DEVELOPMENT OF SHORT RANGE REPULSIVE INTER-PARTICLE FORCES IN AQUEOUS Si_3N_4 SLURRIES WITH CHEM-ADSORBED SILANES

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Abstract

Different chem-adsorbed silane molecules have been used to produce weakly attractive silicon nitride particle networks for aqueous colloidal processing. Silanes with diamino and polyethyleneglycol hydrophilic heads yielded slurries with the lowest viscosity, longest sedimentation stability and highest packing density. Chem-adsorbed silane molecules protected silicon nitride and yttrium oxide, a common processing aid, from hydrolysis at pH's between 5.5 and 11. A novel approach was used to produce short range repulsive potentials neccessary to yield the weakly attractive networks. Addition of salt to dispersed silicon nitride slurries with particles coated with polyethyleneglycol-silane, caused the collapse of the 22 atoms long chains and residual electrical double layer. This produced a weakly attractive network which persisted during consolidation to yield a plastic body with a flow stress that was dependent on the counterion size. When 0.5 M tetramethylammonium chloride was used at pH 10, plastic bodies had a flow stress similar to clay, whereas lithium counterions produced bodies with a much higher flow stress.

1 Introduction

Colloidal processing can improve the strength of structural ceramics by reducing the size of strength degrading heterogeneities by filtration prior to consolidating an engineering shape.[1,2,3] Pujari et al.[1] showed that this approach could not only lead to a significant increase in average strength, but also to the appearance of a threshold strength because flaws within the powder greater than a given size were removed, thus truncating the flaw size distribution prior to consolidation.

Filtering the slurry to remove flaws greater than a given size requires a dispersed slurry, and thus a repulsive interparticle pair potential. The filtered slurry should not be dried because of the probability of reintroducing heterogeneities. Instead, the engineering shape could be fabricated directly from the slurry by methods used for traditional, clay based ceramics. Clay based slurries are shaped either by slip casting and pressure filtration, as the particles are being consolidated, or after consolidation by extrusion and forging. Consolidated clay bodies are generally plastic whereas consolidated bodies made with other powders are normally brittle. Recently, it has been shown that clay-like bodies from weakly attractive particle networks can be produced by developing a short-range repulsive potential between the particles that partially 'shields' attractive van der Waals potential.[4,5]

Short-range repulsive potentials can be produced by different methods. In one method, a surface charge is developed on each particle when neutral -M-OH surface sites are reacted with either acid or base (producing charged $-M-OH_2^+$ or $-M-O^-$ groups) followed by an increase in the salt concentration to produce a highly compressed cloud of counterions. The particles are attractive due to van der Waals forces until their counterion clouds begin to interact.[4] The free energy of the particles increases as the concentration of

counterions between them is increased when particles are pushed togehter. When the slurry contains a low concentration of counterions, the thickness of the counterion cloud is large, and the net interparticle forces are repulsive. When salt is added to the slurry to increase the counterion concentration, counterion cloud shrinks to a finite thickness. This allows the van der Waals force to cause the particles to attract one another until the counterion clouds interact at short separation distances. This approach is effective for colloidal processing because a pH generally exists that allows the interparticle forces to be repulsive at small concentrations of counterions. The dispersed slurry is needed to first filter the heterogeneities from the slurry. After filtration, salt can be added to compress the counterion clouds and produce the desired short-range repulsive potential.

In the second method, molecules are covalently attached to the surface of the particles by a chemical reaction to form a dense 'brush' that protrudes from the surface. When the 'brush' on the surface of one particle begins to penetrate the 'brush' on a second particle, the free energy of the two increases due to the decreased entropy by molecular confinement and the increased strain energy within the 'brushes'. Long molecules produce thick 'brushes' that effectively shield the attractive van der Waals potential, and thus produce dispersed slurries. Short molecules produce thin 'brushes' that only partially truncate the van der Waals potential, and thus produce a short-range repulsive potential once the particles are attracted to one another via the van der Waals potential. For these weakly attractive networks, the equilibrium separation distance can be approximated by twice the 'brush' thickness (twice the molecular length).[6]

Silicon nitride is an important high temperature structural ceramic material due to its low thermal expansion coefficient and modest elastic modulus, which minimize thermal stresses during thermal transients, and its high strength due to its fibrous microstructure that imparts high fracture toughness.[2] Two different sites terminate Si_3N_4 surfaces,:

silanol sites (-Si-OH) and double amine sites, $-Si_2=NH$ groups.[7] Hydrolysis and oxidation[7] can change the ratio of these two surface sites. In water, this ratio can change in a matter of hours, depending on pH.

Attempts to produce short-range repulsive potentials with silicon nitride using compressed counterion clouds have not been effective because the potential is insufficient to keep the particles from being pushed together during particle packing.[8] Kramer and Lange [9] showed that low molecular weight alcohols could be reacted with the -Si-OH surface sites to chemically bond hydrocarbon chains to the silicon nitride particles. The strength of saturated, consolidated particle networks was shown to be inversely proportional to the length of the hydrocarbon chain. Longer hydrocarbon chains kept particles farther apart by truncating the van der Waals attraction at a greater separation distance. Kramer and Lange showed that consolidated bodies with a high particle packing density could be plastic, with a yield stress that could be altered by changing the length of the bonded hydrocarbon chain. Unfortunately the use of hydrocarbon chains has two serious problems relative to the objectives of colloidal processing. First, this method yields hydrophobic particles, and thus, a non-aqueous liquid must be used to formulate a slurry. Second, and more serious, is that short hydrocarbon chains can only produce a short-range repulsive potential and not the long-range repulsion neccessary to filter the slurry to remove heterogeneities. Long chains produce slurries with repulsive networks and low sedimentation stability. Bodies consolidated from such slurries are brittle.

