differential shrinkage either during densification. In addition, the slurries produced with the increased volume fraction reported here were also used to mold bar specimens via a colloidal iso-press forming method developed at UCSB. Prior to the demonstration that SRI could fill the shell with a slurry of the same volume fraction as used to form the shell, it was thought that the colloidal iso-press forming method would be useful for consolidation both the shell and the filled composition during in a single operation. This research was carried out by, Reto Joray, a Masters Degree student from the Technical University of Zürich for his diploma work. Mr. Joray spent approximately 6 months at UCSB and returned to Zürich at the end of May, 1999.

2. Slurry Reformulation, Characterization and Consolidation

AS800 Si_3N_4 slurry received from AlliedSignal was characterized and optimized for colloidal iso-press forming, primarily by influencing the pair potentials of silicon nitride particles within the slurry. PEG-silane was used at a concentration of 2 w/o of solids to produce both steric and electrostatic repulsion. In later process, the double layer was compressed to form a weakly attractive network. Initially, tetraethylammonium chloride (TMACl) was used. In an effort to eliminate possible chloride impurities, tetraethylammonium nitrate ($TMANO_3$) was used in later stages. The lowest concentration of TMACl where consolidated bodies would still liquefy, was 0.5 M.

AS800 was characterized by measuring the average particle size, particle size distribution, and zeta potential of the suspended particles.

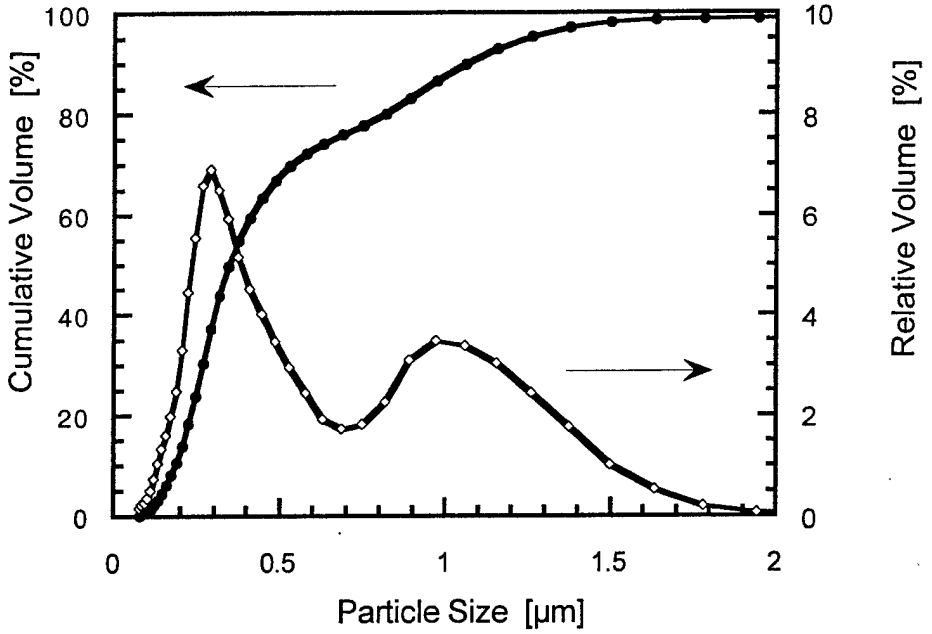

Figure 1. Particle size distribution of AS800 (batch A, reacted with 2 wt% PEG-silane, measurement # 1)

The zeta potential was shown to change with aging and also varied batch to batch. The average isoelectric point was 5.5.

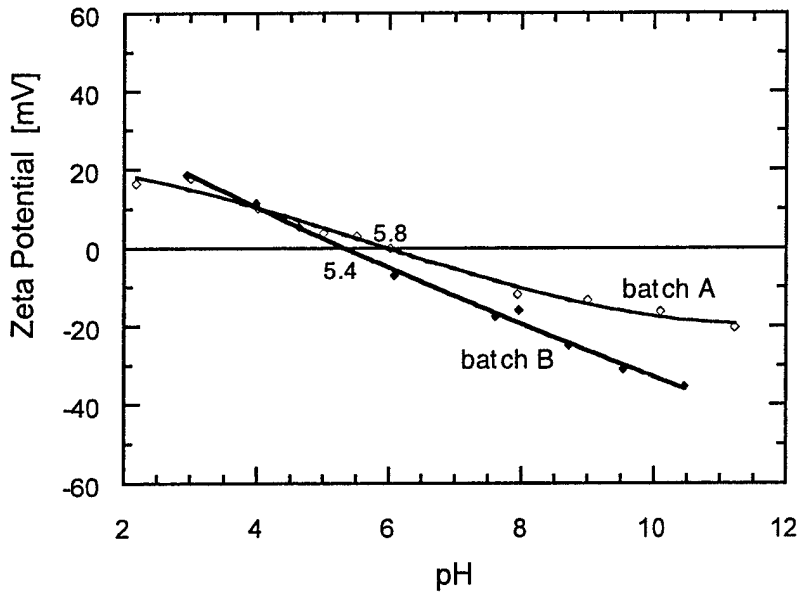

Figure 2. **Variation of the zeta potential of AS800 over time (batch A, 2 wt% PEG-silane)**

The viscosity of these slurries was measured with a cup and couette cell. Viscosity as a function of strain rate was measured for salt concentrations of 0.0 M, 0.1 M, 0.25 M, 0.5 M, 0.75 M, and 1.0 M. These measurements were carried out near the isoelectric point at pH 6 and also under normal processing conditions at pH 10.1. The dispersed slurry had a low viscosity and exhibited nearly Newtonian behavior. The flocculated slurry was very thick and exhibited strong shear thinning behavior. The addition of salt causes an increase in viscosity shear thinning instead of Newtonian behavior. The salt effect saturated at 0.5 M. At this

concentration the viscosity of the dispersed slurry was approximately one-half of an order of magnitude lower than that of the flocculated slurry.

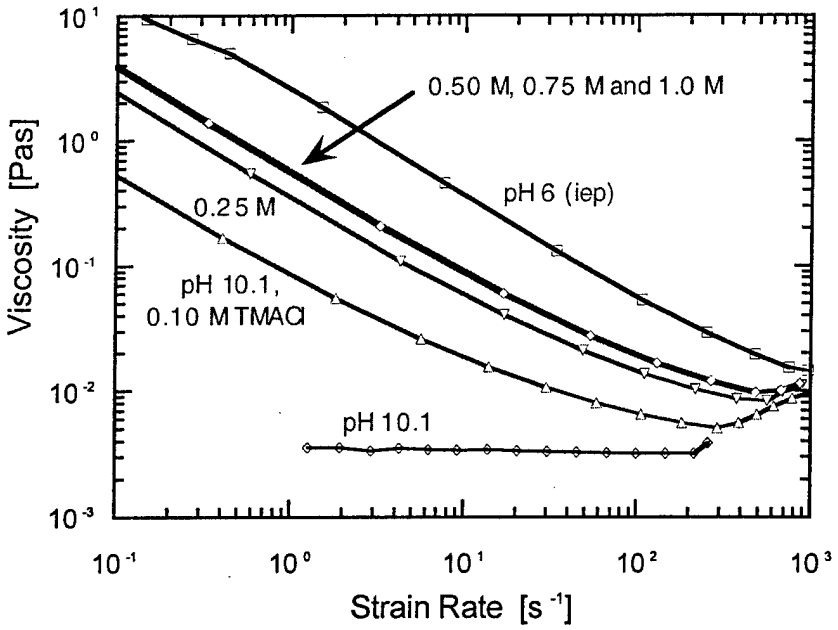

Figure 3. Viscosity of AS800 (batch A, 2 wt% PEG-silane) diluted to 20 vol% in the flocced state (at pH 6) and in the dispersed state (at pH 10.1) at different concentrations of TMACl

These slurries were then consolidated to higher packing densities in a filter press. Applied pressures ranged from 0.5 MPa to 50 MPa in order to characterize the ductile to brittle transition.

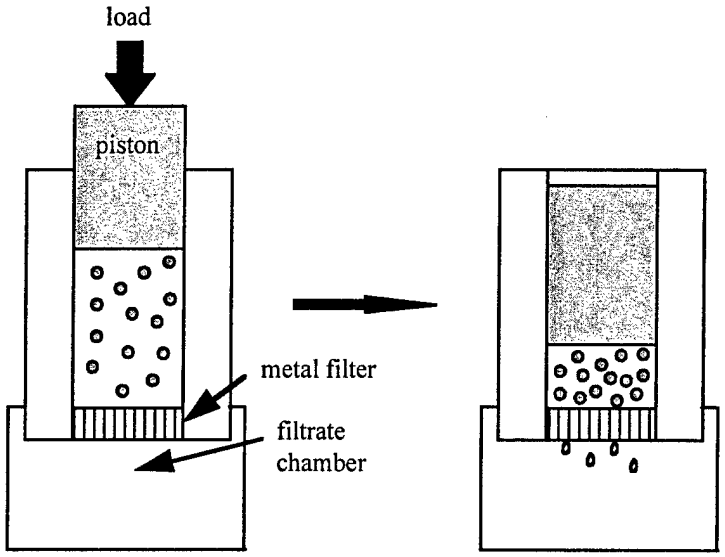

Figure 4. Pressure filtration mechanism

After consolidation at 2 MPa, selected slurries were fluidized and characterized by dynamic rheology. Fluidized slurries showed dilatant behavior. Dynamic stress sweep tests at constant frequency of 1.0 rad/s were performed to determine the shear modulus and yield stress.

batch	A	A	A	B
PEG-silane [wt%]	2	2	1	2
salt	TMACl	$TMANO_3$	$TMANO_3$	$TMANO_3$
salt concentration [M]	0.5	0.5	0.5	0.5
pH	10.1	10.1	10.1	8.7
consolidation pressure [MPa]	2	2	2	2
shear modulus [MPa]	1.3	0.9	13	4.5
yield stress [Pa]	294	406	213	684

Table 1. Shear moduli and yield stresses of consolidated slurries for different compositions

Saturated consolidated bodies were subjected to uniaxial compression to determine the peak stress for flow in plastic specimens and failure in brittle specimens. Even with displacement rates as low as 0.2 mm/min, flow was not observed in any specimens. Some specimens were not truly brittle, however. Bodies consolidated above 5 MPa showed brittle behavior. Pieces consolidated below 5 MPa could be liquefied after mechanical testing. This is evidence of a ductile to brittle transition in this regime. It has been theorized that plastic flow would be observed with slower displacement rates.

