

**STRUCTURE/PROPERTY BEHAVIOR OF INORGANIC/ORGANIC
SOL-GEL DERIVED HYBRID MATERIALS**

by

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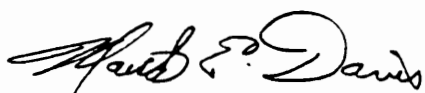
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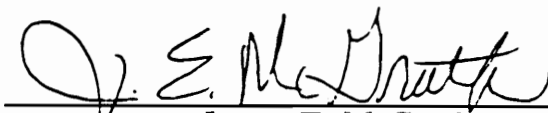
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(ABSTRACT)

A novel class of inorganic/organic hybrid materials referred to as CERAMERs have been successfully prepared by a sol-gel process using a polymeric acid catalyst, poly(styrene sulfonic acid), to form a network from tetraethylorthosilicate (TEOS) and triethoxysilane end capped oligomers of poly(tetramethylene oxide) (PTMO). The structure-property relationships were determined for these hybrid networks from their dynamic mechanical behavior, mechanical properties, and SAXS behavior. Thermal gravimetric data coupled with FTIR analysis were used to obtain a qualitative measure of the extent of conversion of the metal alkoxides as a function of acid catalyst.

Another new class of CERAMERs was successfully developed by the sol-gel processing of three different metal alkoxides in conjunction with the triethoxy silane end capped PTMO oligomers. The first novel hybrid is based upon complexes of aluminum tri-n-butoxide with ethyl acetoacetate or titanium tetra-iso-propoxide with ethyl acetoacetate reacted with the triethoxysilane end capped PTMO. The

hybrid networks were optically clear and could be easily formed as relatively large monoliths. A novel method of preparation of stable sols without the use of ethylacetoacetate, developed by Dr. Bing Wang in this laboratory, led to more stable CERAMERS of titanium tetra-iso-propoxide (TiOPr) reacted with the functionalized PTMO as well as a fourth inorganic/organic hybrid material based upon zirconium tetra-n-propoxide and PTMO. Indeed, the mechanical properties of the TiOPr/PTMO CERAMERS and ZrOPr/PTMO CERAMERS were significantly enhanced over the TEOS/PTMO CERAMERS in terms of both Young's modulus and stress at break. The structure-property relationships of these materials were adequately described by the morphological model originally developed for the CERAMERS based upon TEOS/PTMO.

Polyimides have been functionalized with the triethoxysilane group for successful incorporation into a hybrid network using either TEOS or TiOPr. The nature of the oligomer structure as well as the synthetic route to the triethoxysilane functionalized oligomers were analyzed in terms of thermal stability and SAXS behavior.

to my family

ACKNOWLEDGEMENTS

The pursuit of knowledge and understanding of the structure/property relationship of polymeric based systems led me to Virginia Polytechnic Institute & State University and the guidance of Professor Garth L. Wilkes. The reputation of the faculty and this university have achieved the highest standards in my opinion. The members of my committee as well as the numerous other faculty and staff members of VPI&SU have demonstrated a level of excellence in both the pursuit and communication of knowledge never before witnessed by me. They have shown me that my knowledge is limited only by my imagination and effort.

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CHAPTER 1

INTRODUCTION

1.1 The Sol-Gel Process

The typical ceramic is produced by blending metal oxides and carbonates in a dry form or slurry followed by thermal treatments to temperatures exceeding 2000°C. The sol-gel process is a series of chemical reactions that together convert a soluble metal alkoxide into a ceramic at relatively low temperatures [1]. The sol-gel process on the other hand produces ceramic structures that only require thermal processing to temperatures of ca. 600°C to 1000°C [2]. This is accomplished by the chemical reactions which metal alkoxides will likely undergo, i.e. hydrolysis and condensation, at low temperatures, i.e. 20°C, although the extent of conversion will be limited by vitrification.

A general representation of the sol-gel reactions is given in Figure 1-1 for one of the most commonly studied metal alkoxides - tetraethylorthosilicate (TEOS) [1], where R is C_2H_5 . There are equilibria indicated for each of the three reactions, yet, it should be understood that numerous factors control their net direction. Indeed, a large portion of the sol-gel literature has been devoted to the study of the variables that control the reactions of the sol-gel process [1]. There are at least two other key components of the sol-gel process, a catalyst and the solvent, which are not listed in Figure 1-1, but are typically used. The catalyst, either an acid or a base, determine the reaction kinetics as well as the final gel structure. The solvents which can be protic, aprotic, polar, etc., are required to provide mutual solubility of the metal alkoxide and the water [1,2,3,4]. The role of the solvent in the sol-gel process varies as a function of the pH of the reaction solution. Water is both a reactant and a product of the sol-gel process and thus the actual pH of the reaction is in a constant state of flux.

The sol-gel derived structure is dependent upon all of the variables listed above and more, including temperature, pressure and time. The level of water added initially will determine the extent of hydrolysis prior to condensation. A low level of hydrolysis of the alkoxides stimulates the formation of linear structures with little to no branching. The opposite of this is high levels of hydrolysis promote branching [5]. Thus, there are distinct differences in the final structure and properties of the materials simply as a function of the water content [1,5,6,7]. The pH of the

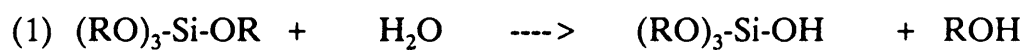
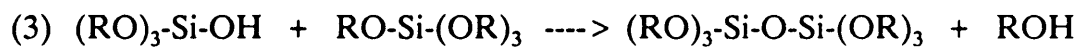
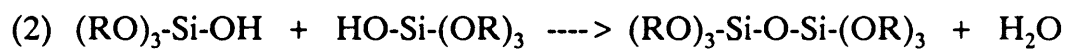
HYDROLYSIS:**CONDENSATION (TWO POSSIBLE REACTIONS):**

Figure 1-1 Simplified Sol-Gel Process

solution has been shown to regulate the role of water in the sol-gel process. The kinetics of sol-gel processing at a low pH are dependent upon the level of water [1]. However, as the reaction pH is increased to above the isoelectric point of, for example TEOS, the reaction rates become much less dependent upon the amount of water supplied. The morphology of the structures formed are distinctly different for the low and high pH conditions [1,8,9,10]. The dependency of structure on water and pH can be extended to the other variables such as the metal alkoxide structure, the solvent, the catalyst, and the reaction temperature [7,10,11,12].

The metal alkoxide is most likely the most significant variable in the sol-gel process [1]. The electropositivity of the metal will determine the overall reactivity of the metal alkoxide. Most evidence available today indicates that the sol-gel process begins by nucleophilic attack on the metal [1]. Thus both the electropositive metal and electronegative alkoxide will determine the overall reactivity of the metal alkoxide. This will control the kinetics of the sol-gel process and the final structure as previously indicated. The solvents can enhance the reactivity of the metal alkoxide by charge stabilization through various mechanisms [1]. But, the metal alkoxide determines the reactivity and thus the structure of the gel.

Monolithic structures are difficult to obtain by sol-gel processing of metal alkoxides [6]. The stoichiometry of the sol-gel process is not indicated in Scheme I, but one will note that for each mole of metal alkoxide hydrolyzed and condensed, there are four moles of alcohol produced and a net of two moles of water released.

The reduction in mass is significant. The removal of the solvent typically involves evaporation and mass transport by capillary action. The associated forces are large and typically cause fractures of the three dimensional inorganic network [1,13]. Drying control chemical agents (DCCA) and special processes at supercritical conditions have been employed successfully to obtain monoliths from sol-gel processed materials [14].

1.2 Organic/Inorganic Hybrid Materials

The definition of organic/inorganic hybrid materials in the context of this work will be rather narrow in scope. An organic/inorganic hybrid material is one prepared by the sol-gel process using a metal alkoxide and a metal alkoxide functionalized organic molecule. Those familiar with the science of silane coupling agents will recognize their use with fillers are the first examples of an inorganic/organic hybrid. A functionalized organic molecule, i.e. isocyanatopropylene, is reacted with triethoxysilane to produce a silane coupling agent (an extensive listing is available in reference [1]). Indeed, the silane coupling agents have been applied to a wide variety of fillers, both inorganic and organic, to achieve a covalent bond between the matrix and filler. The alkoxide portion of the silane coupling agent is reactive toward surface silanols whereas the organo functional group can be selected from a variety of reactive species, i.e. epoxide,

acrylate, isocyanate etc.. The silane coupling agents have improved the performance of fillers. The alkoxide functionality of the silane coupling agents have also been used to enhance bonding of numerous substrates that exhibited poor adhesion previously.

Professor Helmut Schmidt was one of the first (publicly anyway) to extend the performance of the silane coupling agents to produce organic/inorganic hybrid materials by the sol-gel process [15]. The silane coupling agents are typically applied to filler particles which are then blended in with the matrix resins. Schmidt produced the filler phase of his system, commonly referred to as ORMOSILs, (these materials have been renamed ORMOCERs within the last year) in situ by the sol-gel process. The inorganic phase composition was controlled by the metal alkoxides employed. The organo functionality of the silane coupling agent was matched to the matrix resin to be used. The second step of Schmidt's process was to combine the inorganic phase with the matrix resin and form a network by catalyzing the reactive organo functionalities.

Professor Garth L. Wilkes successfully developed a novel class of organic/inorganic hybrid materials commonly referred to as CERAMERs [16,17,18,19]. The properties were both ceramic like and polymer like which is the derivation of the term CERAMER. Wilkes' approach was to functionalize oligomers (either organic or inorganic) with metal alkoxides. The functionalized oligomers were then combined with metal alkoxides by a sol-gel

process. The hybrid networks produced in this manner are typically monolithic and optically clear. The relative volume fraction of each component as well as the chemical structure of the functionalized oligomer determines the ultimate properties of this novel class of organic/inorganic hybrids.

Another approach to producing organic/inorganic hybrid materials by the sol-gel process has been reported by a number of groups. Mark et. al. have swollen networks of poly(dimethylsiloxane) (more recently poly(phenylmethylsiloxane) with metal alkoxide solutions and then catalyzed the sol-gel reaction to form inorganic particles within the network [20,21]. Mauritz et. al. have prepared hybrid materials in a similar fashion using perfluorosulfonic acid films (Nafion) [22]. Parkhurst, et. al. combined poly(dimethyl siloxane) oligomers with TEOS and titanium isopropoxide to form hybrid networks similar to Wilkes CERAMERs [23]. Each of these systems represent organic/inorganic hybrid materials that exemplify the opportunities the sol-gel process offers in terms of developing new materials.

1.3 Research Objectives

The primary objective of the research presented here was to develop a better understanding of the structure-property relationships that determine the behavior of CERAMERs. A significant contribution to this objective has been made through the efforts of others that have preceded this work

[16,17,18,19,24,25,26,27,28,29]. It was therefore essential to design systems that could add to a well established foundation of information which describes the structure-property behavior of CERAMERs.