Luther et al.[10] attempted to overcome the two problems associated with the use of covalently bound hydrocarbon chains with the use of short surfactant molecules to produce the short-range repulsive potential. Surfactant molecules have a hydrophilic head group that terminates a hydrocarbon chain. The head groups can be cationic, anionic nonionic or zwitterionic. Surfactants are attracted to the charged surfaces where they usually phys-

adsorb, even though some molecules such as amines or carboxylic acids can chem-adsorb onto the oxide surface of the same sign of charge.

Luther et al.[10] and Ducker et al.[11] showed that different surfactants did allow for aqueous processing and the change from long - to short-range repulsive potentials, but also showed that plastic bodies could not be formed because the surfactant molecules could be easily pushed away from between the particles as the powder was consolidated. That is, although specific surfactants could produce either dispersed or weakly attractive particle networks by changing the pH in the slurry state, they always produced brittle bodies after consolidation, probably due to surfactant desorption from the surface. These results clearly showed a need for the molecules that would strongly bind to the surface of Si_3N_4 .

Leong and coworkers used carboxylic acids such as citrate and other multivalent anions like phosphate to disperse zirconia powder for colloidal processing.[12] They showed that the strength of the particle network was inveresly proportional to the size of the adsorbed ion. In short, they showed that larger anions produced slurries with lower viscosity and yield stress at the respective particle isoelectric point where no electrostatic forces played a role. We tried this approach but citrate molecules were also displaced from the surface during consolidation process.

Many different organic molecules can be covalently grafted to powder surfaces by a reaction involving the -M-OH surface sites.[13] Silanes are a general class of molecules that appear appropriate for Si_3N_4 because they can be synthesized with reactive end groups (e.g., $-Si-(OR)_3$ and $-Si-Cl_3$) that upon hydrolisis strongly bond to the -Si-OH sites on the Si_3N_4 surface, and they do not add unwanted elements to Si_3N_4 powders. The reactive end group and a large variety of hydrophilic head groups (e.g., carboxyl, amino, ethyleneoxide, hydroxyl, etc.) can be separated with a hydrocarbon chain, of different

lengths. Lea and Hlady[14] coated silicon nitride wafers with silane molecules containing extended polyethylene glycol groups of 2000 or 5000 daltons MW. Using the atomic force microscope with silicon nitride cantilever tips and silane coated Si_3N_4 wafers they showed that the large molecules produced strong repulsive forces in water, as expected. On the other hand, when salt was added, the salt could collapse the extended polyethylene glycol chains to produce attractive surfaces with a short range repulsive interaction. Buchta and Shih[15] reacted the aminosilane ($Si(OC_2H_5)_3(CH_2)_3NH_2$) reagent with a Si_3N_4 powder. They showed that the powder coated with the aminosilane produced a much better dispersion and a higher packing density at low pH (1.5-3). This is not a surprise since both the pKa of the amino group and the isoelectric point of the aminosilane coated silicon nitride powder are around pH 10. At pH below 3, the aminosilane coated powder is far from its isoelectric point. Unfortunately, silicon nitride processing aids such as yttria are not stable below pH 6.

Bowen and coworkers[16] used silanes with hydrocarbon chains to improve dispersability of silica particles in organic solvents. While short molecules (up to 18 atoms in the chain) showed great promise in the improved processing of large particles, they were insufficient in length to prevent the flocculation of small particles with diameters of 100 nm or less.

In the present study, silicon nitride powders were coated with different silane molecules to achieve high packing density, a desired viscosity, high sedimentation stability and a powder that was relatively non-reactive with water. Short chain molecules such as diaminosilane with seven carbon atoms in the linear chain were sufficient to produce well dispersed networks with larger, 0.7 μm (Ube Industries, E03) powders, but a longer molecule of polyethylene glycol (PEG) silane with 22 carbon atoms in a linear chain was necessary to disperse the smaller, 0.2 μm, (Ube Industries, E10) powders (data not

reported here). Of greater significance, consolidated bodies of Ube E3 powder coated with PEG-silane were plastic with a flow stress comparable to a commercial throwing clay when large cations, such as tetramethylammonium, were added to PEG-silane coated powder slurries formulated at high pH.

2. Experimental

The Si_3N_4 powder (Ube Industries, Japan, E03) was used, 'as received', in this study. The average particle size, measured in our laboratory and reported by the manufacturer, was 0.7 μm. Although a number of different silanes were studied, only two that produced useful and contrasting properties will be reported. N-(2-aminoethyl)-3-aminopropyltrimethoxy silane is denoted "diaminosilane" and N-(triethoxysylilpropyl)-O-polyethylene oxide urethane with 4 to 6 CH_2CH_2O units, denoted as PEG-silane were purchased from Gelest Inc., Tullytown, PA. Both molecules are schematically shown in Fig. 1. Slurries were formulated in deionized water with the conductivity of 1 micromhos/cm. Salts, including LiCl, CsCl and tetramethylammonium chloride (TMACl) (Sigma Chemical, St. Louis, Missouri), were used for dispersed slurries formulated with excess counterions. Basic slurries prepared with the appropriate hydroxide (e.g. LiOH, TMAOH. etc.) were emphasized due to the greater stability of oxide densification additives (e.g., Y_2O_3) at high pH that are mixed with Si_3N_4 powders to formulate commercial structural ceramics. Analytical grade chemicals were used.