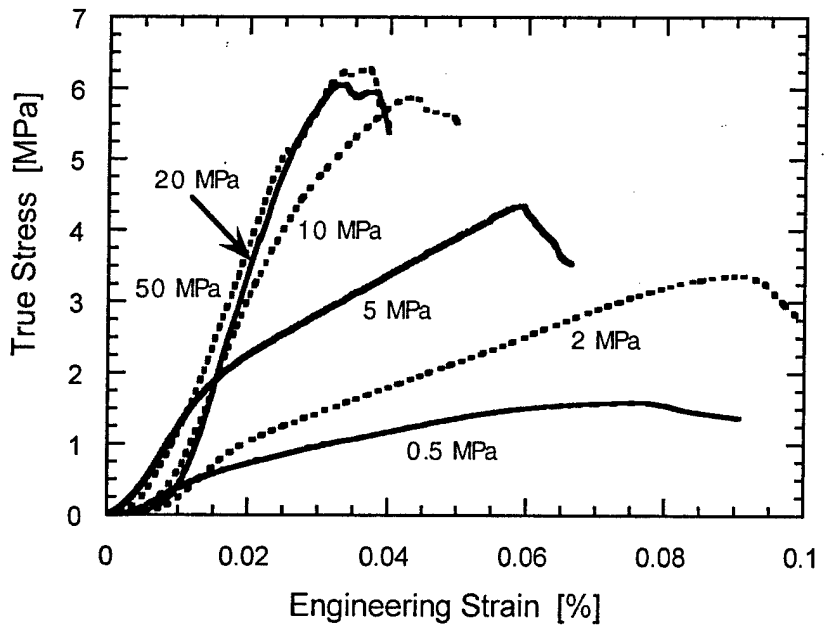

Figure 5. True stress versus engineering strain curves for different consolidation pressures (AS800, batch B, 2 wt% PEG-silane, 0.5 M $TMANO_3$, loading rate: 1 mm/min)

Consolidated slurries were also liquefied for iso-pressing. These slurries were injected into silicone molds. Porous alumina plates were used for removal of water during pressing.

The relative densities of filter-pressed and iso-pressed specimens were determined. The specimens from dispersed slurries(no salt) produced the highest packing densities and also exhibited brittle behavior. 2 w/o PEG-silane produced optimum dispersion.

batch	PEG-silane [wt%]	salt	salt conc. [M]	pH	rel. density filter-pressed [%]	state	rel. density isopressed [%]
A	2	-	-	10.1	57.9	brittle	
A	-	TMACl	0.75	10.1	47.8	not extrudable	
A	1	$TMANO_3$	0.5	10.1	48.4	not extrudable	
A	2	TMACl	0.5	10.1	50.6	extrudable	57.8
A	2	$TMANO_3$	0.5	10.1	51.8	extrudable	60.1
B	2	$TMANO_3$	0.5	8.7	51.3	extrudable	61.7

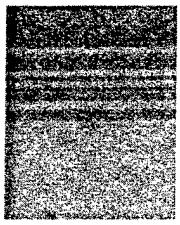

Table 2. Relative densities after pressure filtration at 2 MPa and isopressing at 200 MPa for one minute

consolidation pressure [MPa]	0.5	2	5	10	20	50
relative density [%]	51.7	52.6	53.4	54.8	55.4	55.3
behavior	plastic	plastic	plastic	brittle	brittle	brittle

Table 3. Relative densities measured after mechanical testing (AS800, batch B, 2 wt% PEG-silane, 0.5 M $TMANO_3$)

Three bars were isopressed, dried, and sent to Allied Signal for densification.

sample	batch	salt	conc. [M]	isopressure [Pa]	time [min]
AS1	A	TMACl	0.5	300	5
AS2	A	TMACl	0.5	200	2
AS3	A	$TMANO_3$	0.5	200	2

Table 4. Sintered specimens, containing 2 wt% PEG-silane, consolidation pressure: 2 MPa

II. Developing a Aqueous Slurry for the SRI Direct Photo Shaping Method

1. Goal

The current slurry used by SRI is based on organics that require organic solvents. It is the goal of this task to investigate the possibility of using an aqueous slurry system. The approach is to use an amino-silane surfactant that has been shown (see Part I, above) to produce strongly repulsive interparticle potentials needed to produce a well dispersed slurry. SRI will develop a new amino-silane molecule with a graphed photosensitive ligand. This new molecule is expected to both produce the desired interparticle pair potential needed to formulate a slurry containing a high volume fraction of AlliedSignal powder, but also to play another role, i.e., to incorporate the photosensitive initiator into an aqueous slurry system. Our initial work in this area was to duplicate the slurry preparation now being carried out at SRI, and to characterize the UCSB formulated slurry. This work was carried out by Ms. Lisa Palmqvist, who had particle support by the Swedish government. She returned to Sweden at the end of June, 1999. Mr. Ryan Bock, a Graduate student in the Materials Department has taken over this task.

2. Initial Experiments

The preparation of the SRI Direct Photo Shaping Si_3N_4 slurry was successfully duplicated in-house at UCSB. This was done with a combination of mechanical mixing and ball milling. Initially, the pre-slurries are mixed with a mechanical stirrer. The mixture was put into a bottle and rolled with silicon nitride milling media. The viscosity of these new slurries compares very favorably with SRI data.

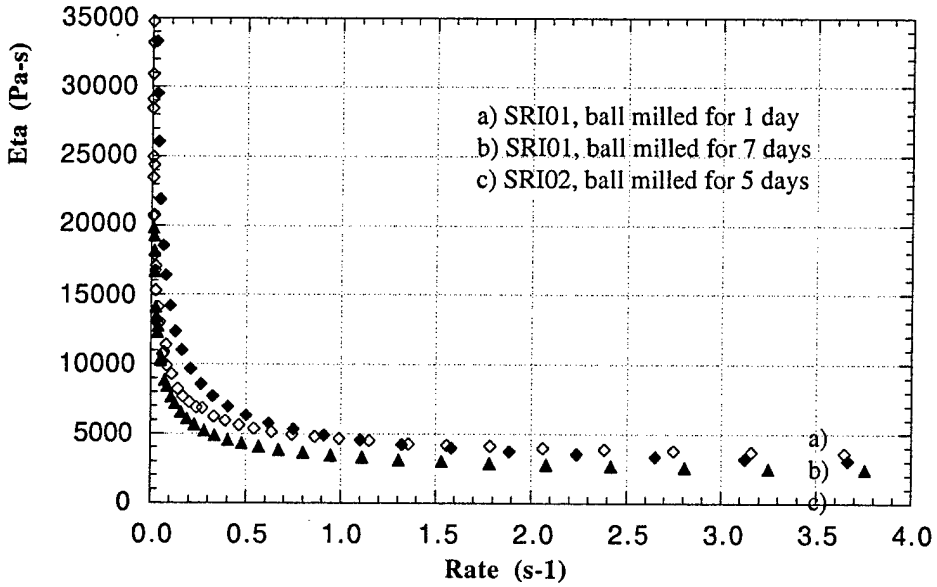

Figure 6. Viscosity of UCSB slurry.

These slurries were aged for up to seven days. As can be seen in Fig. 6, the slurries were stable over the time range of these measurements.

Dynamic rheology tests were performed on original composition slurries. The yield stress was determined to be 0.42Pa as shown in Fig. 7.

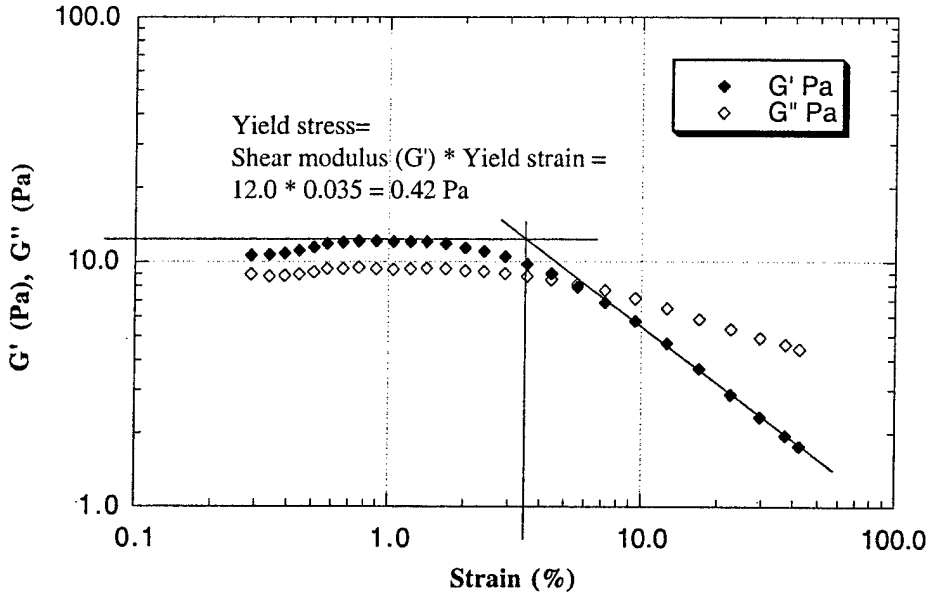

Figure 7. G' and G" vs. strain at a frequency of 1 rad/s for the original slurry composition.

Original composition viscosities were measured after a period of near rest (0.01 s^{-1} shear rate) after one minute at high shear rate (100 s^{-1}). This rest period varied from 0 to 20 minutes. Initial viscosity increased proportional to rest time. However, as shown in Fig. 8, after further shearing all viscosities approached a uniform value.

