Polysiloxanes Derived From the Controlled Hydrolysis of Tetraethoxysilane as Precursors to Silica for Use in Ceramic Processing

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POLYSILOXANES DERIVED FROM THE CONTROLLED HYDROLYSIS OF TETRAETHOXYSILANE

AS PRECURSORS TO SILICA FOR USE IN CERAMIC PROCESSING

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SUMMARY

Synthesis, properties, and potential applications in ceramic processing for two polysiloxane silica precursors derived from the controlled hydrolysis of tetraethoxysilane (TEOS) are presented. The higher molecular weight TEOS-A is a thick adhesive liquid of viscosity 8000 to 12,000 c.p. having a SiO_2 char yield of about 55 percent. The lower molecular weight TEOS-B is a more fluid liquid of viscosity 150 to 200 c.p. having a SiO_2 char yield of about 52 percent. The acid catalyzed hydrolysis of TEOS to hydrated silica gel goes through a series of polysiloxane intermediates. The rate of this transition increases with the quantity of water added to the TEOS; thus, for ease of polymer isolation, the amount of water added must be carefully determined so as to produce the desired polymer in a reasonable time. Excess water must be avoided to prevent too short a gelation time. The water to TEOS mole ratio falls in the narrow range of 1.05 for TEOS-A and 0.99 for TEOS-B. Further polymerization or gelation is prevented by storing at -5 °C in a freezer. Both polysiloxanes thermoset to a glassy solid at 115 °C. The liquid polymers are organic in nature in that they are miscible with toluene, and ethanol, slightly soluble in heptane, but immiscible with water.

For both polymers, results on viscosity versus time are given at several temperatures and water additions. Also their thermal decomposition properties are discussed. Based on these results, some examples of practical utilization of the precursors for ceramic fabrication are given. These examples include use of TEOS-A as a binder for the formation of an oxide ceramic compact. Good green body properties were obtained after cold pressing and up to the final sintering. Curing at 115 °C produced an oxide bound by a solid polymer matrix. At higher temperature, the oxide particles are held together via reaction bonded silicates formed from SiO_2 derived from the pyrolysis of TEOS-A. A second example involves the use of TEOS-B as a precursor to SiO_2, which when mixed with high surface area alumina and fired forms mullite. TEOS-B in a third application may be used to infiltrate already formed ceramic bodies. The formation of SiO_2 and silicates in the pores on firing serves to increase density without effecting shrinkage.

INTRODUCTION

The need for oxidation resistant materials for high temperature application has directed our interest toward the synthesis of refractory silicates (e.g., mullite) and their use in the fabrication of monolithics and fiber reinforced ceramic matrix composites. Results of an investigation of sol gels for this purpose indicated that, while they are well suited for the synthesis of silicate powders, sol gels have limited application in fabricating ceramic

shapes. This is largely due to the low oxide char yield of sol gels (typically 10 to 15 percent) because of their high solvent content. Their high solvent content, usually water, results in considerable shrinkage during solvent evaporation in processing the sol gel to the final sintered compact.

The hydrolysis of alkoxy silanes is unique in relation to alkoxides of other metals, in that liquid polysiloxane intermediates can be readily isolated. The object of this investigation was to develop a silicon dioxide precursor for use in the fabrication of silicate monolithics and ceramic matrix composites. Desirable precursor properties include:

(1) A liquid thermosetting polymer
(2) Low vapor pressure
(3) Stable over long time periods
(4) Readily pyrolyzed to pure silica
(5) High silica char yield--low shrinkage
(6) Inexpensive
(7) Nontoxic reaction products produced during thermosetting and pyrolysis

The approach has been the synthesis of two polysiloxane polymers, TEOS-A and TEOS-B produced by the controlled hydrolysis of tetraethoxysilane (TEOS). TEOS-A, the higher molecular weight of the two, is a viscous glue like liquid with good adhesive properties (viscosity about 10 000 c.p.) and TEOS-B is a relatively low viscosity liquid (viscosity about 150 c.p.).

Investigation of reactions involved in the hydrolysis of tetraethoxysilane (TEOS) began over 140 years ago (ref. 1), long before practical use of sol gels was realized. Ebelman reported the formation of well defined siloxane oligomers on hydrolysis of TEOS. Recently, because of the increased interest in sol gels, the mechanism of TEOS hydrolysis has been extensively studied (refs. 2 to 10).

When water is added to a solution of TEOS in ethanol, rapid hydrolysis and relatively slower condensation polymerization reactions occur. These can be represented simplistically according to the following chemical equations. The first reaction is the hydrolysis of TEOS:
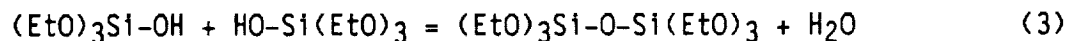
$$Si(OEt)_4 + XH_2O = Si(OH)_x(OEt)_{4-X} + XEtOH \qquad (1)$$
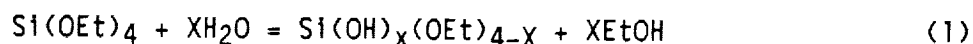
Depending on the mole ratio of H_2O to TEOS (from 1 to 4), more than one ethoxy group (OEt) can be replaced by hydroxyl groups (OH) on the same molecule. Because we are mainly concerned with a H_2O/TEOS mole ratio near unity, the equations will represent the reaction of equal moles of H_2O and TEOS.

The hydrolysis step in the sequence is

$$(EtO)_3Si-OEt + H_2O = (EtO)_3Si-OH + EtOH \qquad (2)$$
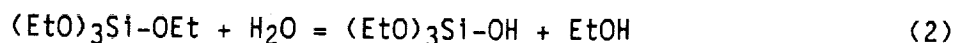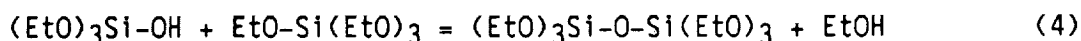
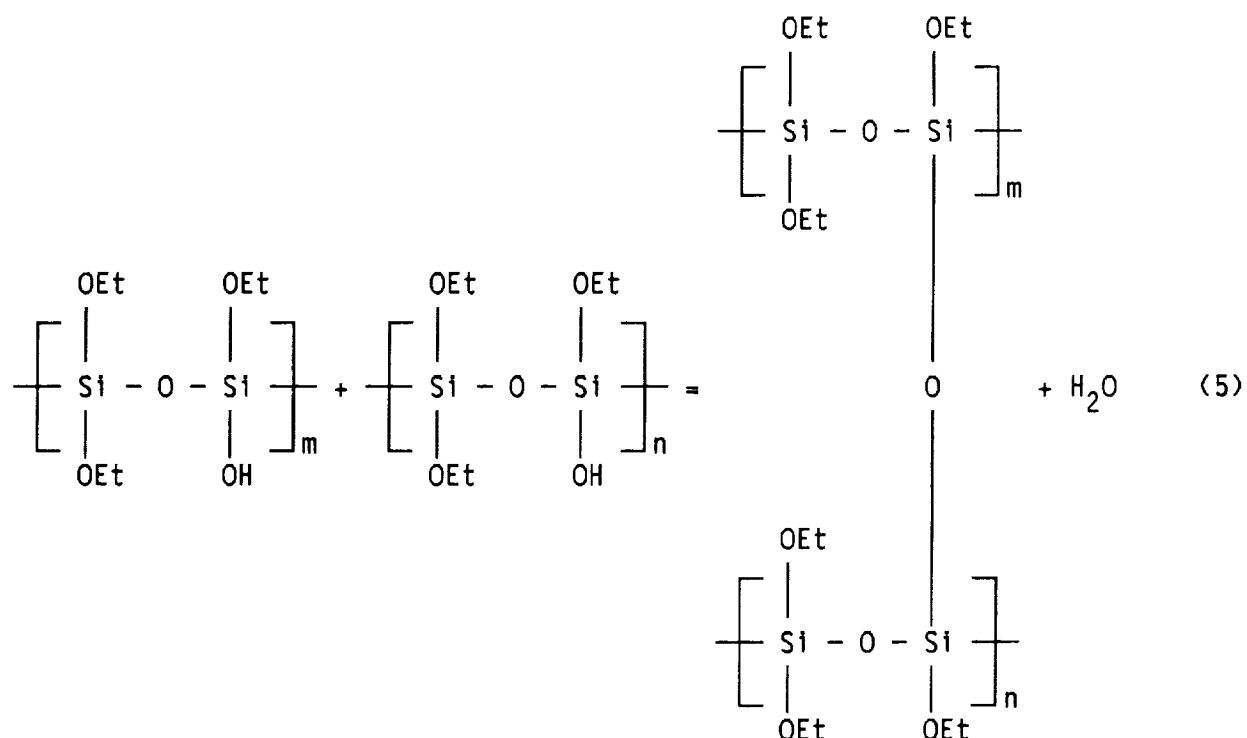where Et is the ethyl group C_2H_5.