A number of goals were established that were considered important in achieving the ultimate objective of this research project. The first was to evaluate the effectiveness of a polymeric acid catalyst in promoting the formation of the CERAMERs prepared with TEOS and poly(tetramethylene oxide) oligomers which were end capped with isocyanatopropyltriethoxysilane (PTMO) [19,24,25,26]. It was believed that a catalyst supported on a polymer would have a lower potential to migrate. The migration of catalytic species (H^+ , Cl^-) were believed to contribute, in part, to the aging behavior identified in these hybrid materials [27,30]. The addition of the catalyst in the form of a high molecular weight polymer was also considered important in terms of the rheology of the CERAMER sols.

A second goal set for this research was to produce CERAMERs in which the total amount of TEOS would be replaced by other metal alkoxides, i.e. titanium isopropoxide and zirconium isopropoxide (The nomenclature that has been developed for these two materials is TiOPr and ZrOPr, respectively. This shorthand notation was better suited for the CERAMER nomenclature system previously developed) [17]. Earlier work by Glaser [27] demonstrated improvements in the mechanical properties of CERAMERs prepared by the incorporation of TiOPr in TEOS/PTMO systems.

A third goal of this project was the substitution of PTMO in CERAMERS with a high modulus, thermally stable polyimide. The polyimide should improve the thermo-oxidative stability of these hybrid materials. The incorporation of a polyimide in these hybrid organic/inorganic networks should also enhance their abrasion resistance for use as protective coatings. Noell et. al. successfully produced hybrid systems of TEOS and functionalized oligomers of poly(arylene ether ketones) (PEK) [29]. The processing conditions for the TEOS/PEK CERAMERs were quite different from the methods used for the preparation of TEOS/PTMO CERAMERs [24,29]. The major emphasis of the incorporation of the polyimides into the sol-gel derived hybrid network was to develop procedures for producing monolithic structures.

CHAPTER 2.0

LITERATURE REVIEW

2.1 Introduction

A comprehensive study of sol-gel science has recently been completed by Brinker and Scherer [1]. This resource in addition to other review articles more than adequately summarizes the volumes of literature dealing with sol-gel processing of materials which has been published in the last 20 years [3,31,32,33]. It, therefore, becomes redundant to describe in complete detail the literature with references to sol-gel processing. This literature review will present the most widely accepted views (as this author believes them to be) of the sol-gel process. An attempt has been made to relate the chemistry with the structures produced. There are three general headings that the sol-gel process will be organized under for purposes of this literature review (Table 1-1). The three categories listed in Table 1-1 are based upon the variables that are considered to be the most critical in sol-gel processes. The first category, 'Chemical Reactions', lists the five reactions that

typify the sol-gel process [1]. These will be described in more detail in section 2.2. The variables that determine the net direction of the chemical reactions and their kinetic rate constants are listed under the heading 'Processing Variables' in Table 1-1. The processing variables will be described in section 2.3 in terms of their influence on the Chemical Reactions and the Structural Factors. The third category "Structural Factors" is a broad summary of the elements that one must consider in terms of all the variables listed and those that do not fit neatly into either of the other two categories. The "Structural Factors" will be reviewed in both sections 2.2 and 2.3. review of the sol-gel derived structures will be presented in section 2.4. The categories listed in Table 1-1 are useful for the purpose of this literature review, but is not intended as a complete description of the very complex sol-gel process.

2.2 Chemical Reactions

A general, simplified scheme for the sol-gel process of TEOS was illustrated in Figure 1-1. The sol-gel process as previously alluded to is actually a very complex series of equilibria that are not totally understood. Figure 2-1 depicts all of the various reactions considered a part of the overall sol-gel process. The reactions portrayed in Figure 2-1 are believed to accurately represent the sol-gel processing of TEOS in an aqueous alcoholic system. The catalyst is omitted as well as the solvent since inclusion of either will bias the reaction equilibria and compound the

Table 2-1 Variables of sol-gel process

CHEMICAL REACTIONS	PROCESSING VARIABLES	STRUCTURAL FACTORS
Hydrolysis	Catalyst	Metal
Water Condensation	pH	Alkoxide
Alcohol Condensation	Stoichiometry	Steric Effect
Esterification	Concentration	Inductive Effect
Alcoholysis	Solvent	
	Temperature	
	Pressure	

complexity of the process.

The overall stoichiometry of the sol-gel processing of TEOS is described by reaction 8 [1]. There are four moles of water consumed and two moles of water released per mole of TEOS condensed. A net total of four moles of the alcohol are generated by the complete condensation of one mole of the metal alkoxide, TEOS. There is a net loss of four moles of solvent with the complete hydrolysis and condensation of each mole of metal alkoxide, assuming four alkoxides per metal atom as is the case for TEOS. Thus, there is a large reduction in mass associated with the hydrolysis and condensation of metal alkoxides. It has been shown that a typical sol-gel process at ambient conditions does not proceed beyond ca. 90% conversion of all metal alkoxides [1,34].

Hydrolysis is the first step in a sol-gel process using silicon alkoxides. The hydrolysis reaction requires one mole of water. One mole of alcohol is liberated for each mole of water consumed in the hydrolysis reaction depicted by reactions 1 through 4 in Figure 2-1. The silanol generated by the hydrolysis reaction is capable of undergoing a condensation reaction with another silanol to form a siloxane bond and release one mole of water (reaction 5, Fig. 2-1). The silanol can also undergo nucleophilic attack by an alkoxide to create the siloxane bond and one mole of alcohol (reaction 6, Fig. 2-1). The reaction pathway that the silanol follows is dependent upon the variables listed under the categories "Processing Variables" and "Structural Factors" (Table 1-1). The condensation reactions (reactions 5 through 7,

Fig. 2-1) resemble the chain propagation steps of a "Step-Growth Polymerization" [35]. This assumes of course the condensation reactions are not reversible. It has been shown, however that each of the reactions in Fig. 2-1 are reversible under certain conditions. Iler [1] and more recently Klemperer et. al. [36] report that there is a strong tendency for alcoholysis of the siloxane bond if the reaction pH is above the isoelectric point of TEOS (i.e pH > 2.0 to 2.3). The explanation of this behavior will be presented in detail in section 2.4. The net reactions defined by the left and right arrows in Fig. 2-1 are dependent upon the variables described by "Process Conditions" in Table 1-1. The reverse reactions are less significant under acidic conditions compared with high pH conditions. (High and low pH conditions are stated with respect to the isoelectric point of TEOS which as previously stated is approximately 2.0.)

The sequence of the reactions as illustrated in Fig. 2-1 does not accurately represent the actual order of the sol-gel process. It is well known that the order depends upon a number of factors including concentration of reactants, pH, solvent and temperature. The hydrolysis reaction precedes the condensation reactions, but depending upon conditions does not necessarily go to completion prior to the onset of condensation. The relative rates of hydrolysis and condensation, as will be shown, determine the final structure. The sol to gel conversion point for the sol-gel processing of metal alkoxides is usually indicated by the point at which flow ceases [1].

2.3 Sol-Gel Processing

The factors listed under the category "Processing Variables" (Table 2-1) exhibit a rather strong interdependence. The pH of the sol-gel reaction is critical in determining the overall kinetics according to Kelts et. al. [9] and Coltrain et. al.[37]. Thus, the water concentration and catalyst concentration as well as solvent and soluble metal alkoxides will contribute to determining the overall solution pH. In addition, the consumption of water by the hydrolysis reactions will shift the effective hydrogen ion concentration and thus the equilibrium of the sol-gel process and ultimately the reaction kinetics. The reaction kinetics are also dependent upon the solvent system and the products of each of the reactions as will be shown in Section 2.4 which describes the structures which are produced by the sol-gel processes. The hydrolysis and condensation reactions described previously will be discussed in terms of each of the processing variables listed in Table 2-1 in this section.

2.3.1 Processing Variables

Aelion [38], Schmidt [3] and Yoldas [7] have demonstrated that the type of catalyst and its concentration determine the hydrolysis rate and the extent of hydrolysis for a given ratio of water to metal alkoxide. Hydrochloric acid (HCl), sulfuric acid (H₂SO₄), nitric acid (HNO₃) and the base ammonia hydroxide (NH₄OH)

are typical of the catalyst used in sol-gel processes. However, a broad spectrum of acid and base catalysts have proven to be effective catalysts for the hydrolysis of metal alkoxides [1,7,22,23,27]. The extent of hydrolysis and the mechanism change dramatically with the concentration of the catalyst used.

Aelion, Loebel and Eirich investigated the reaction kinetics of the sol-gel process using TEOS and two different catalysts HCl [38]. The stoichiometry of the reactants TEOS and water were systematically varied with the catalyst concentration for three different solvents, methanol, ethanol and dioxane. The amount of water consumed or generated were analyzed by Karl Fischer titration. The amount of solvent generated was determined by distillation from a higher boiling solvent. There are some drawbacks associated with these methods, but overall their accuracy is acceptable [1]. Aelion, Loebel and Eirich's results were significant in terms of the trends they identified for the different catalysts and catalyst concentrations. The hydrolysis reaction proceeds rapidly and nearly to completion at high concentrations of water and HCl. The rate of hydrolysis followed a first order dependence on the acid concentration. The apparent order of the hydrolysis reaction was second order with respect to the ethylsilicate and water [38]. There was no apparent dependence of the hydrolysis reaction on the solvents for the high concentrations of HCl, i.e. a low solution pH. The ratio of water to TEOS was varied from nearly 7:1 to a low of 2:1. A high concentration of acid at the high water to TEOS ratio caused rapid hydrolysis and condensation of the TEOS. The hydrolysis rates were reduced by

lowering the acid concentration while maintaining the high water to TEOS ratios [38]. Aelion, Loebel and Eirich observed that as the pH exceeded a value of 2.7 the system gelled rapidly [38].

There are both similarities and differences to be noted as a function of the hydrogen ion concentration in Aelion, Loebel and Eirich's study. The base catalyzed reaction rates also exhibited a strong first-order dependence on the concentration of the base catalyst, ammonium hydroxide. However, the reaction rates only held for very low concentrations of the silicate and with high amounts of water, i.e. 8:1, water to TEOS. A precipitate formed in reactions at the higher pH ($\text{pH} > 3$) when more monomer, TEOS, was added. This did not occur for reactions at pH of less than 3. The concentration dependence of the base catalyzed reaction, hydrolysis and condensation, was first-order with respect to TEOS, but only under very dilute conditions [38]. Aelion, Loebel and Eirich also measured a strong dependence of the base catalyzed reactions on the solvent which was opposite of the acid catalyzed reactions [38]. The silicate solubility was decreased significantly as the solvent was changed from methanol to ethanol to dioxane. The reaction changed from a homogeneous to a heterogeneous one according to Aelion, Loebel and Eirich since the precipitate reaction rate slowed but continued [38].

The conclusions that Aelion, Loebel and Eirich made indicated that the reaction rates were similar to those predicted by an acid catalyzed reaction. Two mechanisms were proposed to explain their results. The first involves a dimolecular

scheme where the acid and water formed a complex with the silicon atom and the alkoxide. The acidic proton is donated to the alkoxide to generate the alcohol and the water donates the hydroxyl to the silicon to form the silanol [38]. The second mechanism involves a termolecular complex where the acid protonates the alkoxide oxygen and the water molecule attacks the silicon. The silicon would then release the protonated alkoxide and the conjugate base would abstract a proton from the hydrated silicon. Further support of an acid catalyzed mechanism offered by Aelion et.al. [38] was that the hydrolysis of TEOS in glacial acetic acid was not a particularly fast reaction. This mechanism was proposed in opposition to one involving the formation of the siliconium ion [38]. They further proposed that the base catalyzed reaction involved nucleophilic attack of the hydroxyl ion on the silicon atom followed by displacement of the alkoxide anion which then reacted with water to generate an alcohol and another hydroxyl anion.