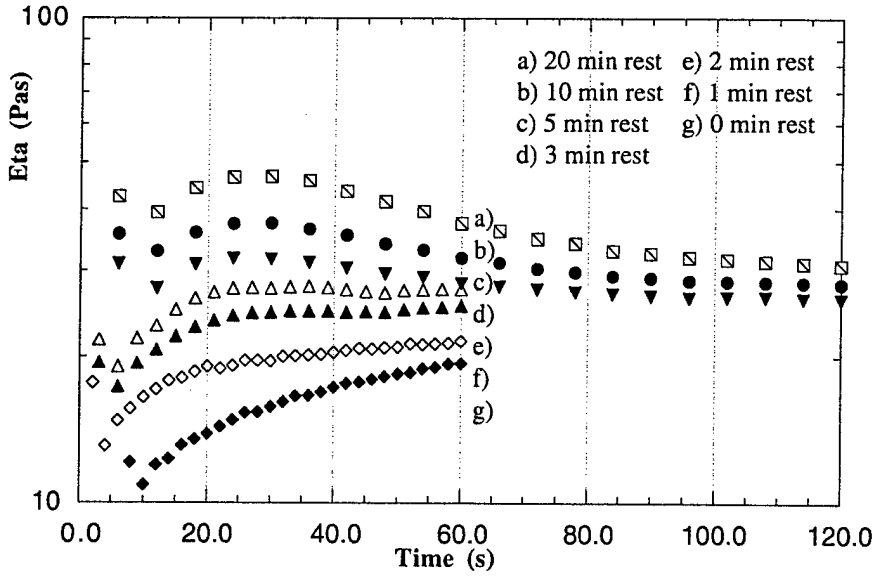

Figure 8. Near rest viscosity (shear rate 0.01 s^{-1}) for original composition after one minute at a shear rate of 100 s^{-1} followed by a period of rest.

3. Slurry Formulation

Following the successful duplication of existing SRI slurries, research was focused on the first photoactive silane developed at SRI and the integration of monomers for the polymerization into the system to produce a water-based slurry for use with the SRI Direct Photo Shaping Method.

Several dynamic and steady state rheological tests were performed on slurries containing the first modified PEG-silane (MPEG1), which was provided by SRI. This modified PEG-silane contains a photoactive ligand. It is hoped that MPEG1 can be used as both a dispersant and a photointiator for aqueous Direct Photo Shaping slurries. For reference purposes, these same tests were also performed on slurries containing unmodified PEG-silane. It has been shown that PEG-silane can be used in aqueous systems with Si3N4 to create a pair potential that corresponds to a good dispersion. The slurries containing modified PEG-silane were aged and tested multiple times. These slurries were formulated by adding 1.73 weight percent (from Si3N4 powder) of either unmodified PEG-silane or MPEG1 to Allied Signal AS800. Prepared slurries were placed on rollers for at least one day prior to testing. Slurries containing the MPEG1 were stored in opaque containers to protect their photosensitive additives. Testing was performed on a Rheometrics dynamic stress rheometer. Tests including dynamic stress sweeps, dynamic frequency sweeps, and steady state stress sweeps were performed. The storage and loss moduli, tanδ, and yield points were observed for slurries containing both the modified and unmodified PEG-silanes.

Dynamic frequency sweeps showed that the MPEG1 slurries were stable in the range of 0.1 to 80 rad/s (see Fig 9). Dynamic stress sweeps were carried out in this frequency range. As seen in Fig. 10, a yield point of 0.6 Pa, G' of ~30 Pa, and G" of ~10 Pa was observed. When the same slurry was aged for three weeks and then retested, a yield point of 1.0 Pa, G' of ~60 PA, and G" of ~20 Pa was observed (see Fig. 11). This aging effect may be due to some of the silane molecules gelling to form an incomplete network.

Dynamic stress sweeps of slurries with unmodified PEG-silane showed a yield point of 0.15 Pa, G' of ~2 Pa, and G" of ~3 Pa (see Fig. 12). Aging studies were not carried out on the PEG-silane slurries.

As can bee seen in Fig. 5 and 6, steady state stress sweeps of both types of slurries showed that the modified PEG-silane slurry (Fig. 13) was more viscous than the PEG-silane (Fig. 14) slurry. When these results were compared with previous tests, it was observed that the modified PEG-silane slurries thickened while they were aged. Both slurries exhibited a lower viscosity than that of the reference data provided for existing SRI slurries. Aging consisted of the slurry being placed on rollers for varying amounts of time.

We formulated more AS800 slurry with both the conventional PEG-silane, and the MPEG1. Our initial attempts to use the modified PEG-silane appeared to produce gelation, even when the slurry was stored in a refrigerator and kept in the dark. It was also discovered that the 'gelled' slurry could be fluidized via vibration. Steady state stress sweeps were performed on as received AS800 (as a standard), AS800 + PEG-silane (for comparison), and AS800 + MPEG1. These slurries were approximately 40 v/o solids. In the latter two, 1.73 w/o (of solids) silane was added. The slurry containing the modified PEG-silane exhibited a higher viscosity than that containing the PEG-silane. Both slurries showed a lower viscosity than the reference data provided by SRI for the existing direct photoshaping slurry. The next step was to add the monomers and eventually the entire monomer system to the slurry mixture.