The silanes were reacted with the Si_3N_4 powders with the following procedure. Silane (1.5 wt. % as of weight of silicon nitride) was added to the water before the addition of 20 vol. % of Si_3N_4. The slurry was sonicated for 5 minutes and stirred overnight to assure the completion of the silane-Si_3N_4 surface reaction. A second reaction route was also used in which a hexane solution containing 5 wt. % of the desired silane was

formulated. Si_3N_4 (10 vol %) was vigorously stirred into the solution for 30 minutes. The hexane slurry was centrifuged and washed 5 times with isopropanol. The washed powder was air dried for 72 hours. Aqueous slurries were then prepared with the dried powder.

Although the second method was expected to produce a thinner layer of silane on the surface of each particle, no significant difference in the processing of the two types of slurries was observed, thus the former was used for most studies. Unless noted otherwise, data reported below are from slurries which contain coated particles produced by the first method. Zeta potential measurements were used to confirm that the silane molecules were bound to the surface of the Si_3N_4 powder.

Zeta potential measurements (Zeta Meter 3.0, Zeta - Meter, New York. N.Y) of the different Si_3N_4 suspensions (20mg/l) were performed after equilibration at pH 4 and a desired ionic strength. Suspensions were dispersed by sonication and pH adjustment was made with additions of nitric acid or an appropriate hydroxide.

The reactivity of uncoated and silane coated Si_3N_4 powders with water was determined at a specific pH with electrophoretic mobility measurements and direct measurements of dissolved silica within the water.[17,18] For electrophoretic mobility measurements, suspensions were prepared and studied at a powder concentration of 1 g/L. These slurries were diluted to 20 mg/l just prior to electrophoretic mobility measurements.

In the second set of experiments to assess the reactivity of Si_3N_4 with water, dissolved silica was measured with the standard colorimetric phosphomolybdate method.[19] In these experiments, the Si_3N_4 slurry (volume fractions from 0.01 to 0.1) was kept at a desired pH for a period of up to 4 weeks. The measurements of the concentration of dissolved silica were perormed after centrifugation at 10,000 rpm. Similar dissolution experiments were performed with aqueous slurries formulated with silane-coated and

uncoated Y_2O_3 (a common densification aid). Dissolved yttrium (as Y^{3+}) was measured with the inductively coupled plasma (ICP) spectroscopy after prolonged centrifugation at 10,000 rpm.

Viscosity measurements were made with a dynamics stress rheometer (Rheometrics DSR) using a couette type measuring cell (29.5 mm diameter, 44 mm long). Slurries were subjected to a high shear rate which was decreased until the measured torque was below the sensitivity of the instrument ($\approx$ 0.1 g-cm).

Slurries were consolidated as saturated cylinders ($\approx$ 1.5 cm height and 2.5 cm diameter) with a pressure filtration apparatus described elsewhere [20] at a pressure within the range of 1 to 60 MPa. The pressure was maintained until an apparent equilibrium packing density was achieved, which was recognized when the movement of the plunger ceased for 10 minutes. The relative density of the consolidated bodies was determined using the weight difference method (volume of water within the consolidated body determined by the weight before and after drying and pyrolysis at 600° C to remove organic molecules). This method measures the relative density of the saturated body; the relative density increases during drying due to volumetric shrinkage.

Load-displacement measurements were performed using a servo-hydraulic mechanical test machine (INSTRON, Model 8562, Canton, MA). The saturated, cylindrical specimens, contained within a plastic bag to prevent evaporation of water, were deformed in uniaxial compression using the displacement control mode of the testing machine as detailed elsewhere [20] Each experiment consisted of applying a compressive strain (0.20) to the specimen at the loading rate of 1 mm/min, while recording the load. The specimen was then unloaded; if the body exhibited plastic flow instead of brittle fracture,[21] it was reloaded to an additional strain of 0.1 to measure the flow stress.

3. Results

Figure 2 reports the zeta potential and the isoelectric point of the E3 Ube Si_3N_4 powder before and after coating with diaminosilane at pH 10 (Fig. 2a) and PEG-silane at pH 10 (Fig. 2b). For the diaminosilane coated powder, the isoelectric point shifted from pH 4.7 for the uncoated powder to pH 10.3 where pKa of the amino group is located ($-NH_3^+ = -NH_2 + H^+$, $pKa \approx 10$). The isoelectric point appears to be unchanged when the Si_3N_4 is coated with the PEG-silane. It was observed that PEG-silane formed a cloudy suspension when first mixed (at 1.0 weight %) with water. Although this solution became clear, without noticeable increase in viscosity after stirring for two hours, some self - assembled structures in the initial solution were large enough to scatter light for zeta potential measurements. Measurements showed that the isoelectric point of the PEG-silane particulates (Fig. 2c) was nearly identical to that of Si_3N_4.