The hydroxyl groups (OH) formed during the hydrolysis reaction become active functional groups participating in the subsequent condensation polymerization reaction shown below:
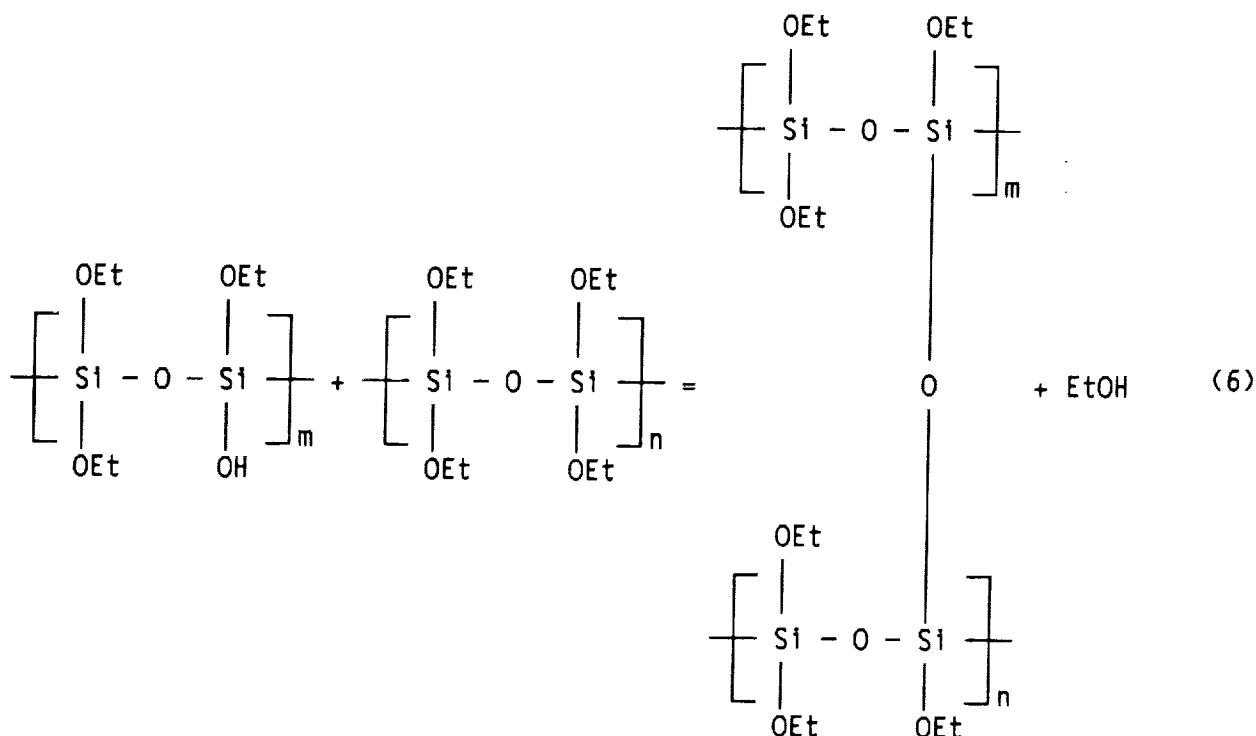
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$$(EtO)_3Si-OH + HO-Si(EtO)_3 = (EtO)_3Si-O-Si(EtO)_3 + H_2O \qquad (3)$$

Also,

$$(EtO)_3Si-OH + EtO-Si(EtO)_3 = (EtO)_3Si-O-Si(EtO)_3 + EtOH \qquad (4)$$

Condensation polymerization continues producing primarily linear or slightly branched polymers of increasing molecular weight as indicated by increasing viscosity. Crosslinking takes place transforming the viscous liquid, first through a gel transition stage, to a hard glass like solid. If sufficient water was added to the TEOS originally, further condensation to cause crosslinking takes place at room temperature in much the same way as condensation polymerization occurs.

$$
\left[\begin{array}{c} OEt \\ | \\ Si-O-Si \\ | \\ OEt \end{array}\right]_m
+
\left[\begin{array}{c} OEt \quad OEt \\ | \quad | \\ Si-O-Si \\ | \quad | \\ OEt \quad OH \end{array}\right]_n
=
\begin{array}{c}
\left[\begin{array}{c} OEt \quad OEt \\ | \quad | \\ Si-O-Si \\ | \\ OEt \end{array}\right]_m \\
| \\ O \\ | \\
\left[\begin{array}{c} OEt \\ | \\ Si-O-Si \\ | \quad | \\ OEt \quad OEt \end{array}\right]_n
\end{array}
+ H_2O \qquad (5)
$$

also,

$$
\left[\begin{array}{c} \overset{\displaystyle OEt}{\underset{\displaystyle OEt}{\overset{|}{\underset{|}{Si}}}} - O - \overset{\displaystyle OEt}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{Si}}}} \end{array} \right]_m + \left[\begin{array}{c} \overset{\displaystyle OEt}{\underset{\displaystyle OEt}{\overset{|}{\underset{|}{Si}}}} - O - \overset{\displaystyle OEt}{\underset{\displaystyle OEt}{\overset{|}{\underset{|}{Si}}}} \end{array} \right]_n =
\begin{array}{c}
\left[\overset{\displaystyle OEt}{\overset{|}{Si}} - O - \overset{\displaystyle OEt}{\underset{\displaystyle OEt}{\overset{|}{\underset{|}{Si}}}} \right]_m \\
| \\
O \\
| \\
\left[\overset{\displaystyle OEt}{\underset{\displaystyle OEt}{\overset{|}{\underset{|}{Si}}}} - O - \overset{\displaystyle}{\underset{\displaystyle OEt}{\overset{|}{\underset{|}{Si}}}} \right]_n
\end{array}
+ \; EtOH \qquad (6)
$$

Once crosslinking occurs as indicated by the separation of a gel phase from the liquid, the polymer cannot be used for the applications described in this report; thus, care must be taken to stop the reaction at the desired stage. This is accomplished by quenching the reaction medium to below -5 °C.

The factors influencing the course and rate of these reactions are (ref. 10):

(1) Molar ratio of water to TEOS
(2) Temperature
(3) Nature and amount of catalyst
(4) Nature of solvent
(5) Chemical reactivity of the alkoxysilane
(6) Concentration of TEOS in solution

The molar ratio of water to TEOS is critical in determining the properties of the final condensation polysiloxane product; thus, this parameter is given major emphasis in this investigation. The last three factors were not researched.

This paper presents some aspects of the synthesis of two polysiloxanes derived from the controlled hydrolysis of TEOS, namely, TEOS-A a very viscous adhesive liquid and TEOS-B, a less viscous more free flowing liquid. Some of their interesting applications as binders and infiltrants for ceramic processing are also discussed.