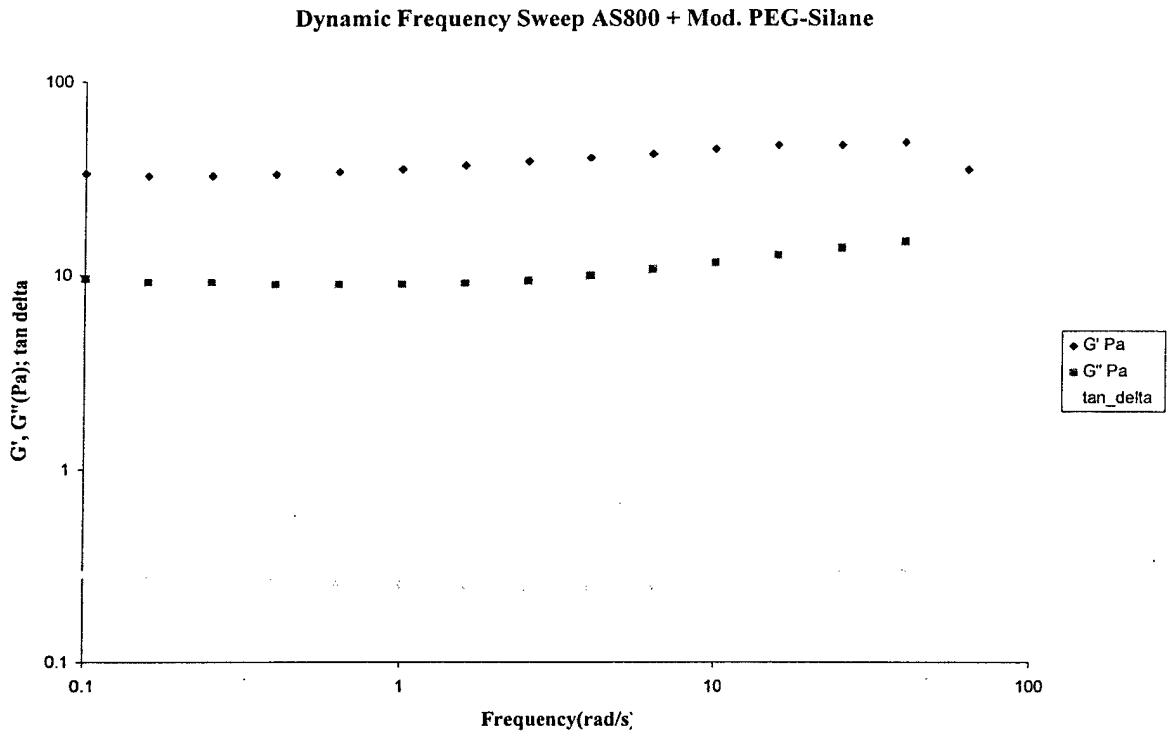

Figure 9. Dynamic frequency sweep with MPEG1 slurry

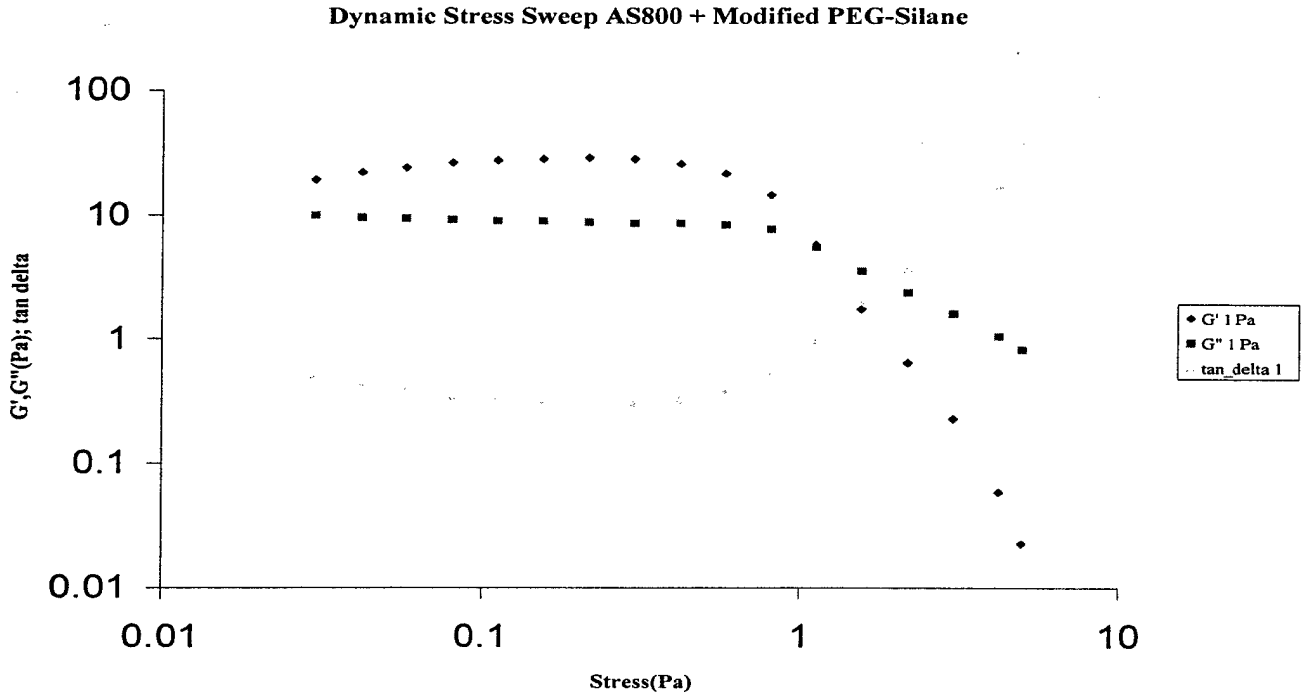

Figure 10. Dynamic stress sweep with MPEG1 slurry

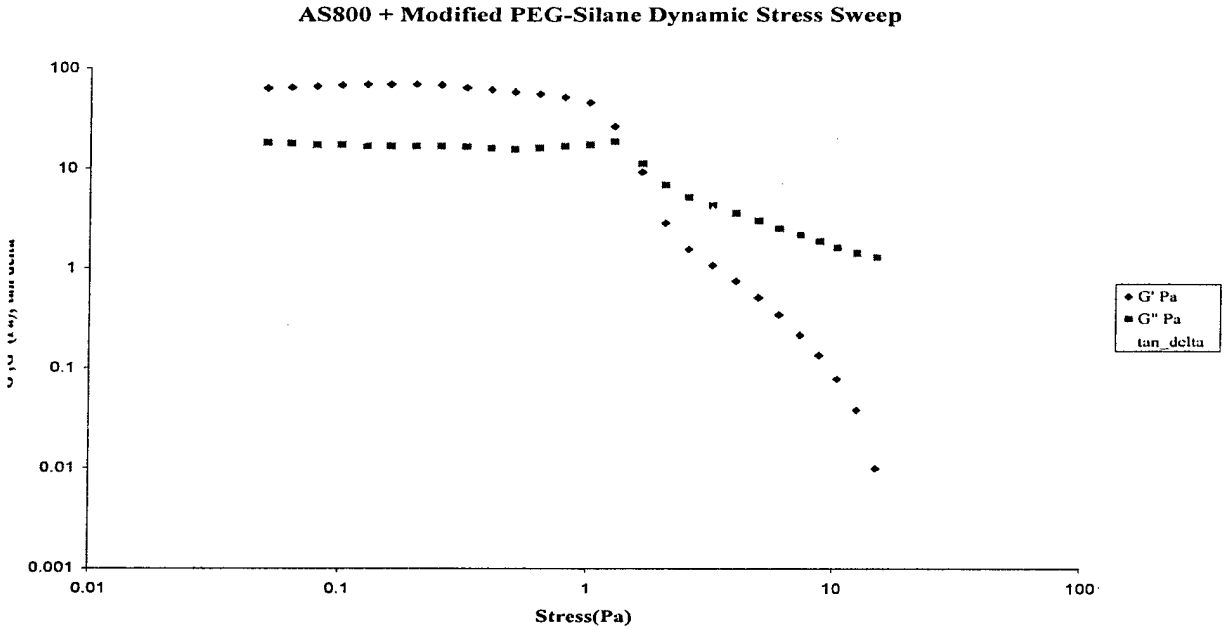

Figure 11. Dynamic stress sweep after aging with MPEG1 slurry

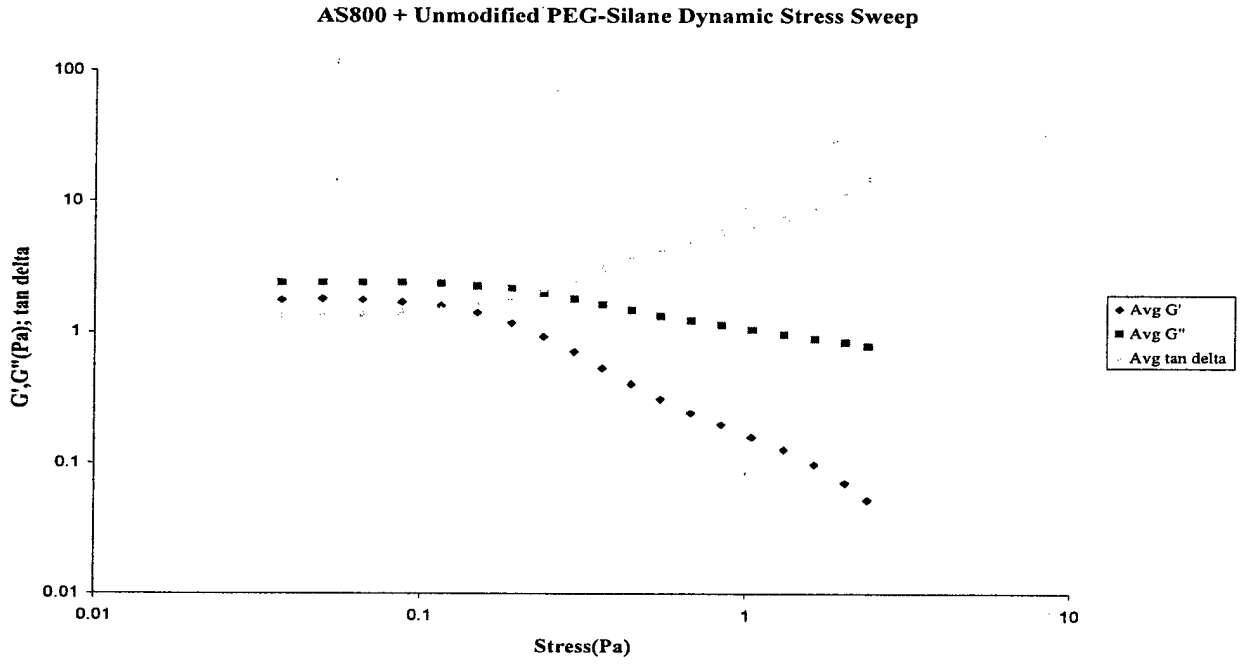

Figure 12. Dynamic stress sweep with unmodified PEG-silane

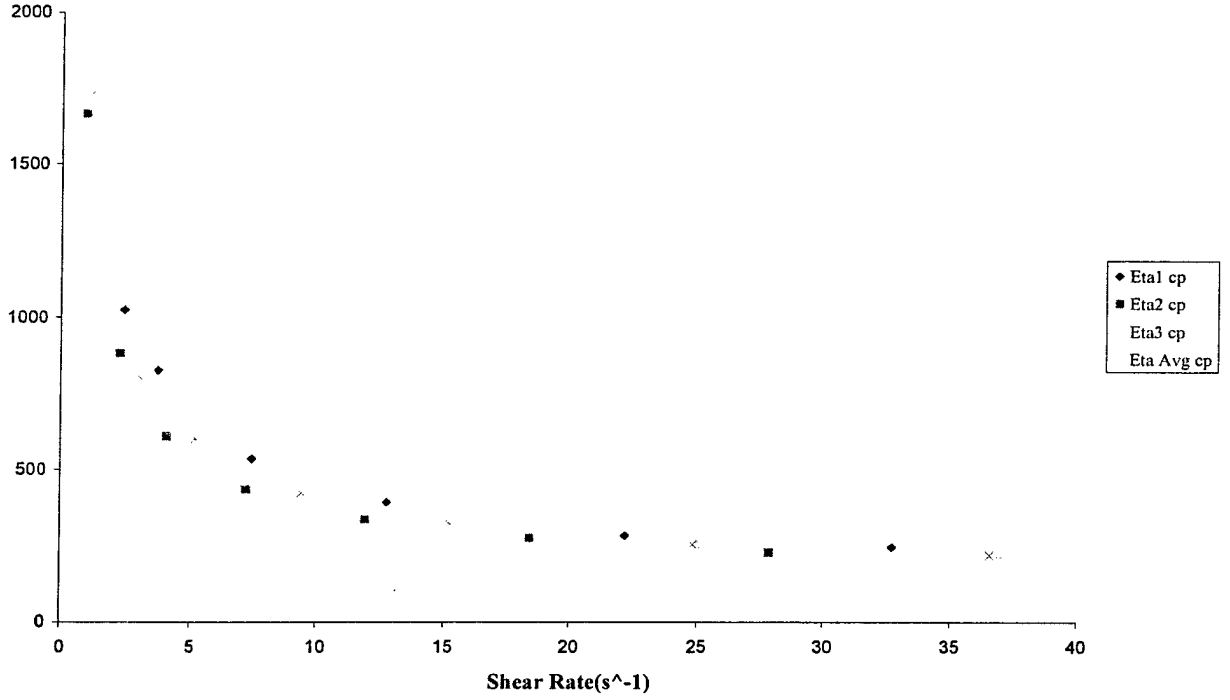

Figure 13. Steady state stress sweep with MPEG1

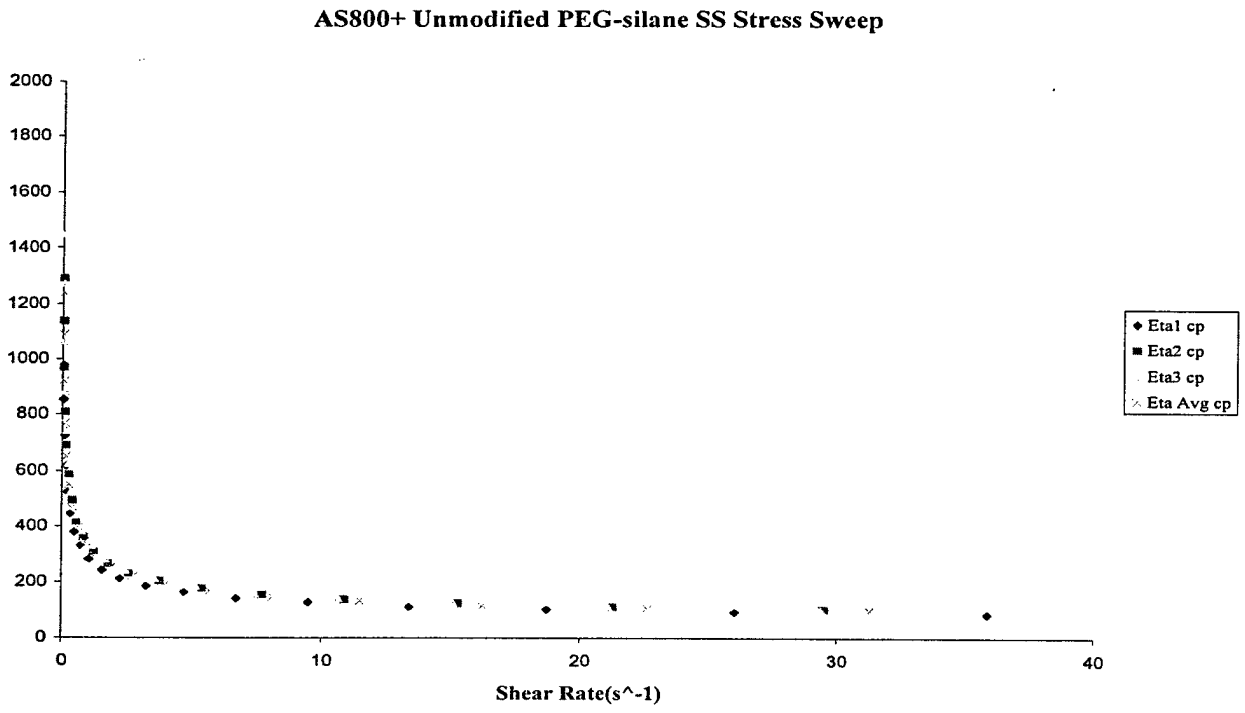

Figure 14. Steady state stress sweep with unmodified PEG-silane

Several slurries were formulated with the monomers from SRI's existing slurry and freeze-dried AS800. The rheological properties of slurries containing MPEG1 were measured under steady state conditions. Slurries

containing unmodified PEG-silane were also measured for purpose of comparison. These slurries were formulated with monomers now used in SRI's non-aqueous slurries and freeze-dried AS800 silicon nitride powder. Some of the earlier slurries contained Ube E-03 Si3N4 powder instead of freeze-dried AS800. The modified PEG-silane and freeze-dried AS800 were both supplied by SRI.

The slurries were formulated by mixing two preslurries and then adding powder while stirring with a mechanical mixer. The first preslurry consisted of deionized water and whichever silane was being used. The second preslurry consisted of pentaerythritol triacrylate(PETA), XB 5180, bisepoxy, and 2-hydroxyethylacrylate(HEA); the four monomers used in SRI's existing direct photo shaping slurry. These monomers were used in their original volume percents relative to each other. The pH of these slurries is kept at or above 10 during this process to insure dispersion.