Figure 3 presents the isoelectric point and zeta potentials of silicon nitride particles which were coated with diaminosilane in water at pH 1 and hexane, respectively. It appears that surface properties of particles coated in water and hexane are different. The isoelectric point of particles coated in water at pH 1 is located at pH 9 and for the particles coated in hexane, at pH 10.5. However, the highest zeta potentials for both powders were observed at pH 2 (≈40 mV). No significant differences in powder procesability were observed at pH 2. As shown in Figure 2a, the highest zeta potentials obtained with diaminosilane E03 silicon nitride coated at pH 10 were ≈60 mV at pH 3. When silicon nitride powder was coated with the PEG silane at pH 10, the most negative zeta potentials (≈ -60 mV) were measured at pH 11.5. Less negative zeta potentials were observed for powders coated in hexane (-45 mV at pH 10). Therefore, most of our work was done with

powders coated with silanes in water at pH 10. All data presented in the following figures (both with diamino and PEG silane coated powders) were obtained with the powders coated in aqueous solutions at pH 10, as described above. Slurries formulated with such powders had the lowest viscosities. Consolidated bodies produced from the slurries with the powders coated at pH 10 also had the highest packing density. **(Last sentence left off).**

Figure 4a shows that storing uncoated Si_3N_4 powder (1 g of powder per 100 ml water) at pH 10 for 3 weeks shifts the iso-electric point from pH 4.7 to pH 7.8. This shift is expected due to the dissolution of silanol groups.[22] Both Fig. 4b and 4c respectively, show that the diaminosilane and PEG-silane coated powders are unaffected by a storage period of 3 weeks at pH 10. These data strongly suggested that the chem-adsorbed silanes are reasonably effective in preventing water molecules from reacting with the surface. Similar information was recently reported for ZnO.[23] Consistent with the data shown in Fig. 4, Fig. 5 reports that the PEG-silane coating significantly reduces the dissolution of surface silica for a 20 volume fraction Si_3N_4 slurry stored at pH 10.3 for a period of $\approx$ 5 days. Namely, after 5 days $\approx$ 10 times more silica (980 ppm) was dissolved from uncoated silicon nitride as opposed to only 92 ppm from PEG silane coated silicon nitride.

Likewise, Fig. 6 shows that coated Y_2O_3 powders are more stable than uncoated powder. The reaction[24] $Y_2O_3 + 6H^+ = 2Y^{+3} + 3H_2O$ caused the pH to dramatically increase from 6.5 to 8.5 in $\approx$ 3hrs, whereas the pH stabilized at 7 for the PEG-silane coated powders, which was more effective than the diaminosilane coated powder. Although not studied in detail, neither coating appeared very effective at pH $\leq$ 5.

Sedimentation stability of Si_3N_4 slurries produced after diaminosilane and PEG-silane coating was investigated with standard penetrometry. In this method, a 5 mm

diameter glass rod is used to penetrate the sediment produced after different periods of slurry storage. Uncoated, dispersed (pH 10) Si_3N_4 slurries produced a very compact sediment after 24 hours in which the glass rod could not penetrate without breaking. Diaminosilane coated slurries with an initial volume fraction between 0.20 to 0.40 produced a very soft sediment for periods up to at least six months as indicated by the complete penetration of the glass rod. Slurries with an initial volume fraction = 0.50, formulated with PEG-silane had somewhat harder sediment, but the glass rod could still penetrate the sediment more than 85% after six months of storage at pH 10.

Figure 7 reports the viscosity vs. shear rate data for un-coated and PEG-silane coated Si_3N_4 slurries (0.20 volume fraction) formulated at a pH where both coated and uncoated powders are dispersed (pH = 10) and where both are flocced (iso-electric point, pH = 5). As shown, the dispersed slurry formulated with the PEG-silane coated powder exhibits Newtonian behavior (shear rate independent) with the lowest viscosity, whereas the uncoated, dispersed powder is nearly Newtonian with a slightly higher viscosity at lower shear rates. Figure 7 also shows that the flocced slurries are strongly shear thinning as expected for an attractive particle network.[25,26] The flocced slurry produced with the uncoated powder has much stronger network (higher viscosity at any shear rate), than the PEG-silane coated powder. Two other sets of data are also shown in Fig. 7, namely data for uncoated and coated powder slurries dispersed at pH 10 with additions of 0.5 M of tetramethylammonium chloride. As shown, both of the slurries produced with the added salt are shear thinning and with a weaker network (lower viscosity at a given shear rate) than their respective slurries produced at the iso-electric point; the weaker network of the two is formulated with the PEG-silane coated powder.

Table 1 lists the relative density of bodies consolidated by pressure filtration at 25 MPa from uncoated and PEG-silane coated slurries formulated at pH 10 (dispersed slurry),

flocculated at the isoelectric point (pH 5), and dispersed at pH 10 and coagulated with 0.5 M of added TMACl. After consolidation, the brittle or plastic rheology of each body was tested with the mechanical testing machine as described above. The relative density for the uncoated powder formulated at the iso-electric point was the lowest (0.48) and was slightly greater (0.51) for the PEG-silane coated powder also formulated at its iso-electric point. Both of these bodies were brittle, i.e., cracked into many pieces without flow. Bodies produced from both powders formulated to produce dispersed (pH 10) slurries had the same, high relative density (0.61), but both exhibited brittle behavior. Bodies produced from PEG-silane powders dispersed at pH 10 and then coagulated with added salt (0.5 M TMACl) had a high relative density and exhibited plastic behavior. Figure 8 quantifies the plastic behavior of this body relative to that of a commercial throwing clay. Also shown are the flow stresses of the bodies produced from the slurries formulated with the addition of some other counterions in the series, Li^+, Na^+, K^+, Cs^+, TMA^+, added as chlorides. Figure 8 shows that the flow stress decreases as the size of the unhydrated counterion increases. This same behavior was previously observed for consolidated bodies formed from Al_2O_3 slurries that were dispersed at pH 12 and formulated with excess counterions in this same series.[27]