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EXPERIMENTAL

Reagent grade or equivalent chemicals were used in all cases. Dehydrated 200 proof ethanol, 99 percent tetraethoxysilane (TEOS), and deionized water were used to prepare the siloxane polymers. Mention should be made as to the origin of the tetraethoxysilane because we found differences using various sources of this compound with regard to water addition requirements and time at 40 °C necessary to produce TEOS-A and TEOS-B. At present we do not have sufficient quantitative data to warrant reporting this as a result in this paper. For the results presented here, we used tetraethoxysilane from Alfa Products in Danvers, MA.

Synthesis

Preparation of polysiloxanes via the controlled hydrolysis of TEOS was accomplished as follows: 1 mol of TEOS was diluted with 2 mol of absolute ethanol. Ethanol is a cosolvent for TEOS and water which by themselves are immiscible. The predetermined quantity of water, 1.05 to 1.10 mol for TEOS-A and 0.90 to 1.0 mol for TEOS-B containing 0.05 mol hydrochloric acid (HCl) catalyst, was slowly added to the well stirred TEOS alcohol solution. In preliminary experiments described in the results, the optimum amount of water needed to form TEOS-A and TEOS-B was established. Three classes of catalysts, were tested: strong mineral acid (HCl or HNO_3) with mole ratio HCl/TEOS = 0.02 and 0.05, HNO_3/TEOS = 0.05; a weak acid (acetic acid) HAc/TEOS = 0.05; and a weak base (aqueous NH_3) NH_3/TEOS = 0.05. The effect of no catalyst was also tested. Although any strong acid catalyst would suffice, HCl was chosen because of convenience, availability, and the fact that HCl is volatile; that is, it is readily removed during pyrolysis of the TEOS polymers.

Shortly after the addition of the acidified water to the TEOS-alcohol solution, a mild exotherm was observed. Stirring was continued for about an hour; then the solution was kept at 40 °C in an open beaker for the specified time as indicated for the results shown in figure 1. During this time, condensation polymerization proceeded and the ethanol solvent was removed by evaporation. As ethanol was lost, the viscosity of the remainder increased. For the synthesis of the highly viscous polysilane designated as TEOS-A, the polymerization was terminated at the point just prior to gelation. At 40 °C, for TEOS-A production, this process took at least 60 hr after which time the polymerization had to be closely watched until the desired viscosity was observed before the onset of gelation. Unfortunately, probably because of the complexity of the reactions involved, an exact time of reaction could not be established with any accuracy. The polymerization was immediately stopped by cooling the polymer to below 0 °C. The TEOS-A could be kept indefinitely when stored in a stoppered bottle in a freezer. To insure a reasonable transition rate, from monomer to viscous liquid, the amount of water added in the beginning must not be excessive, yet carefully controlled so that the viscous stage of TEOS-A could be reached in a reasonable time. If too much water was added at the beginning, the transition from viscous phase to gelation occurred too fast to insure convenient isolation. Also, the presence of an excess of water increased the instability of the TEOS-A, sometimes resulting in gelation even during cold storage. Because of the lower H_2O/TEOS = 0.90 to 1.0 involved in the formation of the less viscous, free flowing TEOS-B, the transition to the gel phase was not as sharp timewise as that for TEOS-A formation; thus, the

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process time at 40 °C was not as critical. The reaction mixture was usually removed from the 40 °C water bath after about 150 hr, then stored in the same manner as TEOS-A.

Properties

The viscosity of the TEOS-A and TEOS-B materials as a function of time was studied (fig. 1). A 100 g sample was placed in a 250 ml beaker and immersed in a 40 °C water bath. For the viscosity measurements, made on a digital viscosimeter,[1] the sample was removed from the bath and cooled to 20 °C. An aliquot used for the actual measurement was afterwards returned to the original 100 g and the beaker again placed in the 40 °C bath until time for the next viscosity reading. This process was repeated for all of the viscosity determinations. For the 110 °C runs, the procedure was similar, except that the liquid in 250 ml covered beakers was placed in an oven at 110 °C. In general, viscosity readings were made at various shear rates; these rates were selected to provide convenient readouts, between 20 to 80 on a scale of 0 to 100. At least two readings at each shear rate were taken. No viscosities were measured once gelation had begun.

The viscosity experiments were continued to determine the effect on viscosity versus time for the addition of more water to aged TEOS-B. For a TEOS-B sample aged for 315 hr at 40 °C and originally synthesized from 1 mol TEOS monomer, 0.99 mol water, 0.05 mol HCl, and 2.0 mol EtOH, 0.21 mol water containing two drops of concentrated HCl was added, all dissolved in the cosolvent 19 ml absolute ethanol. Then viscosity (now increasing at a relatively rapid rate) was measured at specified time intervals until gelation occurred. The modified TEOS-B, in terms of total water used, required 0.99 mol originally used to make TEOS-B plus 0.21 mol added after 315 hr, which then equaled a total of 1.2 mol of water per mole of the TEOS monomer.

To understand the thermal decomposition properties of TEOS-A and TEOS-B, an incremental weight loss experiments were performed on about 20 g samples each of TEOS-A and TEOS-B. Two samples of each were poured into open weighing bottles and heated at 115 °C for 200 hr in a laboratory oven after which time crosslinking and solidification were accomplished. The solid samples were weighed and the percent weight loss was then calculated from the before and after weight differences. The weighing bottles containing the solid cross-linked materials were returned to the oven and the temperature was increased to 200 °C and maintained at this temperature for 24 hr. After this time the samples were again weighed. The samples were then quantitatively transferred to tared ceramic crucibles which are more resistant to high temperature than the pyrex weighing bottles. The crucibles containing the samples were put into a muffle furnace and subsequently maintained at temperatures of 300, 500, and finally at 980 °C for 24 hr at each temperature. Percent weight losses at the various temperature increments were all based on the weight of the sample after 24 hr at the indicated temperature and weight of the original liquid TEOS-A or TEOS-B.

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[1]Brookfield Digital Viscosimeter.

In addition to the incremental TGA just described, a continuous TGA analysis using a relatively small amount, about 17 mg, of solid crosslinked TEOS-A powder was made using a Thermogravimetric analyzer.[2] Instead of starting with the viscous liquid, TEOS-A, it was more convenient, in terms of loading the analyzer, to begin with the finely powdered crosslinked material.

To find the SiO_2 char yield after pyrolysis of TEOS-A and TEOS-B, it was assumed that the white residue remaining after both the incremental and scanning TGA, was pure SiO_2; thus, the final weight of the residue was used to calculate char yields. This is a logical assumption since, when silicon-oxygen containing materials are pyrolyzed at 800 °C or above in an oxidizing environment, SiO_2 is the only nonvolatile compound that can form under these conditions. Also, in that high purity starting materials were used, no other metal oxides should be present. This assumption was confirmed by a standard analytical technique for SiO_2. A known amount of TEOS-A or TEOS-B was crosslinked at 115 °C for about 100 hr and the solid material was first digested with H_2SO_4 with additions of concentrated HNO_3 to help oxidize organic material. The insoluble dehydrated SiO_2 formed at the end of the digestion was then removed and fired at 1000 °C for 12 hr. The actual procedure could be simplified because no foreign metals were present; thus, no separations were necessary.

Application Evaluation

One potential important application of TEOS-A, making use of its good adhesive properties, is in the fabrication of ceramic compacts. To evaluate this fabrication approach, ceramic oxide powder such as SiO_2 was first thoroughly mixed with a designated amount of TEOS-A (between 8 to 15 percent TEOS-A) via a mortar and pestle. The mixture was then cold pressed at about 10,000 psi. The green body compacts were cured at 110 to 120 °C for at least 24 hr to thermoset (crosslink) the siloxane polymer. The compacts were then slowly heated in 100 °C increments, with a 1-hr hold at each temperature, 200, 300, and 400 °C until 500 °C was reached. The sample was kept at this temperature for 12 hr allowing organics to be lost and amorphous silica to form. This slow heating program was used to avoid carbon deposition in the compact.