Similar studies by other groups have produced rather contradictory results. Schmidt [39] reported there was not a rate dependence on the hydrogen ion concentration as observed by Aelion et. al. [38]. Schmidt proposed that the acid acted only as a catalyst. Schmidt offered a mechanism involving a siliconium ion as an explanation for his results as well as the rate equations provided by Aelion et. al. The siliconium ion mechanism was originally proposed by Swain et. al. and partially supported by the work of Khaskin involving the use of ^{18}O labeled water [1,38]. Campostrini et. al. have identified the existence of the trivalent siliconium ion by

mass spectrometry [1]. A number of other reports have offered support for the formation of the pentavalent siliconium ion, yet, no one has reported the isolation of such a species [1].

Kelts, Effinger and Melpolder [4] used ^1H NMR and ^{29}Si NMR to study the hydrolysis and condensation of TMOS and TEOS at different pH levels, in different solvents and with different stoichiometries of water to metal alkoxide. The water was actually deuterium oxide. Although the equivalence of deuterium oxide with water in sol-gel processes had not been determined, the authors assumed no significant effect on the reaction kinetics. Thus, the pH* values reported were of the deuterium oxide solution as measured by a glass electrode immediately after combining all of the reactants [4]. TMOS at the low pH* (< 1) underwent rapid and practically complete hydrolysis, according to analysis by ^{29}Si NMR, whereas at the upper pH* ($= 7.8$) the hydrolysis reaction was very slow. The monomer concentration remained very high throughout the sol-gel processing of TMOS at high pH*. At gelation the high pH* solution contained 70% unreacted TMOS according to the analysis by Si NMR [4]. Sixty percent of the species identified by ^{29}Si NMR in the high pH* solutions, as having undergone one condensation reaction, were tetrasubstituted. This is contrasted by the low pH* solution in which only twenty-six percent of the condensed species were tetrasubstituted. Thus, the relative amounts of the tetrasubstituted, trisubstituted and disubstituted silicon species in solution varied with the pH* of the solution. This information and the different rates of hydrolysis for

high and low pH* solutions demonstrates the hydrolysis reaction is the rate limiting step at high pH* [4]. This is contrasted by rates at low pH which indicate the condensation reaction is the rate determining step. Similar behavior was observed with TEOS in ethanol with the pH* varied over the same range ($1 \leq \text{pH}^* \leq 7.8$) [4]. Thus, the trends in relative rates of hydrolysis determined by Aelion et. al. were substantiated by Kelts, Effinger and Melpolder using NMR.

More recently, Coltrain, Melpolder and Salva [37] provided further insight into the role of the catalyst and the solution pH in the sol-gel process. Coltrain, Melpolder and Salva studied the pH dependence of the hydrolysis and condensation reactions using TEOS and TMOS in alcoholic solutions. The water to alkoxide ratio was approximately 4 to 1. Their study compared the times to gelation for HCl, H₂SO₄, p-toluene sulfonic acid, trifluoroacetic acid and nitric acid at different concentrations. Ammonium hydroxide, ammonium nitrate, and nitric acid were used in a two step reaction using TMOS in ethanol. There were two separate pH determinations made for each reaction monitored. The first value was the pH of the aqueous acid solution prior to addition to the metal alkoxide solution [37]. The second pH value was from a measurement of the reaction mixture at 60°C one hour after the aqueous acid solution was added [37]. The pH was varied from a low of one to a high of about six. The maximum time to gelation occurred when the reaction pH was between 1 to 2 [37]. The minimum time to gelation was close to a reaction effective pH equal to 4. The times to gelation reflected a sensitivity to the

acid catalyst used when plotted as a function of the pH of the aqueous acid solution. However, when plotted as a function of the effective pH of the reaction solution, no distinct dependence on the acid catalyst used was observed. Thus, the rates were a function of the total hydrogen ion concentration [37]. Coltrain, Melpolder and Salva attributed the differences between the various acid catalysts to the acid dissociation constants. The acid dissociation constants are dependent upon the solvent used.

A remark, or two, about the temperature of the reaction mixture may be important to consider at this point. Aelion, Loebel and Eirich determined that at temperatures greater than 50°C the condensation reaction in dioxane did not go to completion [38]. However, an increase in the temperature from 20°C to 45°C caused a ten fold increase in the rate of hydrolysis [38]. One must assume at this point that the reaction temperatures do not change the dependency on the solvent or lack of it as is the case in acid catalyzed reactions [38]. Klemperer, Mainz and Millar [36] have shown that restrained siloxane bonds are more susceptible to hydrolysis at elevated temperatures. Thus, temperature is a critical variable in determining the rate of hydrolysis, but also the overall reaction rates. A study similar to that of Coltrain, Melpolder and Salva would be useful if the temperature dependence were measured.

The effect of the hydrogen ion concentration on the reaction rates were correlated to the surface charge of the particles [37] in the two step hydrolysis of TMOS. The two step process allowed the reaction to proceed half way to the time

of gelation at one hydrogen ion concentration, at which time the hydrogen ion concentration could be either lowered by the addition of base or raised by the addition of more acid. A method was used to measure the effective surface charge of the colloidal particles as a function of the solution pH and extent of reaction by Coltrain, Melpolder and Salva [37]. They determined that the surface charge on the particles also scaled with the reaction solution pH [37]. A maximum surface charge on the particles developed at an effective pH of ca. 1 to 2, or where the maximum time to gelation was measured. The minimum surface charge of the particles correlated with the minimum time to gelation and thus the effective pH of ca. 4 [37]. Coltrain, Melpolder and Salva concluded that the effective hydrogen ion concentration of the reaction was critical in determining the reaction rates of TEOS and TMOS in ethanol. The solvents role in the sol-gel process, according to Coltrain, Melpolder and Salva, would change as the surface charge of the silicate species changed [37].

The role of a solvent in the sol-gel process is not clearly defined but appears to be a function of the solvents polarity and ability to donate protons. It appears that the solvent influences the rate of hydrolysis in a number of ways. The solvents interaction with the reactive metal alkoxide or the oligomers was minimal at a pH below ca. 2, but significant above the isoelectric point according to Aelion et. al. [38]. Based on these results Aelion, Loebel and Eirich concluded that under acidic conditions ester exchange between the solvent and metal alkoxide was unimportant.

Peace, Mayhan and Montle, however, showed that ester exchange was a significant factor in the hydrolysis of TEOS under acidic conditions [40]. Brinker et. al. also showed by gas chromatography that ester exchange with the solvent was significant in the sol-gel processing of TEOS under acidic conditions [41]. Brinker et. al. found that hydrolysis of TEOS under acidic conditions required only 90 minutes to go to completion in isopropanol compared to nearly 24 hours in ethanol [42].

Some solvents become involved in the reaction as a coreactant. Formamide is known as a drying chemical control agent or DCCA due to its ability to slow the hydrolysis rate sufficiently that a monolithic structure is produced [42]. The pH of a TMOS/MeOH/Formamide/H₂O mixture decreased as the reaction began. The formamide concentration also appeared to decrease as the reaction progressed. Orcel and Hench concluded that the formamide complexed with the reactive species in some manner to effectively slow the hydrolysis rate. Boonstra, Bernards and Smits [43] studied the role of formamide in the sol-gel processing of TEOS under acidic and basic condition using ²⁹Si NMR and ¹H NMR. As reported by Orcel and Hench, formamide decreased the hydrolysis rate of TMOS under acidic conditions [42]. Formamide did not effect the hydrolysis rate or condensation rate of the base catalyzed system. There was no evidence of either a silicon-formamide complex or consumption of water by the formamide under acidic conditions [43]. Boonstra, Bernards and Smits proposed that the decrease in the hydrolysis rate with the addition of formamide under acidic conditions was due to the consumption of the

acid cation by the amine on the formamide. The lower basicity of formamide with respect to the base catalyst employed, i.e. NH_4OH , was the reason for no change in reaction rates at high pH [43]. Artaki et. al. [44] investigated by ^{29}Si NMR the effect of formamide on the rate of hydrolysis of TMOS under neutral conditions. Artaki et. al. attributed the reduced hydrolysis rates of TMOS to a higher solution viscosity as well as hydrogen bonding between formamide and the reactive metal alkoxides. The conclusions made by Artaki et. al. were based upon reaction temperatures of 50°C [44].

The ratio of water to the metal alkoxide is another key factor in determining the rates of polymerization in sol-gel processes. The studies by Aelion et. al. [38] included water to alkoxide ratios ranging from nearly 7:1 to as little as 2:1. Coltrain's [37] results were based upon a water to alkoxide ratio of approximately 4:1 compared with Artaki's [44] reaction ratios of 10:1 for water and TMOS. Brinker et. al. [41] used a two step process in which an initial ratio of water to TEOS was increased to a ratio of 5:1 in the second step. Bechtold, Vest and Plambeck studied the effect of varying the water to TEOS ratio from 2:1 to 11:1 [45]. The overall trend that all of these studies have is that the higher the water to metal alkoxide ratio the faster the rate of hydrolysis. This does assume that the acid concentration, the temperature, and the reactants are not varied. Pouxviel et. al. [46] concluded from ^{29}Si NMR studies that at low water to TEOS ratios (0.3 to 1) hydrolysis was rapid, but not complete. The extent and rate of hydrolysis increased with higher ratios of

water to TEOS [46]. The opposite trends are seen in the range of higher pH as indicated previously, where the water concentration was important only at low concentrations of the alkoxide species, i.e. dilute systems under basic conditions [38].

The extent of condensation is largely dependent upon the pH of the solution and concentration of water with respect to the monomer. Condensation of the silanol groups formed by hydrolysis of the TMOS is the rate limiting step at low pH according to Kelts, Effinger and Melpolder [4]. The hydrolysis reaction proceeds rapidly and to completion faster than the first NMR spectrum could be obtained. Initially disubstituted, trisubstituted and tetrasubstituted oligomers were detected in the ^1H NMR and ^{29}Si NMR spectra of the low pH reaction ($\text{pH}^* < 1.7$) [4]. The level of substitution dropped off rapidly as the pH was raised to above the isoelectric point (ca. 2.3). The intermediate and high pH reactions produced a relatively uniform distribution of the four condensation products. Kelts and Armstrong [9] have shown by ^{29}Si NMR that at gelation the high pH reactions contained nearly 70% unreacted monomer whereas no unreacted monomer was detected in the low pH solutions. Pouxviel et. al. [46] predicted that the condensation rate increased as the hydrogen ion concentration decreased. The time to gelation however decreases at significantly high values of pH and thus other factors must be considered.