Table 2 reports the effect of pH on the relative density of aqueous, diaminosilane coated Si_3N_4 slurries (20 vol. %) consolidated by pressure filtration (5 MPa). The highest packing density occurs at pH 3 (relative density = 0.55) where the slurry is well dispersed, and has the highest zeta potential ($\approx$ 60 mv). The lowest packing density occurs at pH 10, the iso-electric point for the diaminosilane coated Si_3N_4 powder. Figure 9 shows the stress strain behavior for the consolidated bodies reported in Table 2. At pH 3 bodies produced from the well dispersed slurries were intially brittle but started to flow like a fluid after the particle network was broken apart during mechanical loading as described Franks and

Lange [20]. At pH 7 the bodies were plastic and also started to flow after they were deformed during flow stress testing. Finally, at pH 10 consolidated bodies were brittle but also flowed after the mechanical testing. In the absence of the adsorbed silane layer, consolidated bodies at pH 10 and 7 broke into many pieces during mechanical testing. This is the behavior typical for very brittle bodies.

4. Discussion

The data reported above shows that N-(triethoxysylilpropyl)-O-polyethylene oxide urethane with 4 to 6 CH_2CH_2O units (PEG-silane) has significant attributes in the colloidal processing of Si_3N_4 powder. It was demonstrated that PEG-silane can be chem-adsorbed to the surface in an easy and practical way, namely by adding it to a dispersed, aqueous slurry. The coated powder produces a well dispersed slurry at pH 10. This is important to filter unwanted heterogeneities greater than a given size, and then formulate a weakly attractive particle network by adding excess salt (e.g., tetramethylammonium chloride,TMACl). That produces a short-range repulsive potentials which persist during particle packing to yield a body with a high particle packing density and with a flow stress similar to that of clay. The PEG-silane can also produce chemically stable slurries by delaying the surface-silica/water reaction.

Although the diaminosilane coated powders had attributes similar to the PEG-silane coated powders, the PEG-silane molecules used here could produce a higher particle packing density and a better weakly attractive network, with added salt, desired for the control of flow stress and forming complex shaped bodies. As detailed elsewhere,[21] bodies consolidated from well dispersed slurries are generally brittle (support crack growth prior to plastic deformation) because the particles can be easily pushed into their deep potential well to form very strong particle network.

It was discovered that the addition of counterions to well dispersed slurries formulated with the PEG-silane coated particles could produce a weakly attractive particle network. The first observation that a weakly attractive particle network could be produced by adding excess salt (excess counterions) to a well dispersed slurry was reported by Velamakanni et al.[5] for Al_2O_3 slurries. Colic et al.[27] have also shown that the strength of the weakly attractive network produced with the addition of excess counterions is inversely proportional to the size of the bare counterion, i.e., decreasing flow stress for Li^+ to TMA^+ additions. This behavior was also observed for SiO_2[31] via measurements with the surface force apparatus. This is contradictory to the widely accepted lubricating hydration force model.[5] The effect of the excess counterions has been attributed [27] to the decrease in the thickness of the counterion cloud (Debye length) to a minimum value with increasing counterion concentration, where the minimum Debye length is proportional to the size of the unhydrated counterion, and its penetration depth within the hydration layer on the particle surface. In the current case, where PEG-silane molecules are chem-adsorbed to the surface, we believe that the counterions cause the collapse of the ethyleneoxide chains associated with the PEG-silane. The counterions may also neutralize any residual charge on the silicon nitride surface. Lea and Hlady[14] showed with the direct force measurements that the addition of salt collapsed adsorbed PEG-silane chains and modified strongly repulsive into weakly attractive forces. Our rheological and consolidation studies correlate very well with their microscopic direct force studies. We believe that cations with high affinity for water such as lithium perturb the water structure more and collapse polyethylene chains more efficiently by generating a poor solvent conditions.

Although most silane molecules are not soluble in water, Plueddeman[32] developed aminosilane reagents for aqueous processing. Aminosilane solutions can be stable for several month.[33] The formation of intramolecular zwitterionic pentacoordinate rings, or

other hydrogen bonded intermolecular structures, may be important to their stability in aqueous solution.[34] When the reaction of hydrolysis and polymerization starts, dimers, micelles, particles or emulsion droplets can be formed. When oxides are added, it has been proposed[34] that the aminosilanes bind immediately through very strong hydrogen bond between silane amines and OH groups at the oxide surface. Covalent bonds can be formed during air or heat curing by flipping the molecules so that silanol groups can bond to the OH groups from the metal oxide surface.[35] Solution pH appears to be the main factor controlling aminosilane adsorption. At low pH's where both the oxide and amino groups are positively charged, the aminosilanes can bind directly with their silanol groups to the surface which usually results in the stronger bond.[36] At higher pH's where oxide surface is negatively charged and amino group positively charged, hydrogen bonding and ionic bonding with proton jumping from the OH group of the oxide to the NH_2 group of the aminosilane can be the dominant mechanisms of adsorption. Aminosilane molecules can also bind horizontally with both their amino and silanol groups hydrogen bonded to the surface.[37] Other important parameters controlling the efficiency of silane deposition are number of silanol groups in the silane molecule and concentration of the silane in water (or solvent) during deposition. [36]