A second potential application is the use of TEOS polymers as precursors to SiO_2 in the synthesis of silicates and at the same time to function as binders to consolidate these silicate compacts. The process used here was to first coat the oxide particles with amorphous silica derived from TEOS-B, then mix these coated particles with a relatively smaller amount of TEOS-A to bind them together to form a compact. The preparation and fabrication of mullite, $3Al_2O_3·2SiO_2$, compacts from Al_2O_3 powder, TEOS-B and TEOS-A (binder) was investigated.

The mullite compacts were made by first thoroughly mixing via mortar and pestle TEOS-B with Al_2O_3 powder.[3] The quantity of TEOS-B used was somewhat less than that required for mullite stoichiometry ($3Al_2O_3·2SiO_2$) such that the total amount used to coat the alumina particles plus the relatively smaller

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[2] Perkin-Elmer TGS-2 Thermogravimetric Analyzer.
[3] Two types of Al_2O_3 powder were used: (1) Alon Fumed Alumina, Cabot Corp.; (2) Linde 0.05 μm Alumina Polishing Powder.

quantity of TEOS-A required for the binder corresponds to the mullite stoichi-
ometry. To be more specific, the specified amount of TEOS-B (61.08 g) was
thoroughly mixed with Al_2O_3 (100 g) in a mortar and the mixture was fired
500 °C for about 10 hr. The fired product presumably comprised an intimate
mixture of amorphous silica and alumina. The fired product (132.02 g) weighed
less than the before-fired mixture because of losses due to burnoff of C-H-O
containing organics. The fired mixture powder was thoroughly mixed with
10 wt % TEOS-A binder (13.20 g), and the resulting mixture was then cold
pressed into cylinders at 10,000 psi. The final complete powder mixture
corresponded to 100 g Al_2O_3 + 39.29 g SiO_2 which is the mullite stoichiometry.
The cold pressed green body was heated at 110 °C for 96 hr to crosslink the
polysiloxane.

The cylindrical mullite compact was then subjected to the following heat-
ing schedule: 1000 °C for 19 hr, 1500 °C for 6 hr and finally, at 1700 °C for
8 hr. After each temperature treatment, the compact was weighed and the height
and volume shrinkage determined. From these measurements the compact density
was calculated. The percent theoretical density was determined from the ratio
of the measured density and the theoretical density for mullite, (3.15 g/cc)
(ref. 12). The identification of mullite was verified by standard x-ray dif-
fraction analysis.

A third general application, especially for the more fluid TEOS-B, is to
increase the density of an already formed ceramic compact by filling the pores
with silica. This was evaluated using a mullite compact produced in the previ-
ous experiment. The mullite compact which was subjected to the previously
described heating schedule up to 1500 °C was maintained at 1700 °C for 2 hr,
then cooled to room temperature. The compact was then vacuum impregnated with
TEOS-B and cured at 110 for 24 hr. After this treatment, the specimen was
heated at 500 °C for 19 hr and finally fired at 1500 °C for 2 hr. The compact
was then evaluated for density increase.

RESULTS

Synthesis

The first part of our work was devoted to the development of synthesis
conditions for useful silica precursor polymers, TEOS-A and TEOS-B, derived
from the controlled hydrolysis of tetraethoxysilane, TEOS. The influence of
various factors on the yield of these precursors was investigated.

A primary consideration was to establish the type of catalyst required to
best promote the controlled condensation polymerization of TEOS. In the ab-
sence of any catalyst, after 140 hr at 40 °C, all of the TEOS-ethanol-water
solution appeared to be lost by evaporation leaving no significant residue. It
was assumed that no polysiloxanes were produced. Addition of a basic catalyst,
aqueous ammonia, having an NH_3/TEOS mole ratio = 0.05, caused immediate precip-
itation of a white hydrous silica which remained in the beaker after unreacted
TEOS had evaporated at 40 °C. In this case, apparently, complete hydrolysis
to hydrated silica $SiO_2 \cdot XH_2O$, occurred rapidly without going through polysilox-
ane formation.

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Unsatisfactory results, in terms of polysiloxane synthesis, were also obtained using the weak acid catalyst (acetic acid). As was the case when no catalyst was added, almost all of the reactants were lost due to evaporation. On the other hand, high polysiloxane yields were observed with strong mineral acid catalysts, HCl/TEOS mole ratios 0.05 and 0.02 and HNO$_3$/TEOS mole ratio 0.05. Because of the high polymer yield, convenience in handling, availability, as well as its volatility, HCl at a concentration of HCl/TEOS = 0.05 was used as the catalyst for subsequent synthesis of TEOS-A and TEOS-B.

One of the most crucial parameters in the synthesis and isolation of TEOS-A and TEOS-B is the amount of water initially added to the alcoholic TEOS solution before the onset of condensation polymerization. A preliminary investigation to determine the optimum H$_2$O/TEOS mole ratio shows that this ratio falls in the narrow range of 0.98 to 1.10. We found that when excess water, H$_2$O/TEOS = 1.50, was added, the transition from viscous liquid linear polymer to the crosslinked thick gel and then solid took place in too short a time at 40 °C to allow for adequate recovery of the desired polymers. Conversely, when the amount of added water was not sufficient, the desired viscosity of the TEOS polymers was not reached even after a month at 40 °C. From these preliminary studies, a standard procedure for the synthesis of TEOS-A and TEOS-B was established. The viscous, adhesive, higher molecular weight TEOS-A is synthesized from an original solution comprising (mole ratio), H$_2$O/TEOS = 1.05, EtOH/TEOS = 2.0, and HCl/TEOS = 0.05. While, similarly, the lower molecular weight, more fluid, TEOS-B used less water, H$_2$O/TEOS = 0.99.

Figure 1 shows some of these results plotted as log viscosity versus time as condensation polymerization of TEOS progresses under specified conditions of initial water content and temperature. The steep slope of the log viscosity versus time curve when excess water (H$_2$O/TEOS mole ratio = 1.2) initially was added shows the rapid rate of viscosity increase. This rapid viscosity increase indicative of a fast polymerization rate made it difficult to terminate the reaction at the desired point because the transition from viscous liquid to gel was too sudden. Thus, the synthesis and isolation of TEOS-A at this water content was judged to be impractical. The same plot for the lower water content (H$_2$O/TEOS = 1.05) indicates a slower transition through the viscous stage prior to gel formation. As shown by the increasing slope of the curve, as the isolation time was approached, the extent of the reaction had to be carefully watched so that termination by rapid cooling could be accomplished prior to the onset of gel formation (crosslinking). Thus, at H$_2$O/TEOS = 1.05, TEOS-A could be readily isolated. The relatively shallow slope of the TEOS-B viscosity rate increase curve for H$_2$O/TEOS = 0.99 illustrates aging time at 40 °C was considerably longer, but far less critical than for the case for TEOS-A. The low viscosity rate increase also signifies that TEOS-B is more stable in storage. Whereas TEOS-A must be kept in a freezer, TEOS-B kept well for a long time at room temperature. The viscosity of the final product ranges from 8000 to 12 000 c.p. for TEOS-A and 150 to 200 c.p. for TEOS-B.

As expected, increasing the polymerization reaction temperature from 40 to 110 °C caused a substantial increase in the slope of viscosity versus time curves. When a sample of TEOS-A was heated at 110 °C, gel formation occurred within about 15 hr. Then from this point, the gel converted to a hard glassy solid. The conversion for TEOS-B was much slower, taking about 100 hr at 110 °C to form a stiff gel. As was the case for TEOS-A, the stiff gel transformed to a glassy solid on continued exposure to 100 °C. The fact that both

TEOS-A and TEOS-B can be thermoset at 110 °C to a crosslinked solid polymer is the basis for the ceramic processing techniques which are evaluated later in this report.