The reciprocal of time to gelation is related to the condensation rate according to Brinker and Scherer [1]. Coltrain, Melpolder and Salva studies of time to gelation as a function of the effective pH of the reaction would indicate a

maximum rate of gelation occurs at a pH of 1 to 2 [37]. Yet, in a two step process using HCl and NH_4OH as the catalysts, the maximum gel time occurred at a pH of 7.8 [37]. Coltrain et. al. related the surface charge of the structure to the effective pH and the rate of gelation. The maximum time to gelation occurred when the surface charge was at a maximum [37]. The conclusions drawn by Coltrain, Melpolder and Salva were that the effective pH of the solution was the critical variable in determining time to gelation and that the acid counterion played a minor role [37].

The ratio of water to the alkoxide restricts the extent of condensation by limiting the extent of hydrolysis. Brinker et.al. showed that the condensation of TEOS under acidic conditions begins almost immediately in a water deficient system, i.e. water to TEOS ratio of less than 2:1 [42]. Sakka controlled the ratio of water to alkoxide for producing formulations that are spinnable [47,48]. The silicate structure was mostly linear with few substitutions along the chain. Pouxviel et. al. NMR studies of condensation products as a function of water to alkoxide ratio revealed that the condensation mechanism changed. At low concentrations of water, condensation occurred between a silanol and a silicon alkoxide. There was always a large residual concentration of the alkoxide species when the reaction was starved of water. Increasing the water to alkoxide ratio to a ratio of 4:1 increased the concentration of silanols and most condensations occurred between two silanols [48].

2.3.2 Structural Factors

2.3.2.1 Ligands bound to Silicon

In addition to the variables discussed in the previous section, the metal and the ligands bonded to it influence the hydrolysis and condensation rates of a sol-gel process. The time to gelation is much shorter for TMOS in methanol than TEOS in methanol at the same pH and water to alkoxide ratio [4,9,49]. The time to gelation was determined for a series of silicon metal alkoxides in different alcohols by Chen, Tsuchiya and MacKenzie [49]. These results are tabulated in Table 2-2. The relative ratios of alkoxide to solvent to water to catalyst were all 1:4:4:0.07. There is no consistent trend for the three alcohols that would indicate the influence of the ligand bonded to the metal. However, Chen et. al. calculated the rate constants for each reaction and determined that the rate constant for hydrolysis decreased with larger alkoxides for a given solvent [49]. This, according to Chen et. al., suggested that the differences may be related to steric hindrance caused by the larger alkoxide. However, when tetrabutoxysilane is reacted in methanol the trend did not persist, for which the authors had no explanation [49]. The general behavior, however, does indicate the ability of the ligand to influence the rates of hydrolysis and condensation through steric factors.

Table 2-2 Gelation times for silicon alkoxides [49]

METAL ALKOXIDE	SOLVENT	TIME TO GELATION [†] (HR)
$\text{Si}(\text{OCH}_3)_4$	Methanol	152
$\text{Si}(\text{OC}_2\text{H}_5)_4$	Methanol	242
$\text{Si}(\text{OC}_4\text{H}_9)_4$	Methanol	243
$\text{Si}(\text{OCH}_3)_4$	Ethanol	44
$\text{Si}(\text{OC}_2\text{H}_5)_4$	Ethanol	108
$\text{Si}(\text{OC}_4\text{H}_9)_4$	Ethanol	64
$\text{Si}(\text{OCH}_3)_4$	n Propanol	131
$\text{Si}(\text{OC}_2\text{H}_5)_4$	n Propanol	246
$\text{Si}(\text{OC}_4\text{H}_9)_4$	n Propanol	550

[†] 0.054 mol. Metal alkoxide, 0.216 mol Alcohol, 0.0216 mol. H_2O , and 0.0037 mol HCl at ambient conditions.

Chen, Tsuchiya and MacKenzie also included silicon tetracetate in their study. The gel time decreased from 242 hours to 1 hour in ethanol when acetate replaced ethoxide as the ligand on silicon [49]. There was no satisfactory explanation for the extremely large decrease of time to gelation by Chen et. al.. However, Coltrain and Kelts [50] determined by ^{29}Si NMR that within 30 minutes of mixing silicon tetracetate in ethanol virtually no acetate ligands remain on the silicon atom. Their explanation for the behavior reported by Chen et. al. [49] is that by alcoholysis the tetracetatesilicate was converted into TEOS and acetic acid. The high concentration of acetic acid catalyzed the rapid hydrolysis and condensation of the TEOS. Coltrain and Kelts verified this by comparing the gelation of TEOS in four moles of acetic acid and silicon tetracetate in four moles of ethanol using HCl as the catalyst with a water to alkoxide ratio of 4:1. Both systems gelled at approximately the same time which corresponded to the times reported by Chen et. al. [49]. According to Coltrain and Kelts, the rapid gelation was due in part to the strong acid behavior of acetic acid in ethanol. It was also reported that ethyl acetate was formed immediately after addition of the acidified water. The authors suggested the lower dielectric constant of the ethyl acetate may also contribute to the shorter gel times [50] based on the earlier work of Coltrain et. al. [37].

The steric effect of ligands and possible inductive effects were studied by Doughty, Assink and Kay [51] using ^{29}Si NMR. The hydrolysis and condensation of hexamethoxydisiloxane in an acidic alcoholic solution was followed by ^{29}Si NMR.

The water to alkoxide ratio was varied from 1:16 to 1:3. The results demonstrated that the rate of condensation was determined by the alcohol and water producing reactions as previously reported by Pouxviel et. al. [46] for a water deficient process. The rate constants determined by Doughty et. al. were larger for the water producing condensation [51]. The rate constants for the two condensation reactions were smaller for the hexamethoxysiloxane than the values determined for TMOS [52]. The authors attributed the slower reaction rates of the dimer to the bulky methoxy groups [51]. The difference in the rate constants was also explained by Doughty et. al. in terms of inductive effects. They assumed that under acidic conditions an equilibrium concentration of non-protonated and protonated silanols is established quickly. The rate determining step is nucleophilic attack by the protonated species on a non protonated silicon followed by elimination of a hydronium ion. This process would be slowed by shifting the equilibrium to the unprotonated silanol. The siloxane of the dimer is more electron withdrawing than the alkoxy or silanol of the monomeric species and therefore could shift the equilibrium away from the protonated silanol. Thus, a lower rate constant would result [51].

The hydrolysis of metal alkoxides most likely proceeds by either an electrophilic attack (low pH) or nucleophilic attack on the metal atom (high pH) [1,50,51]. The electron donating or withdrawing nature of the ligands therefore might be expected to influence the reaction rates of the sol-gel process. Schmidt et. al. [39] determined the rate of hydrolysis for a series of alkylalkoxysilanes with the general

formula $(\text{CH}_3)_n\text{Si}(\text{OC}_2\text{H}_5)_{4-n}$. The value of n was varied from 0 to 3. The different metal alkoxides were hydrolyzed in ethanol using either HCl or NH_4OH as the catalyst [39]. The rate of hydrolysis (as reported by Schmidt) was increased significantly at low pH as the value of n was increased. However, there were no products of hydrolysis detected in the reaction at the higher pH [39]. The inductive effect of the alkyl group was attributed by Schmidt as stabilizing a positive charge on the silicon atom. This hypothesis is based upon the mechanism involving a siliconium ion [1,38,39].

Coltrain and Kelts have shown that coreaction of methyltriethoxy silane (MeTEOS) and TEOS in ethanol under acidic conditions produces a blocky structure [50]. The MeTEOS preferentially reacts with itself in the mixture. Approximately 69% of the MeTEOS monomers were homopolymerized within 30 minutes after addition of the acidified water. There was only 31% of the TEOS reacted within the same time frame. Forty-four percent of the the MeTEOS silicons were reacted with MeTEOS silicons [50]. Thus, the inductive effects of ligands bound directly to the silicon or metal atom can cause significant changes in the reaction kinetics that ultimately effect the structure.

2.3.2.2 Other Metal Alkoxides

The nature of the ligands on silicon was shown in the previous section to strongly influence rates of hydrolysis, condensation and gelation. The inductive and bulky requirements of the ligands are the most dominant factors in terms of their effect on reaction kinetics. The structure of the metal atom, however, determines the reactivity of the metal alkoxides in sol-gel processes [1]. The substitution of titanium for silicon in silicon tetracetate produces a very stable metal alkoxide [50]. The difference in reactivity is attributed to titanium's ability to expand its coordination number to five. The acetate ligand coordinates with the titanium as a bidentate which blocks the metal from reaction, i.e. hydrolysis, condensation [53]. Silicon tetracetate is not able to increase its coordination and therefore is much more susceptible to attack directly on the silicon or the carbonyl of the acetate ligands [50].

Livage et. al. have developed a system to predict the behavior of metal alkoxides in a sol-gel process [54]. The metal atom and the ligands are assigned an equilibrium value of the partial charge. The value of each partial charge is determined by the electronegativity of the metal and ligand in the case of a metal alkoxide. The sol-gel process under acidic conditions is believed to occur via a nucleophilic substitution on the metal atom [1,38,50,51,54]. Thus, a more electropositive metal atom should be more reactive in the sol-gel process assuming the ligands, solvent and pH are the same. The trends predicted by Livage's model

and observed experimentally match quite well [54]. The reactivity of a few metal alkoxides are listed (Table 2-3) along with their equilibrium partial charge (as calculated by Livage) in order of decreasing reactivity from top to bottom [1,54].

The other factor to consider in comparing relative reactivity of different metal containing metal alkoxides is the coordination number [55]. The ability of titanium to expand its coordination from four to six is one example [53]. The normal coordination of metals are not always satisfied in metal alkoxides and thus they tend to undergo an expansion of their coordination [55]. The result of this is that the metal alkoxides can form coordinate structures that satisfy their coordination, but reduce their reactivity. Two examples are titanium tetrabutoxide and titanium tetraethoxide which both exist as oligomers in the alcohol corresponding to their ligand [54]. However, titanium tetraisopropoxide remains as a monomer in isopropanol. Sanchez et. al. also indicate that $\text{Ti}(\text{OC}_2\text{H}_5)_4 \cdot \text{HOH}_5\text{C}_2$ complexes are formed by titanium tetraethoxide in ethanol [53].

The full coordination of the transition metals can also be fulfilled by the use of a coordinating ligand such as a carboxylic acid or a chelating agent such as acetyl acetone or ethylacetoacetate [1,53,54,55,56]. Doeuff et. al. used FTIR to characterize the structure of sols prepared by the addition of acetic acid to titanium tetrabutoxide [53]. FTIR bands were assigned by Doeuff et. al. to the vibrational modes of coordinated complexes between acetate ligands and the titanium tetra n-butoxide. There were two bidentate structures proposed and one monodentate

Table 2-3 Partial charge values of selected metal alkoxides [53,54]

METAL ALKOXIDE	PARTIAL CHARGE $\delta(M)$
Zr(OEt) ₄	+ 0.65
Ti(OEt) ₄	+ 0.63
W(OEt) ₆	+ 0.43
Si(OEt) ₄	+ 0.32

complex [53]. The bidentate structures could be formed by the coordination of the carboxylate anion with one metal, i.e. like a chelating agent. The other possible bidentate complex would be the bridging of two titanium atoms by a carboxylate anion [53]. The monodentate complex was the result of coordination between the titanium and the carbonyl of the acetate ligand. Doeuff et. al. demonstrated that the reactivity of the bridging acetate was highest and the chelated bidentate the lowest. Similar results were shown for zirconium tetra n-propoxide reacted with acetic acid [54,56].