Initial slurries contained 41.4 v/o silicon nitride powder, 40 v/o water, 18.6 v/o monomers, and 1-2 w/o of solids(Si3N4) modified or unmodified PEG-silane.

The first slurry evaluated during this period, SRI 10, was formulated with unmodified PEG-silane(1.32 w/o), Ube E-03 silicon nitride powder(41.4v/o), water(40 v/o), and HEA(18.6 v/o). This produced a stable slurry with a relatively low viscosity as can be seen in figure 15.

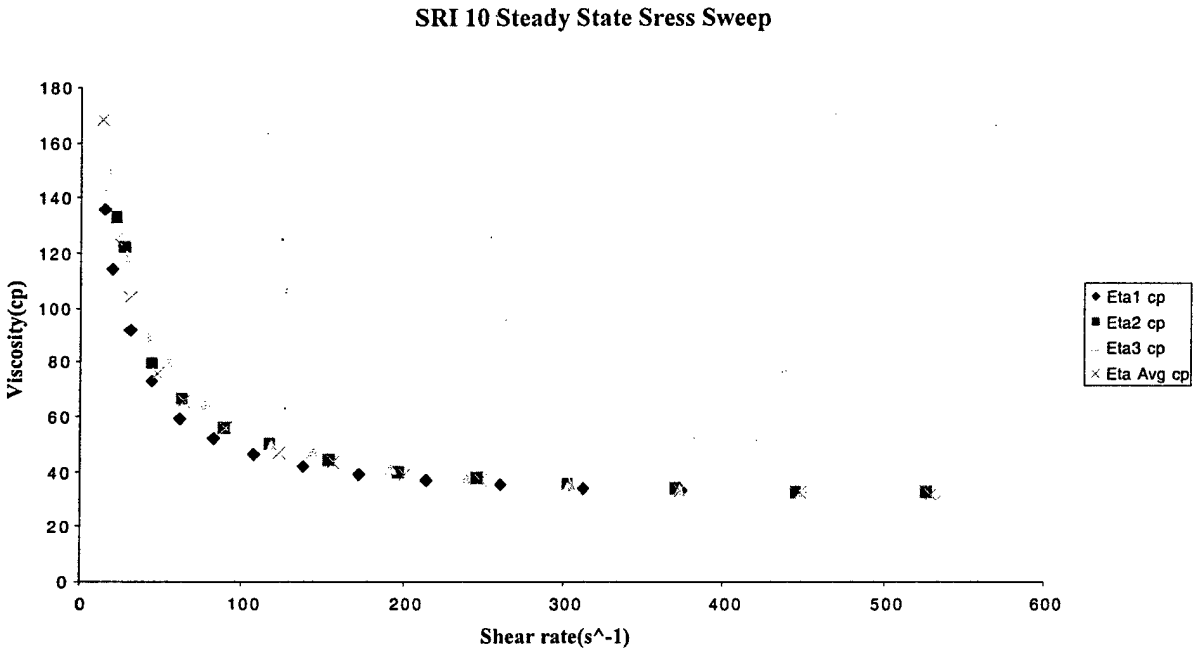

Figure 15. Steady state stress sweep of SRI 10

The next slurry, SRI 11, was of similar formulation. The only difference was that instead of using only HEA, all monomers were added such that their total concentration was 18.6 v/o. More water had to be added to this slurry during formation to keep it fluid. The recalculated concentrations of SRI 11 are as follows: 47.3 v/o water, 36.3 v/o Si3N4, 10.42 v/o HEA, 2.7 v/o XB 5180, 1.78 v/o PETA, and 1.39 v/o bisepoxy. The initial viscosity was high, but this lowered after rolling overnight with Si3N4 media. Fig. 16 shows the low viscosity of SRI 11.

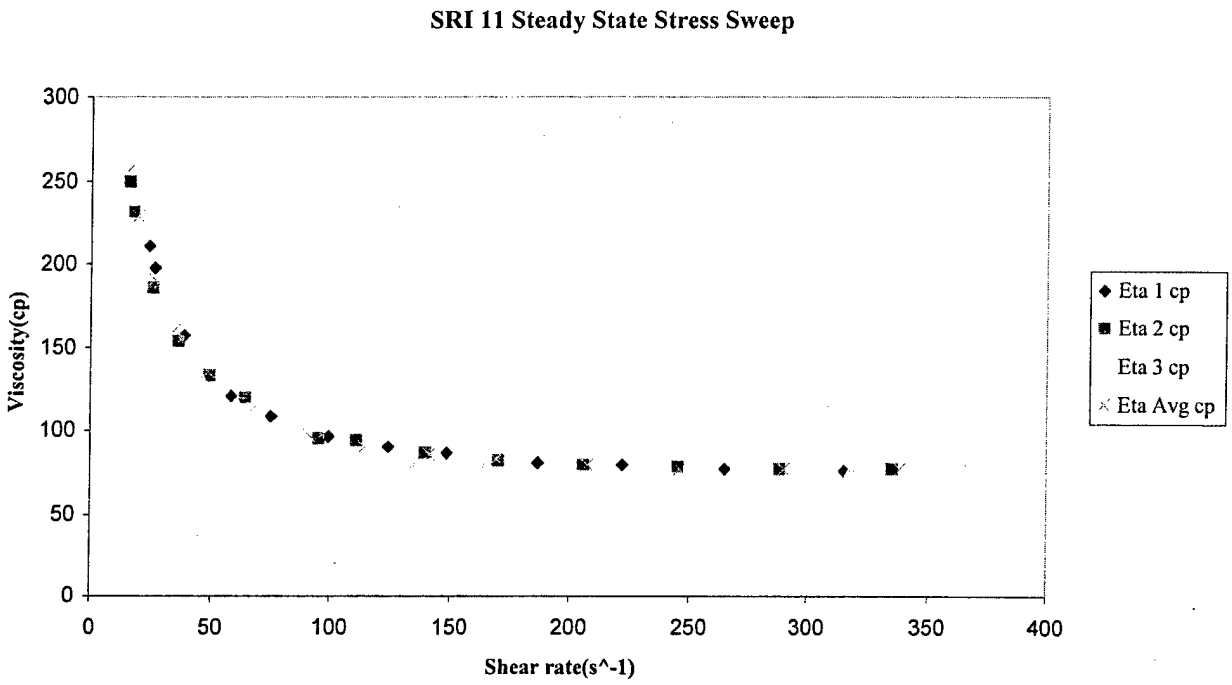

Figure 16. Steady state stress sweep of SRI 11

SRI 12 was batched to SRI 11's original specifications, i.e., 41.4 v/o Si3N4(E-03), 40 v/o water, 18.6 v/o monomers, and 2 w/o of solids modified PEG-silane. By waiting to add some of the powder after rolling with Si3N4 media, a stable dispersion was produced. Figure 17 shows the relatively high viscosity of SRI 12.