PEG silane molecule is essentially an aminosilane in which one amino group is replaced with the polyethylene glycol chain, leaving one free nitrogen proton, i.e., PEG silane is an aminosilane derivative. It may bind to the surface through the hydrogen bonding between the nitrogen proton and the silanol groups on the silicon nitride surface. The polyethylene glycol group can also hydrogen bond to the surface silanols. Moreover, since we observed that PEG silane stays on the surface after 5 washing cycles with isopropanol it appears that at least some PEG silane molecules are covalently bond to the surface. A very strong proof that PEG silane stays on the surface is the production of

plastic silicon nitride bodies after consolidation at 25 - 40 MPA in the presence of 0.5 M of TMACl at pH 10. Without silane coating, bodies produced from similar silicon nitride slurries are brittle. A futher indication of chem-adsorbtion, is that the hydrocarbon chains linking the surface reactive groups with the hydrophilic terminal groups protect the surface from the hydrolitic water attack. This stabilization is probably possible through entrapping water within polyethylene or diamino groups. Chemical stability of yttrium oxide was also improved from hydrolytic water attack at a pH above 5.5. PEG-silane seems to be more successful in preventing water molecules from reaching the surface relative to the diaminosilane, probably because of better entrapment of water molecules in the longer ethyleneoxide chains of PEG-silane and/or the slower diffusion of reactants and products through these longer chains with strong affinity for water[30].

5. Conclusions

Silicon nitride particles were coated with the chem-adsorbed silane molecules with different chain lengths and terminal groups. Excellent sedimentation and chemical stabilities along with low viscosity and high packing density of the slurries were obtained. A novel approach was used to produce plastic consolidated bodies where long chain (22 atoms) PEG silane was used to coat particles and produce well dispersed slurries. Addition of salt was then used to collapse polymer chains and obtain weakly attractive particle networks. Different size counterions were used to control the flow stress of the consolidated bodies. A flow stress close to that of a clay was obtained with E03 silicon nitride, PEG silane coating and 0.5 M TMA chloride at pH 10. Lithium ion produced bodies with the higher flow stress and slurries with higher viscosities than cesium or TMA cations. Lithium perturbs the hydration layer more efficiently due to its high affinity for water, therefore depleting the chains of water. Deeper penetration inside hydration layer of the residual noncoated silicon nitride surface is also probable. Cesium and TMA cations

are binding water less efficiently and do not show such behavior. Recently developed statistical mechanics model predicted such behavior.[38] Colic and coworkers[27] and Chapel[31] observed such behavior with alumina and silica slurries, respectively.

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TABLE 1. Packing density and consolidated body rheology of the E03 Ube silicon nitride powder consolidated at 25 MPa.

Powder/slurry	dispersed (pH 10)	flocced (iep, pH 5)	dispersed, (pH10) + 0.5 M TMACl
uncoated Si_3N_4	0.61 (brittle)	0.48 (brittle)	0.515 (brittle)
PEG coated Si_3N_4	0.61 (brittle)	0.515 (brittle)	0.57 PLASTIC!

TABLE 2. Packing density and flow behavior of bodies consolidated from 20 vol% E03 silicon nitride slurries precoated with diaminosilane in hexane.

pH	Packing Density, Vol%	Flow Behavior
3	55	brittle
3 (+2 M NH_4Cl)	53	brittle
5	53	plastic
6	53	plastic
7	52	plastic
10	49	plastic

LIST OF FIGURES

FIGURE 1. Schematic presentation of diaminosilane and PEG silane molecules.

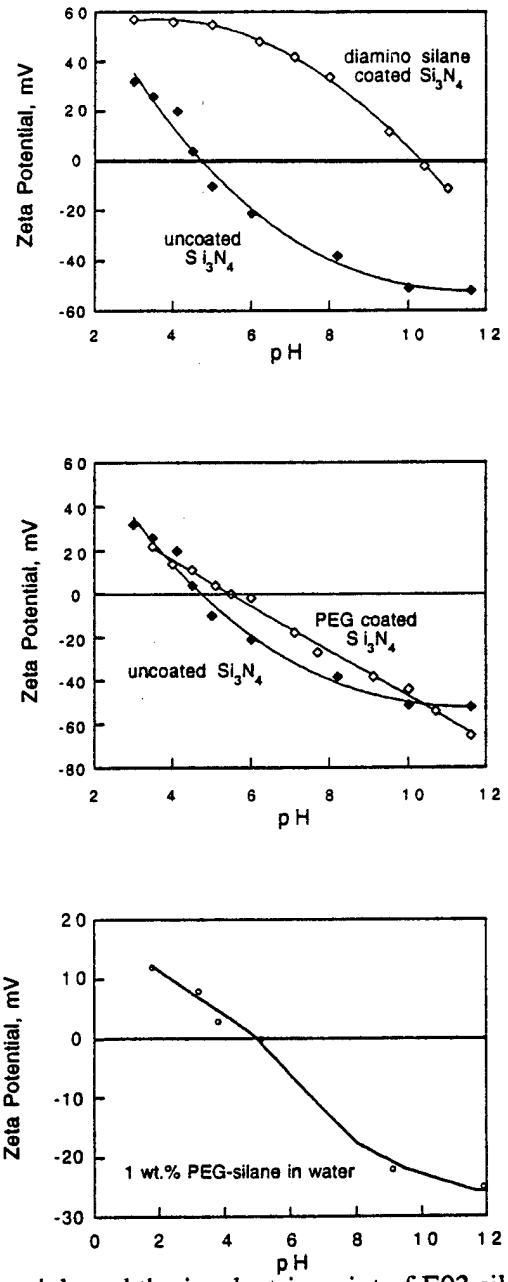

FIGURE 2. Zeta potentials and the isoelectric point of E03 silicon nitride powder before and after coating with (a) diaminosilane and (b) PEG silane, and of PEG silane particulates without powder addition (c).