Acetylacetone has also been studied in sol-gel reactions to reduce the reactivity of titanium, zirconium and aluminum alkoxides [3,54,55,56]. Acetylacetone added to titanium tetraisopropoxide in an equimolar ratio increases the coordination of titanium from four to five [54]. The addition of water to the solution causes the titanium coordination to increase to six [54]. The functionality of the titanium metal alkoxide can be changed by varying the ratio of the acetylacetone to the metal alkoxide. A ratio of 1:1, titanium alkoxide to acetylacetone, produces a slower reacting metal alkoxide that can form a network. However, increasing the ratio of acetylacetone to metal alkoxide to 2:1 yields a non-network forming system, which Sanchez and Schmidt have used for fiber drawing applications [3,54].

Aluminum alkoxides will also form stable complexes with β -diketones such as acetylacetone or the β -diketoester ethyl acetoacetate [57]. Aluminum alkoxides will form tris β -ketoester complex when reacted with the β ketoester in a 1:3

stoichiometry under reflux conditions [57]. The titanium alkoxides will form a bis β diketonate under the same conditions. Bradley et. al. cite work in which zirconium tetraisopropoxide formed a tetra kis acetylacetonate complex. Thus, the structure of the central metal atom in a metal alkoxide determines the type of complexes it can form with the chelating agents [56,57].

2.4 Sol-Gel Structures

The structure of sol-gel derived materials are as diverse as the variables described in the previous sections. The first stage of the sol gel process involves the formation of a stable colloidal dispersion of solid-like particulates. The particulates are formed by the hydrolysis and ultimately condensation of the reactive precursors, i.e. metal alkoxides. The gelation of these particles occurs when their molecular weight increases to infinite values. This process is dependent upon the metal alkoxide and processing conditions as well. The exact physical description of a "gel" may be rather difficult, but in the context of this work is best given by Brinker and Scherer. A gel consists of two phases, a continuous structure and a fluid, both being of colloidal dimensions [1]. The restrictions of these dimensions are of course the colloidal dimension. Brinker and Scherer limit the size of each phase to 1 micrometer. Consider a line segment, that originates in one phase and continues perpendicularly to the regime occupied by the same structure it originated in, the

overall length of the line segment would be on the order of $1\ \mu$ long [1]. The gel formed still contains a significant quantity of sol and thus will typically "age". Many gels will undergo spontaneous shrinkage as new bonds are formed and fluid is squeezed out. This shrinkage is referred to as syneresis [1]. The removal of the liquid from a gel during either drying or as a result of syneresis causes deformation of the solid network structure. There are two general terms xerogel and aerogel that define the structure after removal of solvent. The xerogel is formed by evaporation under normal conditions. The large capillary pressures that develop during this process cause large dimensional changes in the gel. A xerogel is typically 5 to 10 times smaller in overall volume than the original gel. The aerogel is prepared by removal of the solvents under supercritical conditions and thus have little shrinkage. The aerogel has a pore volume fraction of typically greater than 0.9 [1].

This section will review the structural evolution of the sol-gel derived materials according to their dimensionality. First NMR studies will be cited to define the initial sol formed as a function of processing conditions. Secondly the results of FTIR will be compared with NMR studies to describe the evolving sol-gel structure. Small angle x-ray scattering has been used extensively to study the morphological and topological features of evolving gels.

2.4.1 NMR and Raman Spectroscopy

The structure of the solids produced by the sol gel processes have been studied extensively by both ^1H and ^{29}Si NMR. ^1H NMR is useful in following the initial stages of hydrolysis and condensation. However, as the degree of polymerization or the extent of condensation the complexity of ^1H NMR makes it difficult to interpret since the developing structure is inorganic. The complexity of the ^{29}Si NMR spectra for the hydrolysis of ca. TEOS can be appreciated by considering an analysis by Brinker and Scherer [1]. A total of 48 chemically different linear trimers and 81 chemically different cyclic tetramers could exist in a reactive sol depending upon the extent of hydrolysis [1].

Kelts and Armstrong using ^{29}Si NMR studied these structures which developed by the hydrolysis and condensation of both TMOS and TEOS [9]. The water to metal alkoxide ratio was varied from 0.5 to 4 and the effective pH ranged from <1 to approximately 7. The most dramatic difference they reported was the large concentration of cyclic oligomers in the TEOS sol-gel process whereas very few were identified in the TMOS systems. (The water to metal alkoxide ratio was 2 under acidic conditions.) This indicates formation of the cyclic oligomers is sterically controlled in some way [1,2]. Other groups have also reported the identification of cyclic oligomers [4,36,58].

Kelts and Armstrong determined that the formation of the cyclic structures was dependent upon reaction conditions as well as the metal alkoxide [9]. A ratio of TEOS to water of 0.5 under acid conditions produced very few of the cyclic trimers. This is easily explained in terms of the relative degree of hydrolysis. The cyclic structures, a disubstituted silicon, requires more water for hydrolysis compared to a monosubstituted silicon in the metal alkoxides. Kelts and Armstrong also identified more cyclic tetramer than the disubstituted linear oligomer in a reaction with nearly two orders of magnitude greater concentration of the acid [9]. There was a very low concentration of the cyclic trimer in this reaction. These results support the observations that at low water concentrations in an acidic system, the rate of condensation is greater than the hydrolysis reaction rate.

Similar results were reported by Balfe and Martinez [58] using TMOS, hexamethoxydisiloxane and octamethoxytrisiloxane under acidic conditions. The water to TMOS ratio was also 0.5 in methanol, but the exact acid concentration was not given. Balfe and Martinez identified the cyclic trimers in the early stages of the sol-gel processing of TMOS, but not in either the dimer or trimer monomers. The cyclic tetramer developed at later stages of the hydrolysis and condensation of both TMOS and the dimer. The trimer, octamethoxytrisiloxane, did not form any of the cyclic species according to Balfe and Martinez [58]. This in addition to the lack of evidence of dimers or monomers formed during the processing of the trimer led the

authors to speculate that if hydrolysis of siloxane bonds did occur, it was insignificant compared with condensation under the conditions they studied [58].

Klemperer, Mainz and Millar [3,36] monitored the hydrolysis and condensation of TMOS, hexamethoxy disiloxane, octamethoxy disiloxane and octamethoxy octasilsesquioxane from the sol to the gel using both solution and solid state NMR. They used an excess molar ratio of water to the metal alkoxide (8:1) and no acid. The expectation is that under conditions of these hydrolysis would proceed at a much faster rate and that the cleavage of the siloxane bonds may occur. Klemperer, Mainz and Millar monitored the hydrolysis and condensation of the reactive trimer for the generation of monomer, tetramer, or pentamer. Any of these species in the reaction would indicate that hydrolysis of the siloxane bond(s) had to occur. Similar arguments could be made for the disiloxane precursor. The disiloxane precursor siloxane bond and alkoxide bonds were hydrolyzed as indicated by the presence of monomer and hydroxyl substituted monomer and dimer. Klemperer, Mainz and Millar were not able to determine if hydrolysis of the siloxane bonds of the trimer occurred. The resolution of their spectrometer was limited such some of the peaks in the ^{29}Si NMR spectra may have been attributable to either dimers or silicons of the trimer. In addition, to the reaction of the dimer and trimer, hydrolysis of the caged structure, octamethoxy octamethyl silsesquioxane, under neutral conditions, produced their corresponding dimers. The ^{29}Si NMR of the caged structure contains only resonances for Q^3 silicon atoms (Q^3 is a shorthand

nomenclature which describes the silicon atom bonded to three other silicones by bridging oxygens). The ^{29}Si NMR of the hydrolyzed products contained the resonances for the Q^3 structures and a single peak assigned to a Q^4 silicon. The dimer formed mostly by the condensation of the alkoxides rather than by hydrolysis of the siloxane bond followed by condensation [36].

Klemperer, Mainz and Millar [3] also reported that cyclic trimers were formed by the acid catalyzed hydrolysis of the linear trimer, octamethoxy trisiloxane. The ratio of water to alkoxide was 2:1 and the acid concentration was given as $6 \times 10^{-6}\text{M}$, but the pH of the solution was not indicated. The formation of the cyclic species under acidic conditions is in agreement with the results of Kelts and Armstrong [9]. However, Balfe and Martinez [4], however were not able to confirm the presence of cyclic species in the sol formed by hydrolysis and condensation of the linear trimer.

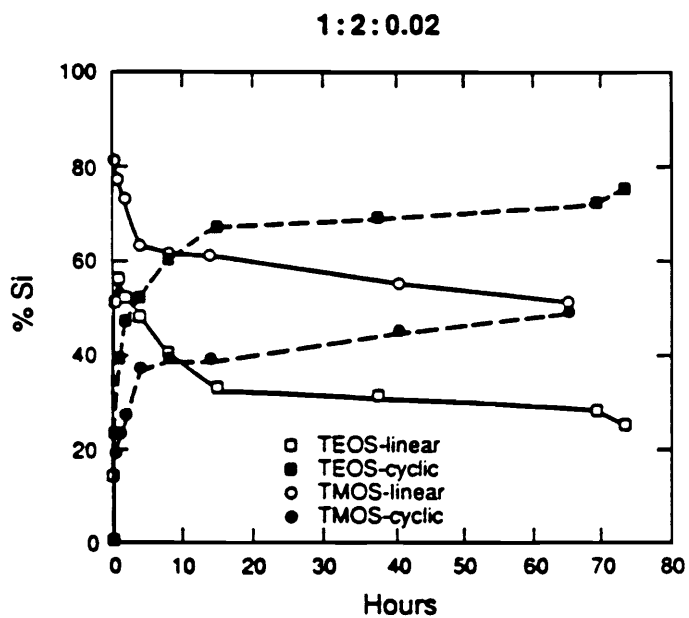
Kelts and Armstrong propose that the structural differences in the early stages of the sol-gel process determine the time to gelation for TMOS and TEOS [9]. The relative rates of hydrolysis and condensation of both TMOS and TEOS do not differ by a significant amount (refer to section 2.3.1) [9]. However, the relative concentration of linear and cyclic oligomers in the sols of TMOS and TEOS were significantly different as indicated in the charts in Figure 2-2 [9]. The TMOS sol has a much higher ratio of linear oligomers to cyclics than the TEOS sol over the time scale of the experiments. The TMOS system gelled after 62 hours whereas the TEOS system had not gelled after 207 hours. An interesting difference to note in

Figure 2-2 is that the linear and cyclic species are converging for the TMOS sol and diverging for the TEOS sol.

Kelts and Armstrong proposed a model for gelation based upon the relative concentration of the linear oligomers and cyclic oligomers [9]. They suggested that the linear or extended polymer structures have more mobility in solution than ring structures. The higher mobility would afford more interactions with other reactive species and thus condensation. The cyclic oligomers would have interactive more slowly and thus have longer times to gelation. Another factor Kelts and Armstrong addressed was that for a given concentration of metal alkoxide monomer, the sol with a higher volume fraction of cyclics would behave as a more dilute solution. Finally, their model suggests that the final structure of the TMOS generated gel should be less dense than one prepared from TEOS [9].