Another interesting property demonstrated in this case for TEOS-B was that the polymerization rate can be increased by the addition of more water. In this way, the rapid polymerization rate of TEOS-B resulting in eventual cross-linking could be initiated. Beginning with a TEOS-B sample which had been aged for 315 hr at 40 °C, figure 1 shows that the batch addition of water, making a total amount of water used of $H_2O/TEOS = 1.2$, resulted in a rapid viscosity increase until gellation occurred. This property indicates that TEOS-B may be used as a ceramic cement with characteristics much like an epoxy resin where the accelerator is added just prior to use. For TEOS-B, the accelerator was acidified water in ethanol solution. Unlike other organic resin systems, TEOS-A is a silica precursor that may have application as a high temperature cement for ceramics.

An interesting general finding derived from these results is the significant apparent change in the course of the condensation polymerization reactions, as indicated by the wide fluctuations in the viscosity-time relationship that took place in the narrow range of added water, at $H_2O/TEOS$ ratios of 0.99 to 1.05. This observation stresses the criticality in the amount of water used to synthesize the TEOS polysiloxanes.

A final point to be made in regard to the viscosity versus time plot in figure 1 is that the data must not be taken as quantitative in terms of a precise reproducible viscosity being obtained at the specified time. In fact, the opposite was observed, attributed to the complexity of the various interactions including control of ethanol evaporation. Poor precision was especially observed at the high water content such as in the synthesis of TEOS-A. For example, assuming an average viscosity of 100 c.p. at a specific time, the data in extreme cases would range from 50 to 150 c.p. for this same time. Greater precision however was found in the results for lower water content such as that used for the synthesis of TEOS-B where, based on an average of 100 c.p., the range varied from about 80 to 120 c.p.. We do believe, however, that the general shapes of the curves are valid indicating that the discussed trends in the data, viscosity versus time, at various water contents and temperatures are accurate. Although not investigated in detail, we found differences between two different TEOS sources. Figure 1 applies to results from Alfa 99 percent TEOS. TEOS supplied by Pfaltz and Bauer, 99 percent, gave somewhat different results, such as, requiring at least 10 percent more water to synthesize TEOS-A and TEOS-B. With these facts in mind, we strongly suggest to those investigators desiring to make TEOS-A and TEOS-B that they generate their own set of results concerning water content, viscosity, time, and temperature relationships corresponding to their particular conditions and TEOS source. Our results, however, provide a good starting point.

Some other pertinent properties of TEOS-A and TEOS-B deserve mention. In general, both polysiloxanes are nearly Newtonian fluids, especially the less viscous TEOS-B. Also, both TEOS polysiloxanes act as organic solutes in that they are completely miscible with typical organic solvents such as toluene, benzene, ethanol, and acetone, although only slightly soluble in heptane. Both TEOS-A and TEOS-B, of course, are immiscible with water.

As expected, the polymerization rate practically ceases at -5 °C; thus, both TEOS polymers may be stored for long time periods in a freezer. At room temperature, however, polymerization continued at a slow rate depending on the initial amount of water added, eventually crosslinking to a rigid gel. Although not anticipated, polymerization was observed to continue even in a dry nitrogen atmosphere and in a tightly stoppered container. We even observed continuation of the polymerization of TEOS-A when in a toluene solution in a stoppered bottle at room temperature. The phenomena was more prevalent when a slight excess of water, H_2O/TEOS = 1.10, was initially added. This result substantiates the fact that pick up of water from the atmosphere is not necessary for the continuation of condensation reactions. To illustrate specifically, when a 50 percent by volume of a TEOS-A solution in toluene was allowed to stand in a stoppered brown bottle at room temperature, a precipitate of cross-linked polysiloxane was observed after 2 weeks time.

Thermal Decomposition to SiO_2

The following section presents the results of our investigation of TEOS derived polysiloxane chemistry with emphasis on thermal properties from which SiO_2 char yields may be determined.

According to a silica material balance, there is little silica lost throughout the synthesis and pyrolysis procedure, based on the original TEOS (28.83 percent weight SiO_2) used to synthesize the TEOS polymers, to the final SiO_2 pyrolysis product at 1000 °C. This signifies that only a small amount of the original TEOS used in the forming of TEOS-A and TEOS-B was lost during the lengthy evaporation procedure at 40 °C at which time all of the ethanol evaporates leaving the polysiloxane residues. Although monomeric TEOS is a volatile liquid in the ordinary sense (boiling point 166 °C), as soon as water containing the acid catalyst (HCl) is added to the ethanol solution of TEOS, condensation must begin immediately with the formation of nonvolatile silanols. This was verified by the observation of a mild exotherm soon after addition of the acidified water. For example, starting with 1 mol of TEOS (208 g), which has a calculated char yield of 1 mol of SiO_2 (60.1 g), the weight of TEOS-A produced was about 104 g with a SiO_2 char yield of 55.09 percent (57.27 g) as determined from the weight of SiO_2 residue found at the end of pyrolysis at 980 °C. Thus, beginning with the equivalent of 1 mol of SiO_2, we end with the ignited residue of 0.917 mol SiO_2, making a SiO_2 loss of 0.083 mol. From this, it follows that the system affords high SiO_2 yields with no significant waste of TEOS. High product yield from simple processing steps is typically a major advantage for practical ceramic fabrication.

Thermal decomposition data for TEOS-A and TEOS-B in terms of weight loss versus temperature are plotted in figures 2 and 3. In the incremental decomposition (fig. 2), the sample was maintained at the indicated temperature for a specified time in air, then rapidly increased to the next indicated temperature and held there for a certain time, the procedure being repeated until 980 °C was reached where only SiO_2 remains. Beginning at room temperature with liquid TEOS-A and TEOS-B and maintaining the two samples at 115 °C for 200 hr caused solidification of the two liquids to a hard glassy solid. During this transition, condensation crosslinking of the linear polysolxane took place with the splitting off of water and possibly some ethanol as indicated in equations (4) and (5). This loss of water and ethanol resulted in a weight loss of

17.85 wt % for TEOS-A and 9.78 wt % for TEOS-B. The greater weight loss for TEOS-A is probably a consequence of a higher OH moiety concentration in the polysiloxane molecule which leads to the removal of a greater amount of OH groups in water formation as well as ethoxy groups lost as volatile ethanol.

A relatively large weight loss was observed for both polymers after 24 hr at 200 °C. At this temperature the condensation crosslinking was complete so that polymer degradation and oxidation was taking place with the removal of organic ethoxy groups. After heating at 300 °C for 24 hr, almost all organics were removed leaving a residue of SiO_2 containing some hydrated silica as well. The total weight loss up to this point is 41.46 percent for TEOS-A and 44.57 percent for TEOS-B. No well defined x-ray diffraction pattern was obtained after 24 hr at 500 °C. Thus we assume that the white fluffy material observed at this point was essentially amorphous silica. Between this increment and 24 hr at 980 °C, only a very slight weight loss was seen. This slight change is attributed to the loss of small amounts of combined water in the silica. The residue final product was assumed to be pure SiO_2. The char yield calculated from the total weight loss of 44.91 percent for TEOS-A and 47.57 percent for TEOS-B is

$$TEOS-A: \quad 100.00 - 44.91 = 55.09 \text{ percent}$$

$$TEOS-B: \quad 100.00 - 47.57 = 52.43 \text{ percent}$$

An important observation having a bearing on processing techniques which require uncontaminated SiO_2 is that rapid firing of solid crosslinked TEOS polymers from 115 to 980 °C in less than 6 hr resulted in the formation of a black glass. Apparently, a carbonaceous residue which formed on quick decomposition of the polymers was incorporated in a glassy network which protected it from atmospheric oxidation. This black material was difficult to burn off even at 1000 °C. With this in mind, processing for highest purity SiO_2 should involve a slow temperature rise treatment with long holding times at certain temperatures especially below 500 °C.