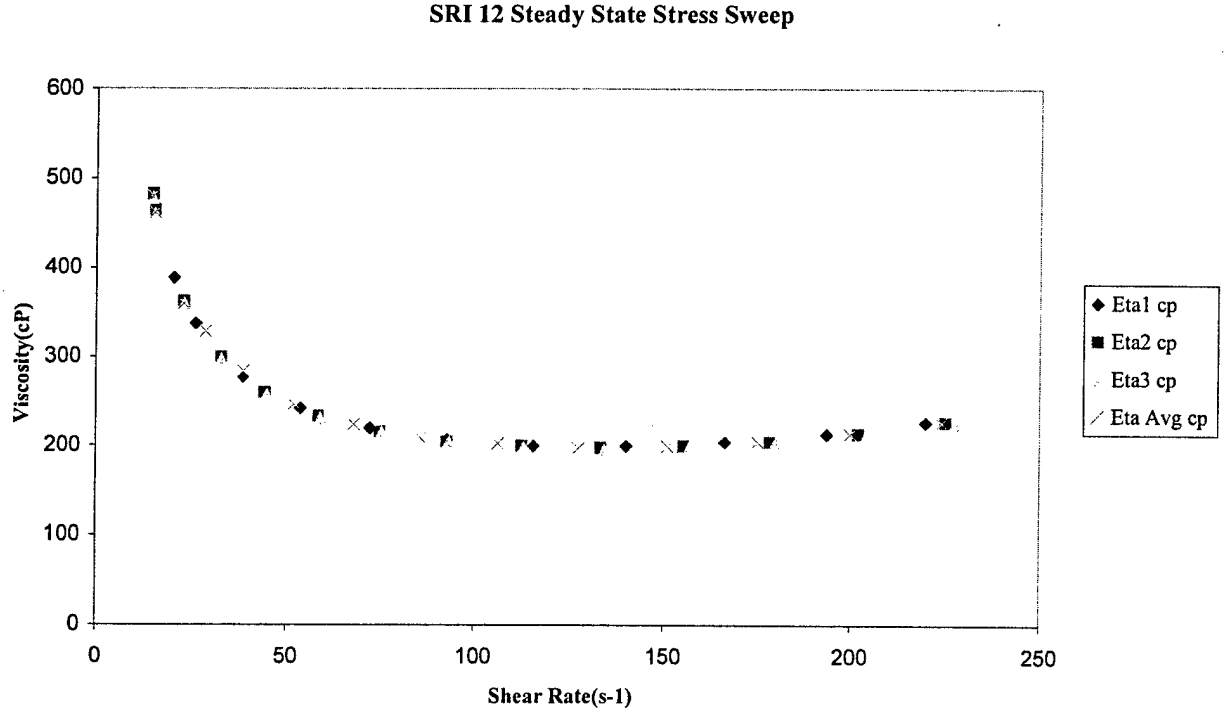

Figure 17. Steady state stress sweep of SRI 12

A slurry containing silicon nitride in water with modified PEG-silane as a dispersant was sent to SRI for freeze-drying.

Next, slurries were formulated with freeze dried AS800 instead of E-03. Agglomeration problems were encountered during the formulation of these new slurries. It is believed that this is due to pH shifting caused by rare earth oxide sintering aids present in AS800. These problems were circumvented by carefully monitoring pH during powder addition. Also, two test slurries without monomers were prepared to see if the freeze-dried AS800 re-dispersed well in water. The first of these contained a mixture of PEG-silanes(1.38 modified and 0.62 unmodified w/o of solids). The second contained 2 w/o of solids unmodified PEG-silane. Both batches produced stable dispersions. The batch with only unmodified PEG-silane exhibited a much lower viscosity, however as seen in figures 18 and 19.

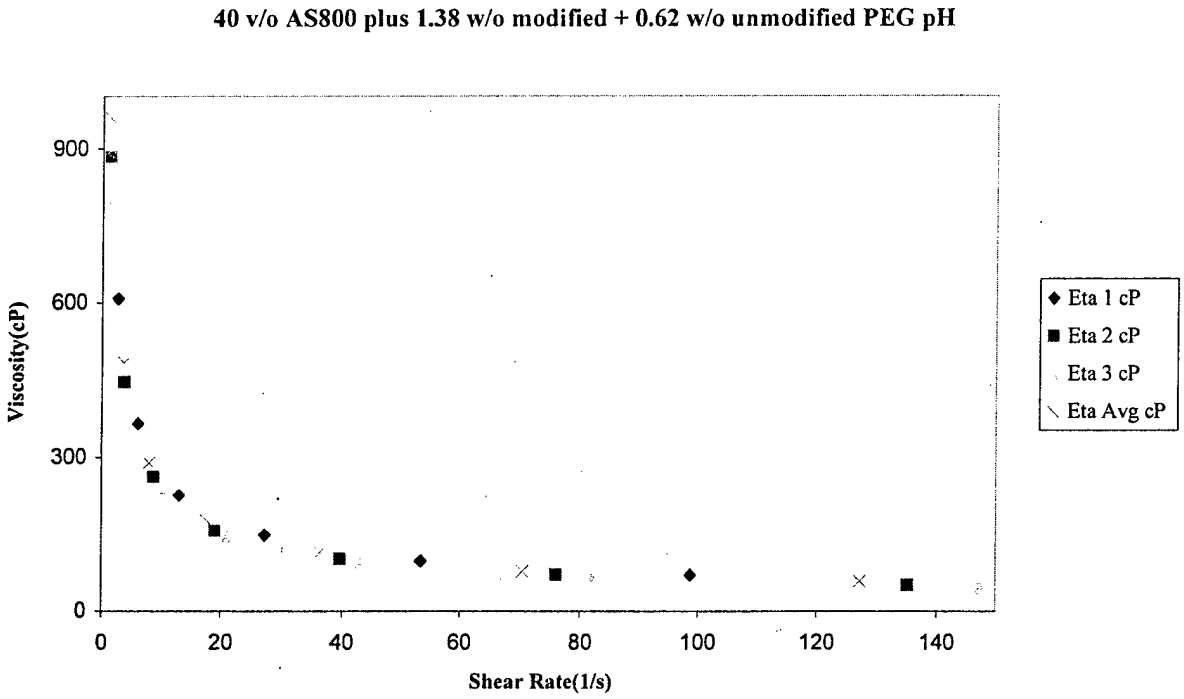

Figure 18. Steady state stress sweep with mixed silanes

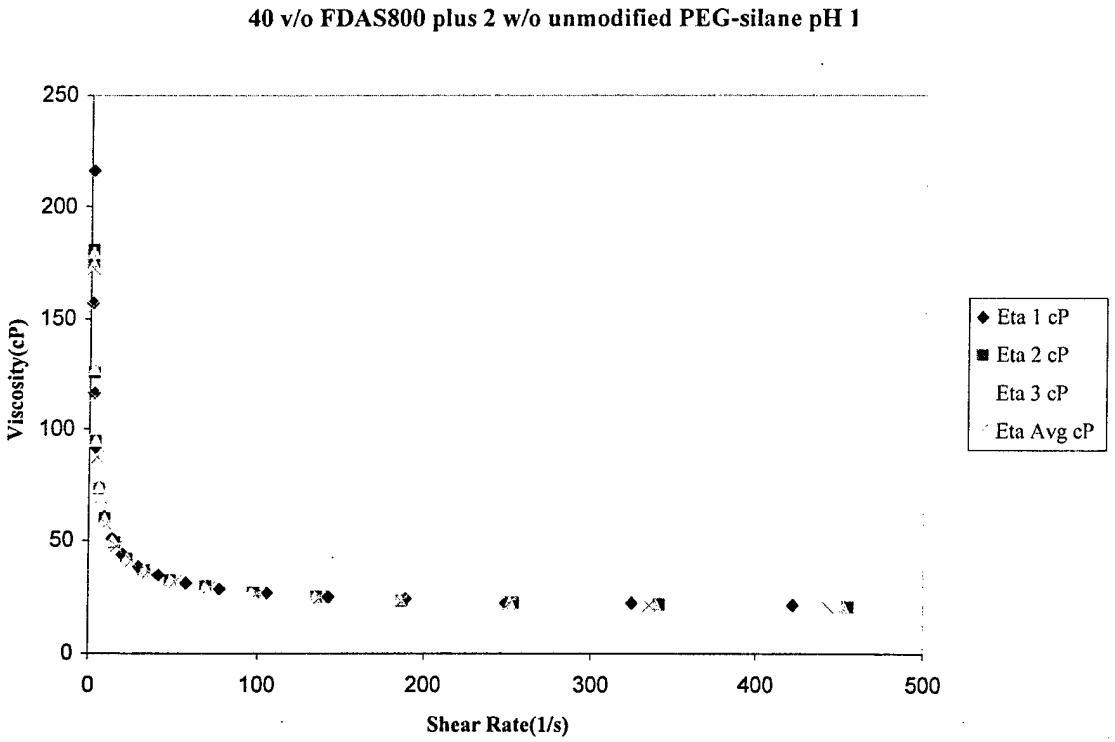

Figure 19. Steady state stress sweep with unmodified PEG-silane

Slurries containing 41.4 v/o freeze-dried AS800 silicon nitride powder, 40 v/o water, 18.6 v/o monomers, and 1-2 w/o of solids (Si3N4) modified or unmodified PEG-silane were formulated.

Attempts were made to add MPEG1 at different stages of slurry preparation. None of these produced a stable slurry. After considerable observation, it is believed that MPEG1 is not soluble in water and will not work well as a dispersant for this new aqueous system.

In light of the solubility problem with MPEG1, SRI produced a new modified PEG-silane molecule (MPEG2) where more polyethylene glycol mers are present along the length of the chain. It was hoped that this would increase the molecule's solubility in water. Unfortunately, it was found that MPEG2 did not exhibit solubility in water either. Pure alcohol and alcohol-water mixtures have been used as solvents for various silane molecules in the past. A mixture of 30 v/o ethanol and 70 v/o water was used to successfully dissolve MPEG2. Several slurries were attempted using MPEG2 and the ethanol-water mixture. After trying several approaches, a pre-slurry approach with milling and sonication led to a stable slurry. SRI 20 was the first successful slurry of this type. Table 5 shows SRI 20's composition.

Component	Concentration
Freeze-dried AS800	41.4 v/o
Deionized Water	28 v/o
Ethanol	12 v/o
PETA	2.04v/o
XB 5180	3.08 v/o
Bisepoxy	1.58 v/o
HEA	11.9 v/o
MPEG2	2 w/o (of solids)
pH 10	

Table 5. Composition of SRI 20

The method used to prepare SRI 20 is as follows:

Pre-slurry 1: AS800 powder is added to the water. During powder addition, the mixture is stirred and sonicated, and the pH is carefully monitored. After most of the powder is accommodated, the alcohol is added to the mixture, which is then sealed and stirred for 30 minutes. Next, the MPEG2 is added. After stirring for 5 minutes, the remaining powder is added while the pH is monitored. Once again, the mixture is sealed and stirred for 30 minutes.

Pre-slurry 2: The monomers are added one-at-a-time to a stirred bath containing the proper amount of HEA. This mixture is sealed and stirred for 30 minutes.