Solid state ^{29}Si NMR has been used to analyze the structure of the gel in the solid state [34,36]. Klemperer, Mainz and Millar used solid state ^{29}Si NMR to analyze the structures generated by the hydrolysis and condensation of TMOS, the dimer - hexamethoxydisiloxane, the linear trimer octamethoxytrisiloxane and the cubic structure octamethoxy octasilsesquioxane under neutral conditions. The systems were gelled in sealed containers with an excess of water and usually at temperatures of 40°C or greater. The key feature of their work was that the siloxane bonds of the cubic structure were hydrolyzed under the conditions of the experiment. This result contradicts their earlier studies of the sol by solution ^{29}Si NMR [9].

a) TMOS sol



b) TEOS sol

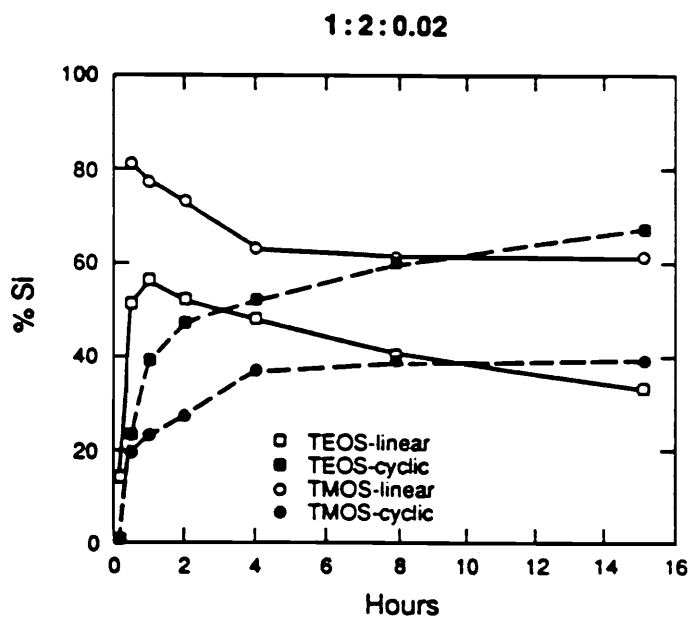


Figure 2-2 Ratio of cyclic to linear structures [9]

Raman bands have been assigned for the majority of the ring structures produced by the sol-gel processing of silicon metal alkoxides [59,60]. Balfe et. al. and Tallant et. al. determined by Raman spectroscopy that cyclic dimers and trimers undergo rapid hydrolysis compared to their linear homologs and the cyclic tetramers [59,60]. Thus the cyclic tetramers tend to contribute to the structure of the gels [60]. This is in excellent agreement with the results of Kelts and Armstrong (Fig. 2-2) [9]. Zerda, Artaki and Jonas [44,61] utilized Raman spectroscopy in conjunction with ^{29}Si NMR to follow the sol-gel polymerization of TMOS as a function of solvent and pH. They identified the cyclic tetramers by ^{29}Si NMR as well as the various linear oligomers [61]. The Raman band assignments correlate quite well with those of Lippert, Melpolder and Kelts [62]. Zerda, Artaki and Jonas using the intensity of the Raman band at 830 cm^{-1} as representative of the concentration of the silicate structure, demonstrated that at 21°C the sol gel reaction continues long after gelation [44].

2.4.2 Small Angle X-Ray Scattering

Brinker et. al. have used small angle x-ray scattering (SAXS) to study the development of the three dimensional structure generated by a two stage sol gel process [41]. SAXS profiles of the scattering intensity versus an angular scattering factor (such as $k = (4\pi/\lambda) \sin(\Theta/2)$, where λ is the wavelength of the incident

radiation and Θ is one-half the radial scattering angle) provides information of structure dimensions of ca. 2 nm to 100 nm. Brinker et. al. analyzed the gelation of TMOS in isopropanol using both acidic and basic catalysts. The first step of the sol gel process was under acidic conditions. The second stage of hydrolysis was either acidic or basic using HCl or NH_4OH , respectively. The analysis of the Guinier region of the (SAXS) behavior of the gels indicated that the acid catalyzed gel dimensions were concentration dependent, whereas the base catalyzed was not. The significance of this observation is that the Guinier region yields information on the dimensions of the scattering source, which in this case is the silicate structure [41]. The Guinier region provides a measure of the radius of gyration of the scattering entities but is restricted to dilute systems. This limitation ensures that there are no interparticle interactions that contribute to the scattering intensity [63]. The acid catalyzed gels increased in dimension (Guinier radius) upon dilution [44]. The expansion of the acid catalyzed gel, according to Brinker et. al., indicates that it must be a linear structure that is highly entangled in concentrated solution. The dimensions measured in the concentrated solution were therefore attributed to interchain dimensions [44]. The base catalyzed gel structure was speculated to be a more compact spherical type structure [44].

The scattering intensity at intermediate angles scales as a power function:

$$I(s) = \sim K^{-x} \quad [1-1]$$

where x is referred to as the Porod slope for a particulate system and K is the scattering vector defined as $4\pi^2 \sin\theta/\lambda$, where θ is one-half the radial scattering angle and λ is the wavelength of the illumination. The magnitude of the Porod slope is related to the geometry of the scattering entity. A log-log plot of the scattering intensity versus the scattering vector K will have a Porod slope of -4 for a sphere. A Gaussian polymer chain in its unperturbed state is predicted to exhibit a Porod slope of -2 [63]. Silicate particles exhibit fractal behavior according to Brinker et. al. [44]. The acid catalyzed sol particles scattering curves had a slope slightly more positive than -2 indicating that the acid catalyzed particles closely resemble linear chains. This is in contrast to the base catalyzed systems where the Porod slope was more negative than -2, ca. -2.06 [44]. Brinker et. al. proposed the base catalyzed was more branched than the acid catalyzed particles, but that both were quite similar [44].

Martin and Wilcoxin have followed the evolution of silicate structures from the sols to gelation using dynamic light scattering [64,65]. The dimensions probed with dynamic light scattering by Martin and Wilcoxin are on the order of ca. 25 to ca. 400 nm [64,65]. The light scattering behavior of the sol to gel transition was determined and correlated with various growth models that have been proposed.

The metal alkoxide, TMOS, was gelled with NH_4OH in methanol at very dilute concentrations. The purpose of this was to monitor the size of the growing silicate structure and analyze diffusion of the structures in the solution. The growth of the clusters as described by Martin and Wilcoxin was exponential due to intracuster interactions in the early stages of the reaction. However, as the clusters reached a critical size and density in the solution the growth rate was closely associated with critical growth of gelation as a result of intercluster growth [16]. The studies of Martin and Wilcoxin reveal an early growth mechanism based upon the chemistry of the system followed by a time where the dimensions of the solid clusters is critical. Polymerization beyond gelation appears to be a function of the initial cluster geometry according to Martin and Wilcoxin [16].

A number of growth models have been used to explain the structure development in sol-gel processes [1,9,16]. Equilibrium growth models are representative of the classical step-growth polymerizations [35]. The Flory-Stockmayer Model uses a Cayley tree or Bethe lattice to describe the location of the reactive species. Bonds form between adjacent sites (reactive species) until an infinite cluster emerges at a certain extent of reaction. The gel point of the system is based upon the average functionality of the reactive monomers which must be greater than 2 [35]. The Flory-Stockmayer model predicts a Porod slope of -2, according to Martin [66], which fits well with most acid catalyzed sol gel processes [44]. However, it does not predict the behavior of the base catalyzed sol-gel

processing of silicates [64,65]. Glaser, Wilkes and Bronniman showed that the Flory-Stockmayer model failed to predict the behavior of an acid catalyzed sol-gel reaction of TEOS, methyltriethoxysilane (MTEOS) and dimethyldiethoxysilane (DMDEOS) [34]. According to the Flory-Stockmayer model the system with a ratio of 1:1 of DMDEOS to MTEOS, the critical conversion level for gelation is 0.68 [34]. However, the system did not gel at a conversion of nearly 0.95 as measured by ^{29}Si NMR [34]. The other equilibrium growth model, bond percolation, was also deemed inadequate by Glaser, Wilkes and Bronniman for their systems gelation behavior. Martin and Wilcoxon studies also noted inadequacies of both the bond percolation model and the Flory-Stockmayer model in predicting the correlation lengths determined in base catalyzed gels [64,65]. The correlation lengths were larger than predicted for the monomers and exhibited a sensitivity to concentration [44].

Kinetic growth models can be summarized by two processes, monomer-cluster growth or cluster-cluster growth [1,67]. These two processes have different requirements in terms of concentration of the reactants and their reaction mechanisms [1]. The monomer-cluster growth model is represented by the sol-gel processing of TMOS under neutral to basic conditions [1]. Kelts, Effinger and Melpolder [4] showed by ^{29}Si NMR that the monomer TEOS was still present in large concentrations at gelation under basic conditions. The acid catalyzed TEOS reaction consumed most of the monomer early to form oligomers [4,9]. Brinker and Scherer provide an excellent overview of the different models [1]. The monomer-

cluster growth model applies to the neutral and high pH sol-gel processes where the monomer concentration remains high. The cluster-cluster growth predicts the condensation behavior of the various oligomers formed early in sol-gel processes at low pH. The kinetic models applied to the sol-gel process appear to produce structures that fit the scattering data quite well [1,64,65].

Thus far, all the results presented have described the structure of alcogels. The conversion of alcogels to either aerogels or xerogels causes dramatic changes in the morphology of the gel [13,36] and ultimately their properties. The details of this will not be covered here. However, recently Hidach et. al. have characterized the mechanical properties and volumetric shrinkage of alcogels and aerogels as a function of pH and aging [68]. TMOS gels were prepared at different pH conditions ranging from acidic to basic. The alcogels were converted to aerogels by heating to 300°C and 20 MPa pressure [68]. The elastic modulus was determined in flexural by a three point bending method. The elastic modulus ranged from a low of 40 MPa to nearly 300 MPa as the density was increased from 0.15 g/cm³ to 0.4 g/cm³ by drying TMOS (neutral) under supercritical conditions as described above. The rate of shrinkage increased with increasing concentration of TMOS and with increasing hydrogen ion concentration in the sols. The total shrinkage varied with amount of TMOS, hydrogen ion concentration, and drying time. There was practically zero shrinkage at a pH of 9 for all conditions. The results were interpreted by Hdach et. al. in terms of the structures identified previously for both

acid and base catalyzed gels. The acid catalyzed gels are more open and less branched compared to the base catalyzed gels. Thus upon drying a larger number of loose chain ends in the acid catalyzed gel condense further and cause a contraction in the structure. The base catalyzed structure is more highly branched and condensed such that it is much less flexible. The base catalyzed structure undergoes very little reorganization.

2.5 Sol-Gel Derived Hybrid Materials

The previous sections were devoted to the processing and structures associated with inorganic oxide networks. There were some references made to organometal alkoxides in terms of the effect of ligands on the rates of hydrolysis and condensation. An entire new field of sol-gel chemistry has developed from the use of the organometal alkoxides with metal alkoxides and with metal alkoxide functionalized polymers. This section will describe the two most prominent classes of these inorganic/organic hybrid materials as well as closely related developments.