The scanning TGA which measured weight loss versus temperature at a heating rate increase of 2 °C/min (fig. 3) showed a similar trend as was observed for the incremental results. An important difference in procedure was that, because of the difficulty in loading and processing the sticky liquid TEOS-A sample in the TGA, the TEOS-A was first solidified by crosslinking. Since the TGA began with the powdered crosslinked polysiloxane, the 100 percent weight in figure 3 corresponds to the sample from the 115 °C point on the incremental pyrolysis plot of figure 2. In the continuously increasing temperature mode of a TGA, decomposition did not begin until about 200 °C. Above this point a major weight decrease was observed which leveled off above 320 °C. This trend is similar to the incremental weight loss curve in figure 2 where most of the weight loss occurs in the same region. This indicates that the polysiloxane polymer can be completely degraded by a long exposure in air at 320 °C. The weight change from the solid polysiloxane to SiO_2 at 799 °C, the maximum temperature of the TGA scan, is 34.96 percent corresponding to a char yield 65.06 percent SiO_2. Taking into account that we started with the crosslinked polymer instead of the original TEOS-A, the char yield based on the original TEOS-A would be 53.45 percent SiO_2. This value is in good agreement with the 55.09 percent char yield calculated from the incremental pyrolysis. The 55.09 percent char yield is probably more accurate because of the considerably

larger samples used, 20 g versus about 17 mg (TGA) in the incremental analysis. A cause for these minor discrepancies in the two char yields may be due to small variations in composition of the TEOS-A samples from batch to batch.

Application Evaluation

Now that we have some background data on the chemistry and some important physical properties of TEOS-A and TEOS-B, we are in a position to present examples of the potential use of these materials in actual ceramic processing.

The sticky, adhesive properties of TEOS-A imply its use as a binder for ceramic oxide powders for the fabrication of ceramic articles. In most cases, organic polymers are used for this purpose, but an inherent objection to purely organic binders is that their binding properties are lost after burn off and before sintering; thus, compacts of poor mechanical strength are produced. In contrast to the organic polymers which leave no char residue after firing, polysiloxanes derived from TEOS-A binder deposit active amorphous silica between the oxide particles which allows reaction bonding via silicate formation at a relatively low temperature; thus, the compacts remain intact up to and after the final firing sequence. In addition, the use of polysiloxane polymers, because of their significant silica char formation, should cause less pyrolytic shrinkage than an equal amount of a zero char yield organic binder. The complete loss of organic binders as volatile organic compounds shows up as a large weight loss, plus shrinkage and/or porosity.

For this first application, we chose Corning 7913 which is essentially SiO_2 for the ceramic powder with TEOS-A as the binder. Weight loss, shrinkage, and density data at increasing heat treatment stages are given in table I. The compact cold pressed at 10,000 psi derived from 15 g of TEOS-A per 100 g of Corning 7913 gave a high quality green body, thereby showing the good adhesive properties of TEOS-A for refractory oxides. When the green body compact was heated at 120 °C for 96 hr, the binder thermoset to a hard polysiloxane bonded solid. At this point the compact was comprised of an oxide powder held in a solid polymer matrix which could be handled readily without damage or material loss. As expected, a slight weight loss was noticed without sample shrinkage. This weight loss was attributed to polymer decomposition. The compact was heated gradually in air to 1000 °C, including a 5 hr hold at 350 °C; the total time from 120 to 1000 °C was about 20 hr. A gentle temperature increase was used to avoid black glass formation. The compact was then kept at 1000 °C for 10 hr. The major weight loss was observed at this point due to polymer decomposition with the formation of SiO_2 and elimination of organics with a small amount of shrinkage and densification. The compact still had good mechanical properties because the amorphous silica that formed around the oxide grains cemented them together. During the 1300 °C heating step, the major part of the densification and shrinkage occurred with an almost negligible weight loss. Total weight loss from the original green body to the final densified compact of 93.3 percent theoretical density was 6.23 percent with a linear height shrinkage of only 3.82 percent. Both percentages are based on the original green body compact. The high density and low shrinkage of the compact without hot pressing and its good handleability in all stages of firing makes the use of TEOS-A promising for making silicate compacts by the method outlined.

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A supplemental use derived from the previous example, which we have not explored quantitatively, is to use TEOS-A to make a moldable putty. This is accomplished by mixing enough TEOS-A with a powdered ceramic oxide such as Corning 7913 to form a pliable dough. This would require somewhat more than the amount of TEOS-A, 15 g per 100 g of Corning 7913, necessary to make the compact described previously. The putty like material thus produced can be shaped either by pressing in a mold or by hand shaping. The preformed objects are then heat treated as described for ceramic compacts. If the ceramic powder is Corning 7913, the heat treatment follows that described in the text and shown in table I. In this way complex ceramic shapes can be produced.

The second potential application illustrates a dual function of the TEOS derived polymers. This application involves the use of TEOS-B as a source of silica for the formation of mullite, $3Al_2O_3 \cdot 2SiO_2$, and, in addition makes use of TEOS-A, as described previously, as a binder. Density and shrinkage data after indicated temperatures are given in tables II and III for fumed alumina and alumina polishing powder, respectively. SEM photographs in figure 4, comparing the two types of alumina, clearly show that the fumed powder is considerably more porous, thus having a larger surface area than the polishing powder. By comparing the data in tables II and III for both grades of alumina, it becomes apparent that the fumed alumina, with its larger surface area, affords better thermal densification characteristics than the polishing powder. After similar temperature treatments, the fumed alumina always provided a higher density. After the final treatment at 1700 °C, the final theoretical density for the fumed alumina specimen was 91.4 percent whereas the final theoretical density for compacts made with alumina polishing powder was only 75.2 percent.

Another advantage of high surface area oxides is that solid state reactions are more readily facilitated. A cold pressed compact derived from the TEOS polymers and fumed alumina in mullite stoichiometry, maintained at 1200 °C for 10 hr provided an almost exclusive x-ray diffraction pattern for mullite; whereas, under the same conditions, a sample made from alumina polishing powder showed unreacted alpha Al_2O_3, not mullite, as the major phase. It should be stated, however, that after exposure to 1500 °C for 8 hr, mullite became the major component according to x-ray diffraction. Also, compacts made from fumed alumina showed slightly more shrinkage than those made from alumina polishing powder. A brief account of the pyrolysis scheme shows similarity with the previous results for Corning 7913. That is, during the first step, after a pre-heat treatment at 350 °C for 10 hr to avoid black glass formation, most of the overall weight loss occurred as a result of organic burn off of the TEOS-A binder with only slight shrinkage. At higher temperature, most of the shrinkage was noted with a relatively low weight loss. An important concluding insight gained from these results is the recommendation that oxides of high surface area be used to fabricate reaction bonded silicate articles from TEOS precursors.

A last potential application of TEOS derived precursors, especially the more fluid TEOS-B, is to infiltrate already formed porous ceramic compacts in order to increase their density without effecting shrinkage. To evaluate this, a ceramic oxide article consisting of partially densified Mullite was immersed in TEOS-B and vacuum infiltrated with this liquid. In this way the liquid SiO_2 precursor became absorbed in the pores of the compact. The compact, with the absorbed TEOS-B was first cured at 110 °C for 24 hr to thermoset the polymer and then fired at above 500 °C to deposit amorphous SiO_2 in the pores.

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The process was repeated to deposit additional amounts of SiO_2 in the pores. On firing at higher temperature, the SiO_2 reacted with the ceramic oxide article.