Pre-slurry 2 is then poured into pre-slurry 1. The mixture is bottled and sealed. The bottle is placed on the roller mill and allowed to equilibrate overnight. The pH is re-adjusted to 10 after equilibration and again before use, if necessary.

SRI 20 was tested in a steady state stress sweep. Figure 20 shows the results of this test. SRI 20 was sent to SRI for further testing. SRI reported moderate success in polymerizing this slurry.

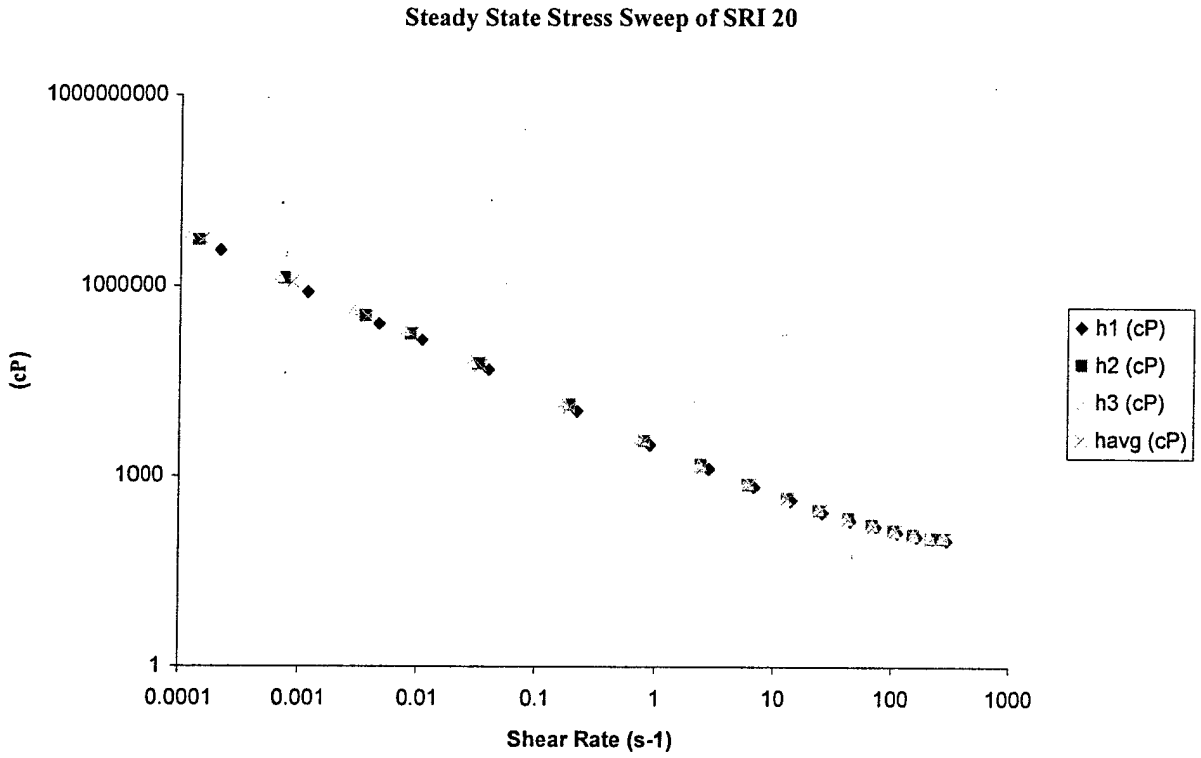

Figure 20. Steady State Stress Sweep of SRI 20

A slurry containing water, freeze-dried AS800, and MPEG2 was prepared and sent to SRI for freeze-drying (SRI 21). The slurry contained 25 v/o silicon nitride and 1.5 w/o (of solids) MPEG2. It was suggested that ethanol be added to promote MPEG2 solubility, and hence bonding to the particles, prior to freeze-drying. This slurry was the last prepared with silicon nitride.

4. Alumina Work

After limited success with the modified PEG-silane/AS800 system, SRI shifted the focus of this work to aluminum oxide slurries in an attempt to simplify the system. Initial work with Alumina slurries involved a

substitution of Sumitomo AKP-50 Alumina powder for the freeze-dried AS800 used previously. The first slurry attempted (SRI 22) contained 49 v/o 7:3 water:ethanol, 51 v/o AKP-50, and 1.5 w/o (of solids) MPEG2. This test slurry was successful. SRI 23 was formulated next. This slurry's composition is listed in Table **. This concentration of powder was too high for the current system, however. This mixture had a paste-like viscosity at an approximate concentration of 47 v/o powder. Next, a slurry (SRI 24) with 35 v/o powder was attempted. Initially, this mixture was fluid, but after overnight equilibration it too had a paste-like consistency. The pH had shifted from 12, the processing pH, to 8.5. No amount of additional base could stabilize this slurry, however.

In light of these results, it was decided that the bonding of the silane molecule to the particle surfaces should be investigated. An iterative process, similar to that used for developing the silicon nitride slurry was proposed. First, an aqueous slurry (SRI 25) containing only alumina and unmodified PEG-silane (1.5 w/o of solids) was formulated. This was tested to see if the PEG-silane had bonded to the alumina surface. A shift in the isoelectric point of the powder would indicate that the peg-silane had bonded to the surface. If this was the case, the next step would be to make slurries with MPEG2. If MPEG2 was found to be attaching, monomers would be added to the system one-by-one to see what interaction was causing gelling.

Slurry compositions were as follows:

All processed at pH 12

SRI 23	SRI 24	SRI 25
51 v/o AKP-50	35 v/o AKP-50	51 v/o AKP-50
15.6 v/o monomers	20.6 v/o monomers	49 v/o water
23.4 v/o water	31 v/o water	1.5 w/o (solids)
10 v/o ethanol	13.3 v/o ethanol	PEG-silane
1.5 w/o (solids) mod. PEG #2	1.5 w/o (solids) mod. PEG #2	

Table 6. Compositions of SRI 23, 24, and 25.

The isoelectric point (IEP) of SRI 25 was evaluated. It was found that the addition of unmodified PEG-silane shifts the IEP from 9, the normal value for AKP-50, to approximately 7.2. This tells us that the unmodified PEG-silane has indeed bonded to the alumina surface. Figure 21 shows the results of zeta potential measurements for SRI 25.

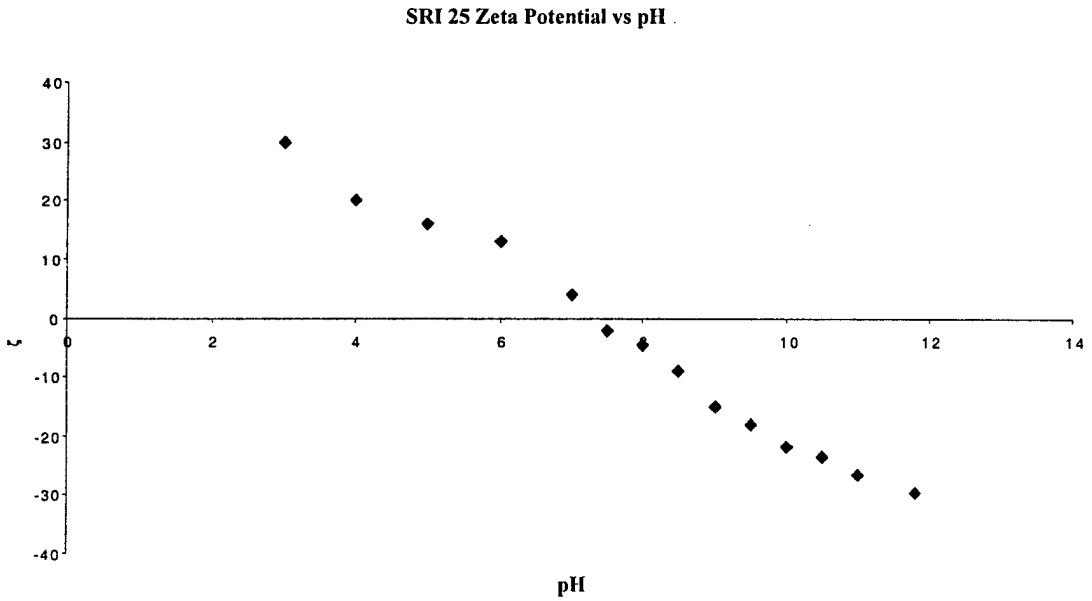

Figure 21. SRI 25 zeta potential vs pH

SRI 26 was evaluated in the same manner as SRI 25. SRI 26 was made with a water/ethanol mixture and modified PEG-silane #2 at a pH of 11. As can be seen from Figure 22, SRI 26 also exhibits a shift in its IEP from ~9 (AKP-50) to 8.5. This shift is not nearly as severe as with unmodified PEG-silane. The limited solubility of the molecule and the use of alcohol in the dispersing medium are probably the two main factors that contribute to this decreased effectiveness.