2.5.1 ORMOSILs (ORMOCERs)

Professor Helmut Schmidt began early in the 1980's reporting on novel materials which were produced by the combination of organosilane coupling agents

and metal alkoxides for use as contact lenses [15,69,70]. Schmidt initially prehydrolyzed a silane coupling agent (glycidyl trimethoxy silane) under reflux conditions in an acidified alcoholic solution with less than stoichiometric quantities of water [69]. The gelled products had poor mechanical strength and failed to remain a solid during drying at 100°C. Schmidt reported that the IR spectrum of this type of material contained a peak at 2870 cm^{-1} which indicated unhydrolyzed alkoxide remained. The next approach was the combination of the silane with TEOS to increase the cross-link density and strength. The components were refluxed with insufficient water to hydrolyze all alkoxides, then in a second step, they were refluxed with excess water and HCl to complete the hydrolysis of all alkoxides and condense the species. The materials produced were optically clear solids with poor mechanical strength. Yet, there was still evidence of the alkoxide species present. Therefore, Schmidt substituted the TEOS with titanium tetraisopropoxide which is a known catalyst for the condensation of metal alkoxides. This required a two stage process to incorporate the titanium into a network with the silane coupling agent to prevent premature precipitation of TiO_2 [69]. The gels produced with the titanium isopropoxide were monolithic, but brittle. This led to the first ORMOCER, which is a term that Schmidt substituted for ORMOSILS in 1989. Schmidt blended the glycidyltrimethoxy silane and the titanium isopropoxide with methacryloxysilane and then prehydrolyzed the mixture to the extent it could then be reacted with methacrylate monomer and a free radical initiator. The system was then cured to

150°C to produce a clear, monolithic structure [69]. The relative portion of the silane functionality was approximately 1:1 with respect to the polymethylmethacrylate.

Since the development of the first ORMOCERs, Schmidt has reported numerous other developments. TEOS, zirconium tetraisopropoxide and titanium isopropoxide were combined with epoxysilane and cured by sol-gel processing at ambient conditions, oven curing at 70°C, or U.V. irradiation at 60°C [70]. The TEOS/epoxysilane materials had poor properties overall. The titanium isopropoxide/epoxysilane ORMOCERs cured to the same extent at ambient as the TEOS/epoxysilane materials did at the elevated temperatures. The zirconium isopropoxide/epoxysilane system reacted to a much higher extent at the elevated temperature compared with the gel cured at ambient conditions [70]. The U.V. irradiation at the elevated temperature accelerated the cure of the titanium isopropoxide/epoxysilane mixture more than just the elevated temperature. The zirconium isopropoxide cured slower than at 70°C and the TEOS did not gel. The faster reaction observed for the titanium isopropoxide/epoxysilane was attributed to a ring opening polymerization of the epoxide initiated by the U.V. irradiation of titanium isopropoxide [70].

Recently, Schmidt and Wolter published a review of ORMOCER coatings for applications such as abrasion resistant coatings, moisture resistant coatings, and coatings for electronic materials [71]. An abrasion resistant coating with low permeability to moisture was prepared by reacting aluminum tri-sec-butoxide with

glycidyl trimethoxysilane, and n-propyl triethoxysilane. The process as described previously by Schmidt [3] requires the aluminum tri sec-butoxide be prehydrolyzed with a small amount of water. The aluminol functionality will condense with the alkoxy silanes spontaneously to produce a three dimensional network [71]. The coating applied to a commercial grade polycarbonate sheet by a dip-coat process and cured to 90°C to 130°C. The moisture resistance and the abrasion resistance of the polycarbonate were improved significantly by the ORMOCER coating. Another coating of similar composition, but with γ -aminopropyl triethoxysilane added as an adhesion promoter, reduced the hydrocarbon permeability of high density polyethylene [71].

An ORMOCER coating for electronic materials was prepared by combining diphenyldichlorosilane, vinyl methyldichlorosilane, and TEOS. The sol-gel processing of these coatings was under acidic and basic conditions. The addition of water to the mixture caused hydrolysis of the chlorosilanes which generated the chloride ion and thus created an acidic environment. The high pH reaction was initiated with ethanolic potassium hydroxide [71]. The solutions were hydrolyzed and condensed initially at ambient conditions followed by a cure up to 250°C. The authors reported that the acid catalyzed condensation reactions were very slow even at 260°C. Schmidt and Wolter attributed the slow reaction kinetics to the bulkiness of the phenyl rings which would inhibit the nucleophilic attack on the silicon atom. However, it might be more plausible that the extremely high concentration of acid

caused by hydrolysis of the dichlorosilane is slowing the gelation of the sol. It was shown by both Aelion et. al. and Coltrain et. al. that at very low pH, the time to gelation is quite long [37,38]. The base catalyzed sols gelled more quickly. The materials prepared by the thermal curing were then dissolved in toluene and ethyl acetate and thermally cured to 260°C. The authors claimed the resultant coatings exhibited excellent chemical resistance and moisture resistance. Two other methods of coating applications, electroplating of an emulsion and photocuring of the prehydrolyzed polymer, were evaluated also by Schmidt and Wolter [71]. The properties of these organically modified sol-gel derived inorganics are distinctly different from either the organic moiety or the inorganic moiety.

2.5.2 CERAMERS

There is one other truly novel class of materials that was developed by sol-gel processing of metal alkoxides simultaneously with organic molecules (or inorganic molecules) which are functionalized with metal alkoxides. These organic/inorganic hybrid networks are the unique combination of the ceramic-like properties of the metal along with the polymer-like properties of the functionalized molecules. Indeed the functionalized molecules are typically oligomers which range in molecular weight from ca. 650 g/mol to a high of on the order of 15,000 g/mol [16,17,18,24]. These

unique materials, commonly referred to as CERAMERs, are usually monolithic and optically transparent.

There is no typical CERAMER to describe, but actually a broad spectrum of materials. The first example of a CERAMER hybrid material was the incorporation of poly(dimethyl siloxane) oligomers and TMOS into a three dimensional network by a sol-gel process [16]. Professor Wilkes, along with his students, reacted the silanol terminated poly(dimethylsiloxane), using two oligomers with molecular weights of 1700 and 3400 g/mol, with an approximately equal weight fraction of TEOS with HCl as the catalyst under reflux conditions (80°C) [17]. These early CERAMERs were monoliths that were both quite flexible and optically clear. The authors attributed these features to the incorporation of the rubbery PDMS into the silicate network and the lack of large scale macrophase separation, respectively. TEOS prepared in the same manner without the PDMS oligomers was inflexible and brittle [17]. The clarity of the samples indicated that if phase separation had occurred the dimensions were not large enough to scatter visible light. Dynamic mechanical behavior was presented for these materials based upon TEOS and PDMS in which the acid to TEOS ratio was varied from 0.022 to 0.111 mol/liter. The storage modulus, a measure of the effective stiffness of the network, was approximately 1 GPa at -150°C and dropped nearly two orders of magnitude and reached a plateau as the temperature was increased to ca. ambient. Upon further heating, the storage modulus rose to approximately 10 MPa at a temperature of 300°C [17]. There was

a trend of the storage modulus to lower slightly with increasing acid content. The $\tan \delta$ behavior of these materials had a maximum at ca -106°C which is approximately 14°C higher than the predicted T_g for PDMS. A second major loss dispersion occurred at ca. -30°C . The authors suggested that the bimodal $\tan \delta$ behavior of the TEOS/PDMS CERAMERs indicated that there was a degree of microphase separation. The shift to the higher temperature of the PDMS T_g was ascribed to a restriction of the polymeric chains by the silicate phases formed from the metal alkoxides. The higher temperature dispersions, from ca. -30°C to nearly 80°C , were attributed to the molecular relaxations of oligomers that were well mixed with the silicate phases. Mechanical properties of the TEOS/PDMS hybrid materials reflected the same trends observed in the storage modulus with regards to the relative acid concentration. The elastic modulus decreased as the acid concentration increased. The ultimate elongation increased with increasing acid concentration. The authors suggested that the relatively higher rates of hydrolysis and condensation with higher acid concentrations produced different morphologies. The theory was that early in the reaction the PDMS silanols self-condensed and phase separation would occur as the molecular weight increased. The TEOS silanols generated at a later stage would then co-condense with the PDMS silanols. The extent of phase separation would therefore depend upon the level of acid in the reaction.

Wilkes et. al. also evaluated CERAMERs with a higher weight ratio of TEOS/PDMS (3:2) as a function of the acid concentration to further investigate their

proposed mechanism. The higher TEOS content increased the storage modulus of the CERAMER in the rubbery region to a value of ca. 100 MPa [17]. The rubbery modulus exhibited a steady increase as the temperature was increased. However, as the acid concentration was increased the storage modulus dropped further and then began a rather sharp increase upon heating beyond 150°C. The $\tan \delta$ behavior of the CERAMERs with a higher ratio of TEOS to PDMS was reduced compared to the compositions with a higher weight fraction of PDMS. This of course is as predicted since the loss behavior is due molecular relaxations of the PDMS chains. There was, however, a higher temperature (nearly 100°C) loss dispersion associated with the higher acid containing CERAMERs (and higher ratio of TEOS to PDMS). The author's ascribe the high temperature loss behavior to possibly better mixing of the two phases and thus, the siloxane chains would be dispersed better. The elongation to break for these CERAMERs was higher than the TEOS/PDMS hybrids with equivalent weight fractions of TEOS and PDMS. Wilkes et. al. concluded that the behavior of the CERAMERs with higher ratio of TEOS to PDMS supported their proposed mechanism [17].

The effects of the amount of acid, the ratio of TEOS to PDMS and the molecular weight of the oligomer were studied in more detail by Huang, Orler and Wilkes [18]. The structure-property relationships of the TEOS/PDMS CERAMERs indicated that there was a degree of microphase separation. The dimensions of the "micro" phases had to be quite small since the hybrid materials were optically clear.