The density increase of a mullite compact after a single impregnation with TEOS-B is shown in figure 11. A somewhat porous mullite compact, which had already been fired at 1700 °C for 2 hr, was cooled to room temperature, vacuum impregnated with TEOS-B, then cured at 110 °C for 24 hr, preheated at 350 °C for 12 hr, and finally fired at 1500 °C for 2 hr. This one shot treatment increased the density from 2.67 to 2.75 gm/cm^3 or, in terms of theoretical density, from 84.8 to 87.3 percent based on the density of mullite, 3.15 gm/cm^3. Repeating the infiltration procedure would most likely lead to a further density increase. Of course, the final compact composition would be slightly rich in silica.

SUMMARY OF RESULTS AND CONCLUDING REMARKS

Two new useful silica precursors, highly viscous TEOS-A and the more fluid, TEOS-B were prepared by the controlled hydrolysis of tetraethoxysilane, TEOS. The synthesis of these polysiloxane precursors depends, most critically, on the accurate weight of water added per mole of TEOS used. The weight of water added must include the amount present in the aqueous HCl catalyst as well as the water present in the ethanol cosolvent if 190 proof alcohol is used instead of absolute ethanol. We have even found that different sources of TEOS vary in their hydrolysis properties; thus, with any given supplier of TEOS, it is advisable to generate an independent set of data for viscosity versus time at various water contents. This is necessary to establish precise H_2O/TEOS ratios for optimum TEOS-A and TEOS-B properties. Our data, shown in figure 1 for TEOS, 99 percent supplied by Alfa Products, serves as a guide to the synthesis and properties of the polysiloxanes. TEOS supplied by other companies should give only minor deviations from our results.

The examples given in this report represent first time applications of TEOS-A and TEOS-B to ceramic fabrication and, as such, should be considered a preliminary exploration with no previously reported background work. Both TEOS-A and TEOS-B are good sources of pure SiO_2, with high char yields, about 55 and 52 percent respectively. When properly fired in air both polymers leave a pure SiO_2 residue free of carbon and other oxides. Although pure SiO_2 can be obtained with sol gels, the yields are considerably lower (about 12 percent) and they lack those desirable properties of the TEOS derived polysiloxanes; sol gels are colloids whereas TEOS derived polysiloxanes are Newtonian fluids. Because of their colloidal nature, sol gels would not be useful for most of the applications discussed here.

The tackiness of TEOS-A makes it a good binder for oxide powders; such green bodies have excellent cold pressed handleability. Firing of these green bodies form dense compacts of oxide particles bonded together by silicate, or in the event that SiO_2 is the oxide, powder firing results in a monolithic compact.

A moldable putty, from which complicated ceramic shapes can be fabricated, is made by adding enough TEOS-A to the finely divided oxide powder to provide the desired consistency. The fabricated green body is then fired to convert

the mixture to a ceramic silicate, or if SiO_2 powder is used, the fired shape is a SiO_2 monolithic.

The more fluid TEOS-B may be conveniently used to infiltrate already fired porous ceramic objects. The porous ceramic shape is vacuum infiltrated with TEOS-B, then fired thereby filling the pores with SiO_2 or silicate. The process may be repeated until the pores are almost complete filled.

Presented here are just a few general applications of TEOS derived polymers. Future investigation should uncover other interesting uses of these materials.

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TABLE I. - HEAT TREATMENT, DENSIFICATION, OF CORNING 7913
(96 PERCENT SiO_2) - TEOS-A COMPACTS

[Cold pressed cylinder at 70 MPa; height, 2.25 cm; volume, 6.4132 cm^3. Green body composition, 15 g TEOS-A/100 g of Corning 7913. Corning 7913 (96 percent SiO_2); Sp. Gr. 2.18; Softening point, 1585 °C.]

Temperature, °C (hr)	Weight loss, percent	Height shrinkage, percent	Volume shrinkage, percent	Density, g/cm^3	Theoretical density, percent[a]
25	0	0	0	1.84	84.5
120 (96)	0.89	0	0	1.83	83.9
1000 (10)	6.19	1.56	6.76	1.85	85.0
1300 (8)	6.23	3.82	15.09	2.03	93.3

[a]Calculated from the ratio of the determined density and the theoretical density (2.18 gm/cc) of Corning 7913.

TABLE II. - HEAT TREATMENT, DENSIFICATION OF FUMED
Al_2O_3 + SiO_2 + TEOS-A COMPACTS

[Total composition, $3Al_2O_3 \cdot 2SiO_2$ (mullite), cold pressed cylinder at 70 MPa; height, 2 cm; diameter, 2.5 cm. $3Al_2O_3 \cdot 2SiO_2$ theoretical density, 3.15 g/cm^3.]

Temperature, °C (hr)	Weight loss, percent	Height Shrinkage, percent	Volume shrinkage, percent	Density, g/cm^3	Theoretical density, percent
110 (96)	0	0	0	1.52	-----
1000 (19)	5.11	2.52	8.32	1.58	50.2
1500 (6)	5.49	13.6	35.8	2.25	71.4
1700 (2)	6.06	18.4	46.0	2.67	84.8
				[a]2.75	[a]87.3
1700 (8)	6.09	22.0	49.7	2.88	91.4

[a]After firing at 1700 °C for 2 hr, sample compact was cooled to room temperature, then vacuum infiltrated once with TEOS-B then fired again at 1500 °C for 2 hr. The density increased as shown.

TABLE III. - HEAT TREATMENT, DENSIFICATION OF Al_2O_3 POLISHING POWDER
+ SiO_2 + TEOS-A COMPACTS

[Total composition, $3Al_2O_3 \cdot 2SiO_2$ (mullite), cold pressed cylinder at 70 MPa; height, 2 cm; diameter, 2.5 cm.]

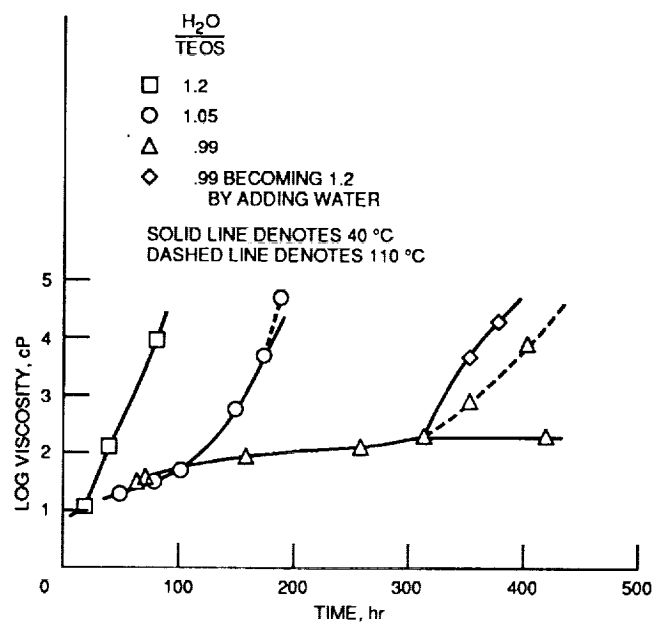| Temperature, °C (hr)	Weight loss, percent	Height Shrinkage, percent	Volume shrinkage, percent	Density, g/cm^3	Theoretical density, percent
110 (96)	0	0	0	1.42	----
1000 (19)	4.91	2.95	9.22	1.48	47.0
1500 (6)	5.27	10.8	28.7	1.88	59.7
1700 (8)	5.70	17.1	43.7	2.37	75.2