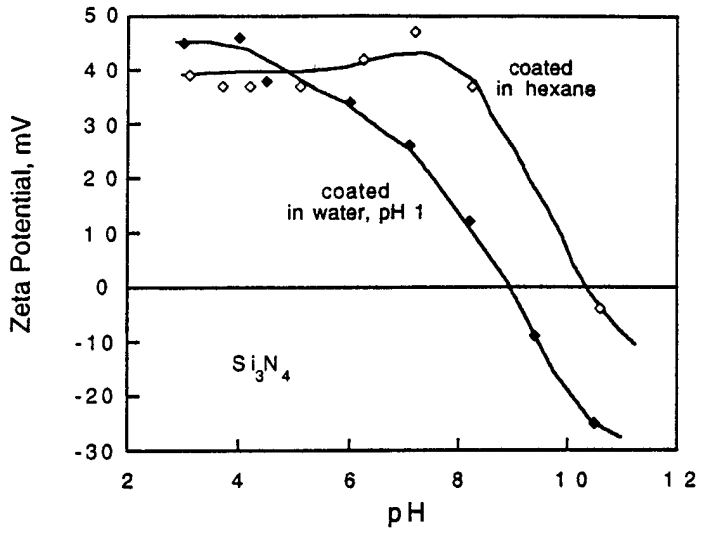

FIGURE 3. The influence of coating solvent (water, pH 1 or hexane) on the zeta potentials and the isoelectric point of diaminosilane coated silicon nitride.

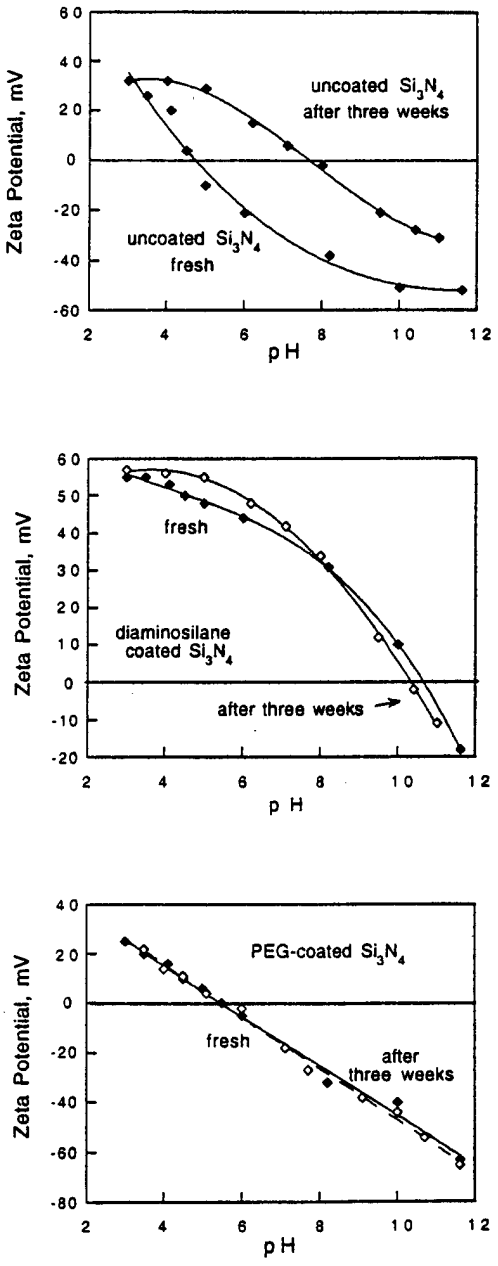

FIGURE 4. Zeta potentials and the isoelectric point of freshly prepared and aged E03 silicon nitride suspensions: (a) without any coating; (b) with diaminosilane coating and (c) with PEG-silane coating.

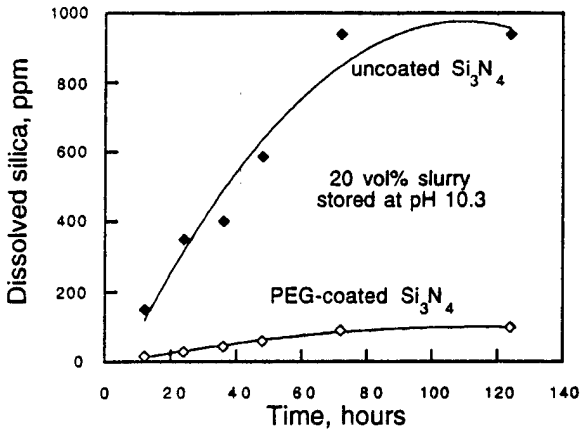

FIGURE 5. Dissolution of uncoated and PEG silane coated silicon nitride E03 powders at pH 10.3 stored for a period of 5 days.