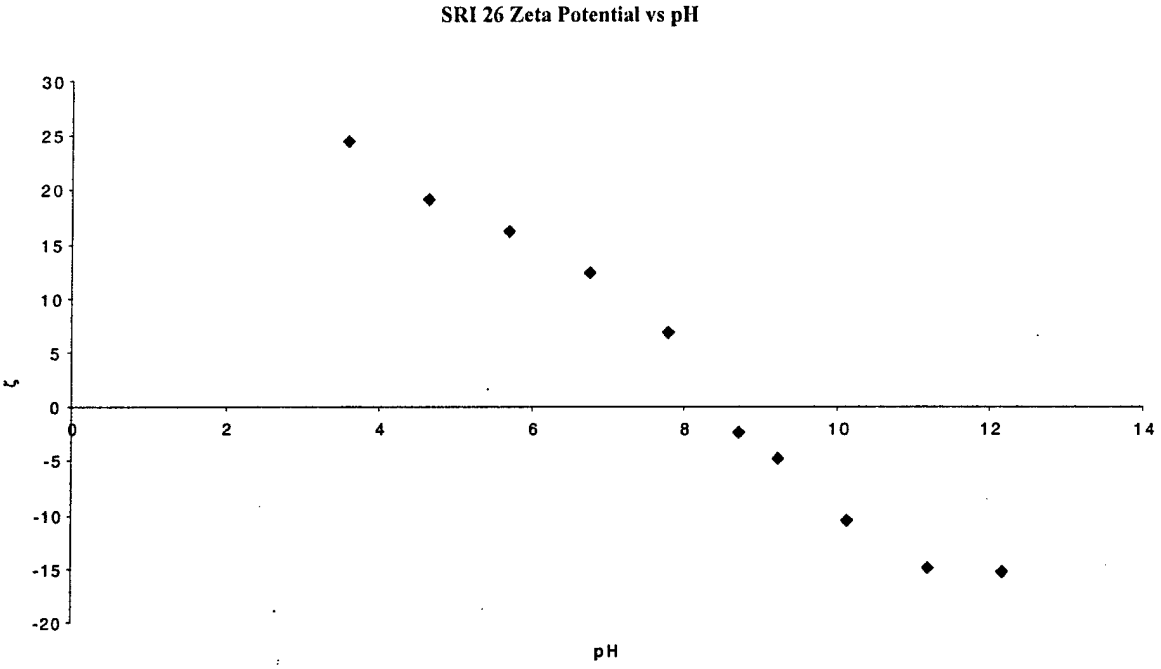

Figure 22. SRI 26 zeta potential vs pH

Batch calculations for the slurries are as follows:

SRI 25	SRI 26
51 v/o AKP-50	51 v/o AKP-50
49 v/o water	34.3 v/o water
	14.7 v/o ethanol
1.5 w/o (solids) unmodified PEG-silane	1.5 w/o (solids) modified PEG-silane #2
pH 12	pH 11

The processing pH was changed from 12 to 11 because gelling has been observed in pH 12 and above alumina slurries in past research.

To further assay if the two PEG-silane molecules were attaching to the alumina surface, rheological measurements of the above slurries were taken at the processing pH, 11, and at their respective isoelectric points. A reference slurry of 51v/o AKP-50 in water was prepared as well. This slurry was taken from the dispersed state (pH 11), to its isoelectric point at pH 9. By comparing the viscosities of the two PEG-silane containing slurries at their IEPs to that of the reference slurry, the effect of the PEG-silane in the absence of electrostactic dispersion forces would be evident. Figure 23 shows a plot of SRI 25 and 26 at pH 11 and at their respective IEPs. The reference slurry is not shown because the slurry was not pourable at its isoelectric point. Since both of the silane-containing slurries were pourable at their IEPs, it is shown that the PEG-silanes are anchored to the alumina surface and do provide a steric barrier to particle-particle contact.

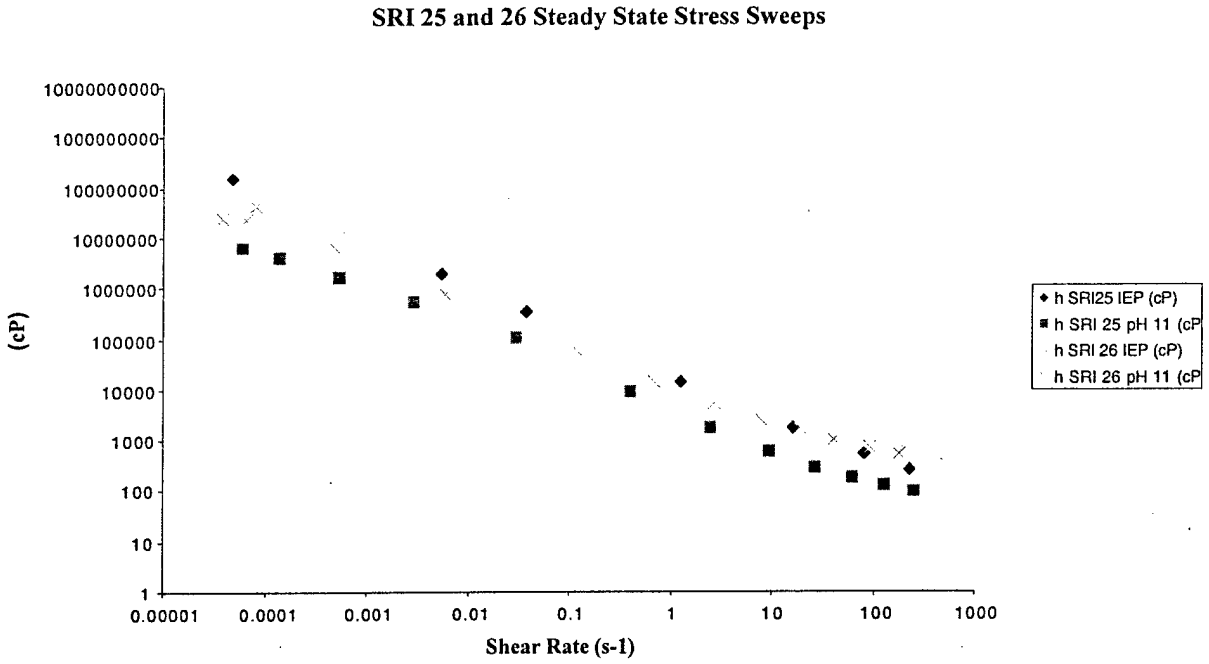

Fig. 23. Viscosity vs. shear rate for SRI 25 and 26.

From the graph it is shown that both the modified and unmodified PEG-silane molecules act as a dispersant in the alumina system. The MPEG2 molecule has less of an effect than the unmodified PEG-silane molecule. This is due to the presence of the non-polar functional monomer group added to this molecule. The functional group precludes water solubility and forces the introduction of an alcohol/water mixture to the system. Electrostatic dispersion is also lessened in the alcohol-water medium. This leads to the decreased performance of the bifunctional silane as a dispersant relative to the unmodified PEG-silane molecule. However, even though the performance is not optimal, the molecule does work as a dispersant. The initial slurries that contained all other monomer compounds probably gelled due to some sort of interactions between the monomers themselves or between the monomers and the medium. As with the previous work involving AS800, further iterative steps need to be taken to determine the cause of the gelling. The success in the AS800 system was achieved by first determining if the modified PEG-silane adhered to the particle surfaces, and then adding monomers one by one to see if any interactions occurred prior to the polymerization step.

III. Compositional Formulation to Develop Residual, Surface Compressive Stresses

1. Goal

The outer portion of the AlliedSignal Vane being made by the SRI Direct Photo Shaping Method will be formulated with a Si_3N_4 material containing a second phase that will be heat treated to produce a compressive surface stress that will impart a greater impact resistance. This material will form the shell, and the shell will be filled with the composition formulated and used by AlliedSignal.

The compressive stress will be produced by a second phase that oxidizes to increase its molar volume; we are currently attempting to develop a compressive stress of 500 MPa. Mr. Ryan Bock, a graduate student in the Materials Department has done the calculations reported below to obtain these residual stresses.

2. Calculations Associated with Compositional Formulation

$Ce_5(SiO_4)_3N$ is a second phase used to produce compressive stresses in Si_3N_4 by the following reaction.

$$\underset{178.6\text{cm}^3/\text{mol}}{Ce_5(SiO_4)_3N} + O_2 \rightarrow \underset{27.67\text{cm}^3/\text{mol}}{3SiO_2} + \underset{24.13\text{cm}^3/\text{mol}}{5CeO_2} + 0.5N_2$$

This oxidation results in a 14.03% increase in volume.

The density of $Ce_5(SiO_4)_3N$ was determined by the following approximation:

The unit cell dimensions of $La_{10}(SiO_4)_6N_2$ were substituted in place of $Ce_{10}(SiO_4)_6N_2$. La^{3+} is nearly the same size as Ce^{3+}.

$a = 9.72$ Å

$b = 7.25$ Å

This is a hexagonal system, so the unit cell volume is equal to $a^2b\sin 60$.

volume = 5.93×10^{-22} cm^3

density = cell mass/(cell volume*N_A)

density = 5.548 g/cm^3

molar volume = molecular weight/density

$Ce_5(SiO_4)_3N$ molar volume = 178.6 cm^3/mol

Calculation of necessary weight fraction of CeO_2 to introduce a 0.5 GPa compressive stress.

We know that the oxidation of pure cerium apatite yields a 14.03% increase in volume. The linear strain can be approximated by dividing this value by three.

$$\varepsilon = \frac{1}{3}(\Delta V/V)$$

$\varepsilon = 4.68\%$

The required volume fraction of $Ce_5(SiO_4)_3N$ to produce the 500 MPa compressive stress can be calculated as follows:

$$f_v\varepsilon = \frac{\sigma}{E}$$

$f_v = (0.5\text{ GPa})/[(310\text{ GPa})(4.68\%)]$

$f_v = 3.42\%$

Where E is Young's modulus for Si_3N_4.

So, assuming $100cm^3$ of this 3.42% $Ce_5(SiO_4)_3N \bullet Si_3N_4$ material to start,

(3.42 cm^3 Ce-apatite)* (5.548 g/cm^3) = 18.97g Ce-apatite

(96.58 cm^3 Si_3N_4)*(2.18 g/cm^3) = 210.54 g Si_3N_4

(18.97 g Ce-apatite)/(990.857g/mol) = 0.0191 mol Ce-apatite needed
The reaction to produce $Ce_5(SiO_4)_3N$ is as follows:

$2Si_3N_4 + 5CeO_2 + 7/4O_2 \rightarrow Ce_5(SiO_4)_3N + 3/2Si_2N_2O + 2N_2$
This assumes the evolution of N_2 and the production of a small volume of Si_2N_2O.

For every mole of $Ce_5(SiO_4)_3N$ produced, we need 2 moles of Si_3N_4 and 5 moles of CeO_2.
Since we need 0.019 moles of $Ce_5(SiO_4)_3N$, we need the following amounts of reactants:

Si_3N_4: 2(0.019) * 140.26 g/mol = 5.33 g
CeO_2: 5(0.019) * 172.12g/mol = 16.35 g

So the total weight of reactants is:

Initial Si_3N_4 + Reacting Si_3N_4 + Reacting CeO_2
210.54g + 5.33g + 16.35g = 232.22g

Finally, the weight fraction of CeO_2 needed is:

16.35g/232.22g = 7.04% CeO_2