Figure 1. - Rate of viscosity increase of TEOS polysiloxane polymers at different water additions. HCℓ/TEOS = 0.05; and EtOH/TEOS = 2. After aging the 0.99 H_2O/TEOS polymer at 40 °C for 315 hours, additional water was added to obtain H_2O/TEOS = 1.2.
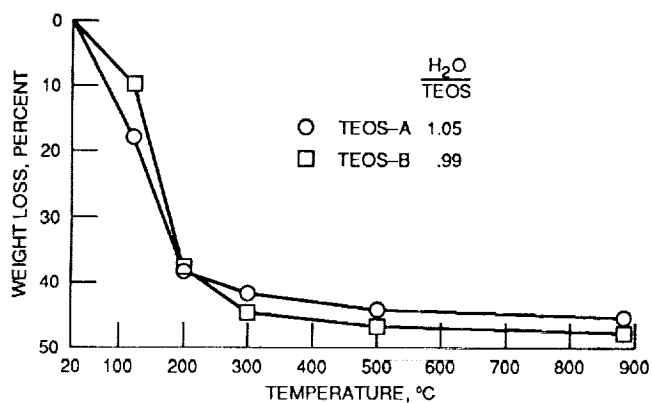

Figure 2. - Weight loss with respect to temperature during incremental pyrolysis of TEOS-A and TEOS-B.
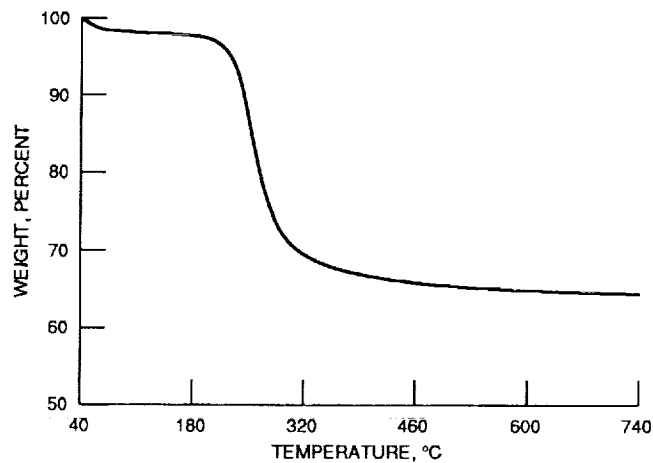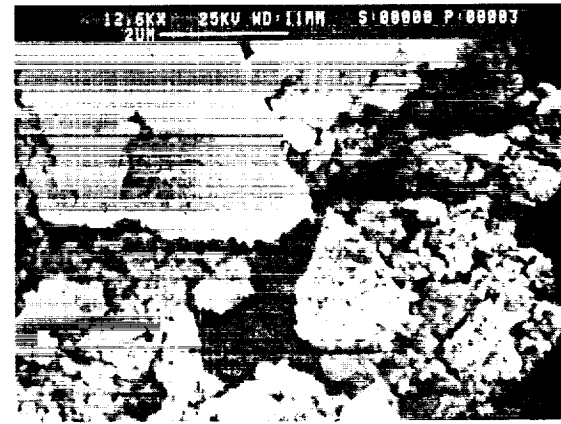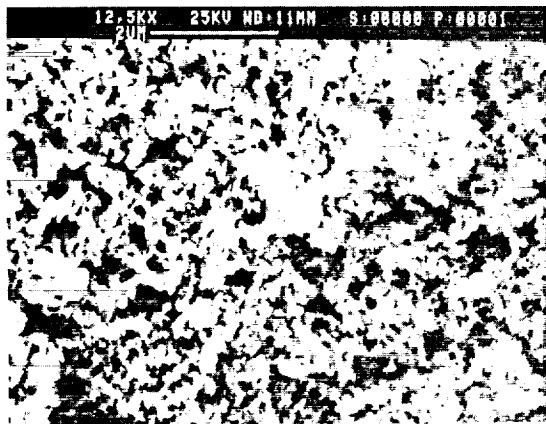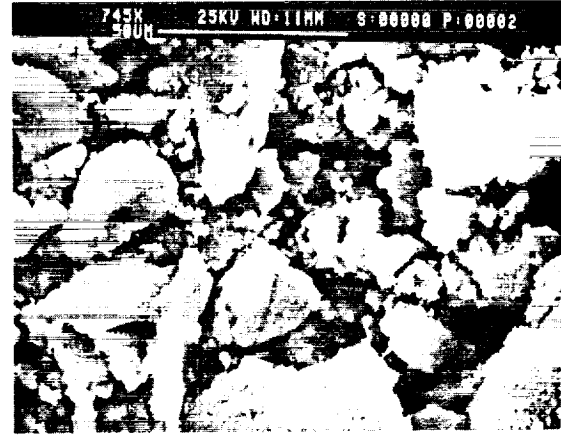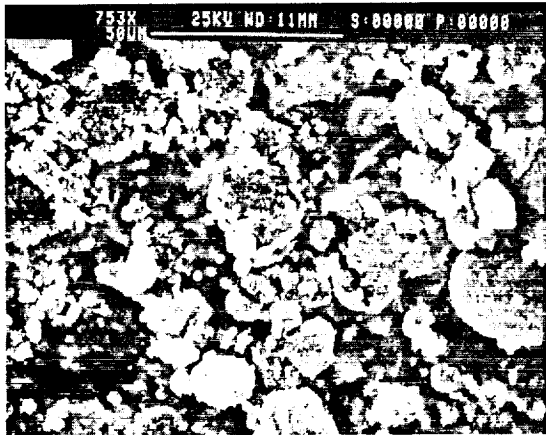

Figure 3. - TGA curve of TEOS-A after thermoset and cured at 115 °C for 100 hours. Weight: 16.8392 mg; rate: 2.00 degrees/min.

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ORIGINAL PAGE
BLACK AND WHITE PHOTOGRAPH

(a) Alon fumed alumina.

(b) 0.05-μm linde alumina polishing powder.

Figure 4. - SEM photographs of fumed aluminum oxide and 0.05-μm polishing powder aluminum oxide.

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15. Supplementary Notes

16. Abstract

Synthesis, properties, and potential applications in ceramic processing for two polysiloxane silica precursors derived from the controlled hydrolysis of tetraethoxysilane (TEOS) are presented. The higher molecular weight TEOS-A is a thick adhesive liquid of viscosity 8000 to 12 000 c.p. having a SiO_2 char yield of about 55 percent. The lower molecular weight TEOS-B is a more fluid liquid of viscosity 150 to 200 c.p. having a SiO_2 char yield of about 52 percent. The acid catalyzed hydrolysis of TEOS to hydrated silica gel goes through a series of polysiloxane intermediates. The rate of this transition increases with the quantity of water added to the TEOS; thus, for ease of polymer isolation, the amount of water added must be carefully determined so as to produce the desired polymer in a reasonable time. Excess water must be avoided to prevent too short a gelation time. The water to TEOS mole ratio falls in the narrow range of 1.05 for TEOS-A and 0.99 for TEOS-B. Further polymerization or gelation is prevented by storing at −5 °C in a freezer. Both polysiloxanes thermoset to a glassy solid at 115 °C. The liquid polymers are organic in nature in that they are miscible with toluene, and ethanol, slightly soluble in heptane, but immiscible with water. For both polymers, results on viscosity versus time are given at several temperatures and water additions. Also their thermal decomposition properties are discussed. Based on these results, some examples of practical utilization of the precursors for ceramic fabrication are given. These examples include use of TEOS-A as a binder for the formation of an oxide ceramic compact. Good green body properties were obtained after cold pressing and up to the final sintering. Curing at 115 °C produced an oxide bound by a solid polymer matrix. At higher temperature, the oxide particles are held together via reaction bonded silicates formed from SiO_2 derived from the pyrolysis of TEOS-A. A second example involves the use of TEOS-B as a precursor to SiO_2, which when mixed with high surface area alumina and fired forms mullite. TEOS-B in a third application may be used to infiltrate already formed ceramic bodies. The formation of SiO_2 and silicates in the pores on firing serves to increase density without effecting shrinkage.

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