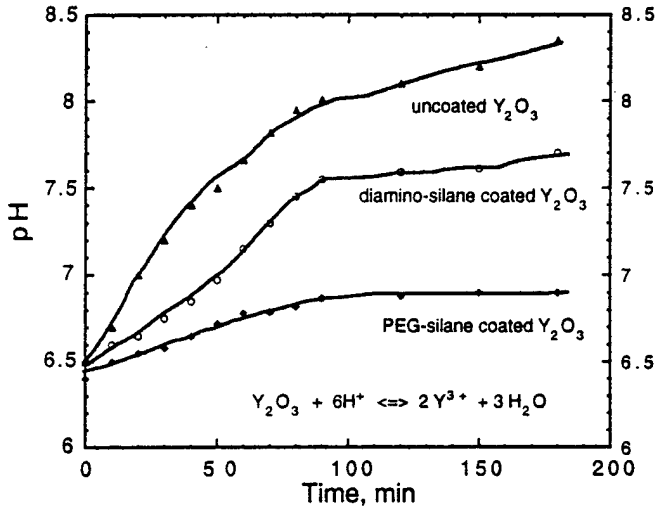

FIGURE 6. Dissolution of uncoated, diaminosilane coated and PEG silane coated yttria at starting pH of 6.5.

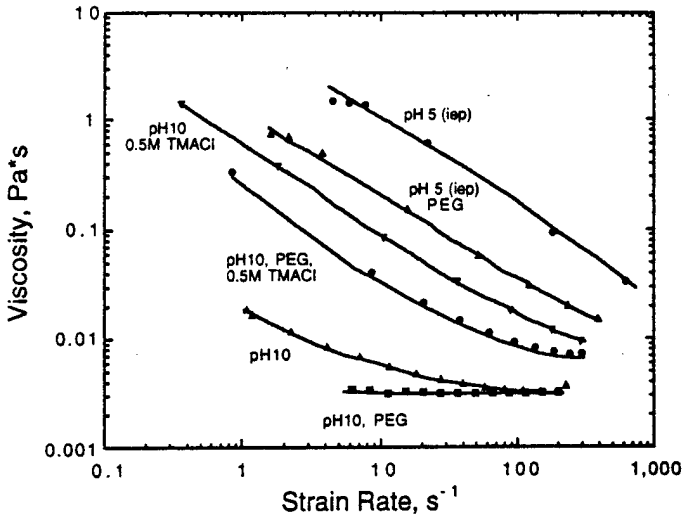

FIGURE 7. Viscosity of uncoated and PEG silane coated silicon nitride slurries at pH 10 (well dispersed), pH 10 and 0.5 M TMACl (weakly attractive) and at the isoelectric point (pH 5).

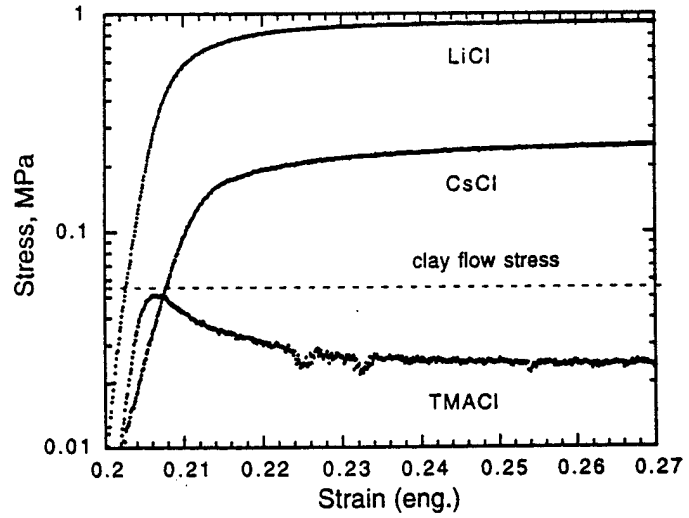

FIGURE 8. Flow stress of the PEG silane coated silicon nitride bodies consolidated at 25 MPa for 30 minutes from the slurries prepared at pH 10 with 0.5 M of Li^+, Cs^+ and TMA^+ chlorides.

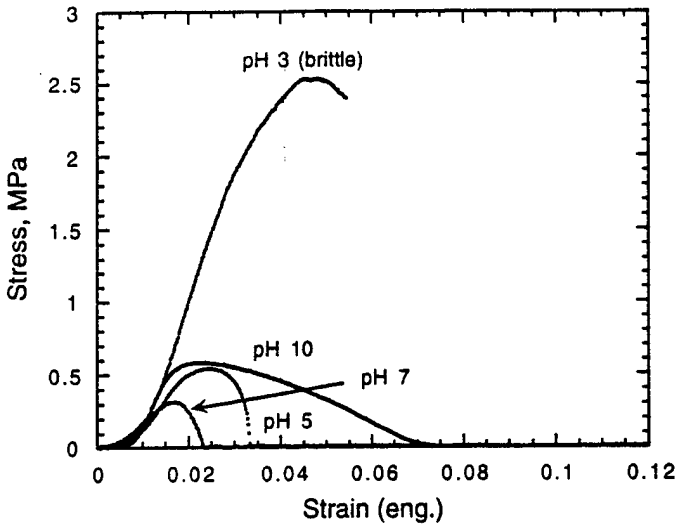

FIGURE 9. Flow stress of the diaminosilane coated silicon nitride bodies consolidated at 5 MPa for 30 minutes from the slurries prepared at various pH's.