There was evidence in both dynamic mechanical behavior and the stress-elongation response of the TEOS/PDMS CERAMERS that as the acid increased the systems were better dispersed. Huang et. al. applied the method of SAXS to the TEOS/PDMS materials to study the nature of the phase separation as a function of acid content. The SAXS profiles as mentioned earlier provide information on any systematic fluctuations in the average electron density of a scattering source. The SAXS profile is a plot of scattered intensity as a function of the angular factor s which is given as $(2\sin \theta)/\lambda$ where θ is one-half the radial scattering angle and λ is the wavelength of the x-ray source. The scattered intensity increases as the average electron density fluctuation increases and tends toward a maximum value if the fluctuation is periodic throughout the scattering source. The opposite is observed as the average electron density fluctuation decreases which is representative of the behavior of a well mixed system. Huang et. al. reported that the SAXS intensity of the TEOS/PDMS CERAMERS did reach a maximum at low values of s and decreased monotonically at larger s values [18]. The decrease in the scattered intensity was systematic in that it correlated with higher concentrations of the acid catalyst. Huang, Orlor and Wilkes concluded the SAXS behavior supported the mechanical properties and dynamic mechanical behavior of the TEOS/PDMS hybrid materials [18]. The higher acid concentration, however, did give rise to two distinct changes, one in the stress-elongation response and the other in the $\tan \delta$ behavior of TEOS/PDMS CERAMERS. A shift from a "Hookean" response to one of

'yielding' was observed in the stress-elongation response of the TEOS/PDMS hybrids when the acid level (actually mole ratio with respect to TEOS) was increased from 0.045 moles to 0.067 moles. A loss dispersion at close to 90°C appears in the $\tan \delta$ spectrum for the TEOS/PDMS materials with the change to higher acid content. The authors explained the data in terms of improved dispersion of the PDMS in the TEOS structure. However, the conditions employed in preparation of the TEOS/PDMS CERAMERs and the hydrolytic instability of PDMS would suggest other possible explanations. The TEOS/PDMS hybrid materials were prepared with less than stoichiometric quantities of water which according to most studies reduces the rate of hydrolysis of the alkoxide [1,4,37]. Another consideration would have to be the potential for ester exchange between the TEOS and isopropanol which would reduce the reactivity of the metal alkoxide [1,38,40]. The higher reactivity of the terminal PDMS silanol (with respect to TEOS silanol) and low concentration of hydrolyzed TEOS species early in the reaction would tend to promote chain extension as Huang et. al. suggests. However, as the acid concentration is raised with respect to TEOS, it is increasing with respect to the PDMS and has a chance of cleaving the chains under the reflux conditions employed, 80°C. The TEOS species could potentially insert into the chain and effectively reduce the molecular weight between network junctions. This in effect would increase the T_g and could explain a shift from the hookean behavior to the semi-yielding behavior of the stress-elongation response as the acid level was increased. This alternate explanation for

the observed behavior is partially supported by the work of Huang, Orlor, and Wilkes where they determined the effect of reducing the PDMS molecular weight to 550 g/mol from 1700 g/mol [18]. The $\tan \delta$ response of the hybrids with short oligomers was dominated by a loss dispersion covering approximately a 200°C range with the maxima shifting from 90°C to 150°C as the level of acid was increased from 0.022 mol. to 0.11 mol.. The scattering intensity of the hybrids prepared with the lower oligomer molecular weight decreased significantly as the acid level was raised. The maximum intensity of the shorter oligomer (550 g/mol) containing hybrid at the low acid concentration was nearly the same as that of the CERAMER with the 1700 g/mol oligomer made with the highest acid content. The structure/property relationships of the TEOS/PDMS could be explained as a function of dispersion of the two phases, but the possibility of chain scission and insertion of the silicate structure is another possible explanation.

The structure/property relationships described for the novel TEOS/PDMS CERAMERs were later demonstrated for a wide variety of oligomers and even a variety of metal alkoxides [24,26,27,29]. Huang, Orlor and Wilkes substituted poly(tetramethylene oxide) oligomers for the PDMS oligomers [24]. The poly(tetramethylene oxide) oligomers' hydroxyl end groups were reacted with isocyanatopropyltriethoxysilane to increase the functionality to six. These functionalized oligomers of poly(tetramethylene oxide) (PTMO) were reacted with TEOS to produce a series of hybrid materials with higher elastic moduli, higher stress

at break and higher elongations [24]. The effects of metal alkoxide to oligomer weight ratio, acid to metal alkoxide mole ratio, solvent, aging, and oligomer molecular weight were all examined by Wilkes and co-workers using TEOS, PTMO, and HCl.

The dynamic mechanical behavior of the TEOS/PTMO CERAMERs as a function of different molecular weight oligomers of PTMO illustrated trends that correlated with the behavior of the TEOS/PDMS hybrid materials. The storage moduli were close to ca 10^9 MPa in the glassy regime of the oligomer (below the T_g which for PTMO is near -70°C), and decline approximately two orders of magnitude as the temperature was increased significantly above the T_g . However, there was a rather distinct incline in the storage moduli of the inorganic/organic hybrid materials evaluated which was associated with a curing of the inorganic phase [24]. The loss behavior of the TEOS/PTMO CERAMERs was defined by a rather broad unimodal dispersion compared with the bimodal dispersions of the TEOS/PDMS hybrid materials [18]. The apparent T_g of the TEOS/PTMO CERAMERs increased with increasing levels of inorganic (TEOS) added into the network. Huang et. al. explained the behavior with respect to two types of motional restrictions on the PTMO segments that account for the loss dispersions:

- 1) **TYPE 1:** The effect of bonding the ends of the chains into the network.

- 2) TYPE 2: The effect of mixing of the PTMO segments with lightly condensed TEOS species. The encapsulation of the PTMO segments by the network forming silicate species.

The restrictions labeled as TYPE 1 and TYPE 2 are based upon the various growth models for acid catalyzed sol-gel processes using TEOS which generally describe a lightly branched, partially condensed silicate network as the structure [67,68]. The trends in both the TEOS/PDMS and TEOS/PTMO materials were explained quite well by their model. The lower molecular weight oligomers had a higher T_g which was explained as a higher degree of mixing in the system, thus a TYPE 2 restriction. The shorter the oligomers of PTMO (or the PDMS) the more likely the silicate phases are continuous, and there would be a higher probability of chain encapsulation. Therefore the system with lower molecular weight oligomers would have a higher modulus compared to that of the hybrid materials with higher molecular weight oligomers [24]. In the other direction, increasing the length of the oligomer reduces the concentration of the inorganic phase with respect to the PTMO and therefore the modulus would decrease.

The TEOS/PTMO hybrid materials compared to the TEOS/PDMS CERAMERs with oligomers of comparable molecular weight, 1000 g/mol versus 1700 g/mol, respectively, (NOTE: The molecular weight of the PTMO was increased by approximately 500 g/mol by the reaction with the isocyanatopropyl triethoxysilane, thus the 1000 g/mol oligomer became a 1500 g/mol oligomer) had higher

extensibility ca. 100% versus 10% and a lower Young's modulus, i.e. 3 MPa versus 12 MPa [24]. Huang et. al. compared the values of the TEOS/PTMO hybrids which were prepared with the 2000 g/mol oligomer of PTMO to the properties of the TEOS/PDMS networks that were made with the 1700 g/mol oligomers of PDMS. The differences in properties were not significant between the two oligomers of PTMO, i.e. 1000 g/mol versus 2000 g/mol [24]. The overall differences in the mechanical properties of the two classes of CERAMERs, i.e. TEOS/PTMO versus TEOS/PDMS, were attributed to differences in the average functionality of the different oligomers. The TEOS/PTMO CERAMERs underwent dramatic changes in mechanical properties after aging at ambient conditions or annealing at elevated temperatures for relatively short times. Huang et. al. showed that the TEOS/PTMO materials Young's modulus increased by a factor of five after aging for approximately one year at ambient conditions [24]. The stress at break of the CERAMER increased by a factor of two and the elongation at break decreased from ca. 100% to 18%. The same magnitude of change was reported for the same composition CERAMER which was annealed for 2 hours at 110°C after aging for 8 days at ambient conditions.

Huang et. al. ascribed the aging of the TEOS/PTMO CERAMERs to further condensation of unreacted silanol and/or alkoxides in the gels. The process has been described previously for network forming reactions by Enns and Gilham in terms of a Time-Temperature Transformation (TTT) phase diagram [72]. A network

forming system typically undergoes a sol to gel transition, sol to glass transition (vitrification) or the glass to gel transition according to the TTT diagram. The sol to gel stage is characterized by a rapid and large increase in viscosity i.e. the material no longer flows under its own weight. The network forming reactions are slowed dramatically by this transition and become diffusion limited by the viscosity of the system. Vitrification effectively occurs when the system T_g reaches the temperature of the reaction. All reactions are in essence stopped when the material vitrifies since all molecular species are in a glassy state with extremely long diffusion rates. The network forming reactions can occur, albeit at a much slower rate in the gelled material if there are any reactive species remaining. The total number of reactive groups in the TEOS/PTMO system is much larger than that in the TEOS/PDMS system due to the functionalization of the PTMO oligomers. Therefore, the TEOS/PTMO systems might continue to form silicate bonds beyond gelation if reactive species remain within close proximity of each other. Huang et. al. referred to Flory's statement that a three dimensional network will form if the systems average functionality is greater than two and thus is independent of the structural characteristics of the reactants (This does not consider however the reactivities of the monomers) [35]. The point of gelation has been predicted fairly well for acid catalyzed sol-gel processes using the Flory-Stockmayer relationship, as previously stated (Section 2.4). The Flory-Stockmayer relationship predicts the TEOS/PTMO system would gel at a degree of conversion of approximately 0.242 versus a value of

0.251 for the TEOS/PDMS system, assuming equal weight fractions of the metal alkoxide and the oligomer (using 1500 g/mol and 1700 g/mol for PTMO and PDMS, respectively). This does not appear to predict the aging effect. However, if one considers the difference in processing temperatures, ambient for the TEOS/PTMO system versus refluxing at 80°C for the TEOS/PDMS materials, it is reasonable. The kinetics studies by Aelion [38] demonstrated the temperature dependence upon the hydrolysis of TEOS. Thus, refluxing the TEOS/PDMS system prior to gelation would most likely hydrolyze all of the alkoxides and promote condensation reactions at a faster rate than allowing the system to react at ambient conditions. The number of reactive groups would therefore be more for the TEOS/PTMO materials than the TEOS/PDMS materials early in the process. Beyond the gel point, however, the reaction, i.e. aging, is slowed and limited by diffusion of the reactive species. The reaction rates are slow, but the condensation of alkoxides and silanol groups do continue for acid catalyzed gels from TEOS after gelation according to Hdach [68].

Similar behavior was reported by Huang et. al. for a CERAMER composition of TEOS, titanium tetraisopropoxide and PTMO (2900 g/mol) in a ratio of approximately 0.8:1.2:3.0. The Young's modulus increased from an initial value of approximately 6 MPa (four days after gelation) to an average value of 50 MPa after aging for 100 days. The higher modulus could also be achieved by annealing the fresh material (4 days beyond gelation) in an oven at 80°C for 4 days [24,27]. The initial modulus of the CERAMERs containing a mixture of TEOS and titanium

isopropoxide was higher by a factor of 3 compared to material prepared in the same manner without titanium isopropoxide [24]. This supports the explanation given above for the aging phenomena since titanium isopropoxide is well known as a condensation catalyst for metal alkoxides [73]. The addition of the titanium isopropoxide to the reaction accelerates the condensation of the TEOS initially. After gelation occurs, however, the remaining reactions become diffusion limited as in systems with TEOS only.

The same trends observed in the SAXS behavior of the TEOS/PDMS hybrids with respect to variations in molecular weight of the oligomer and level of TEOS were exhibited by the TEOS/PTMO CERAMERS. There was a more discrete maxima in the TEOS/PTMO materials SAXS profiles of scattered intensity versus the angular factor s , which decreased with the molecular weight of the PTMO oligomer [24]. The position of the maxima in the SAXS profiles of the TEOS/PTMO system shifted to lower values as the molecular weight of the PTMO oligomer increased. The maximum intensity of the SAXS profile increased as the weight fraction of TEOS was raised and as the materials aged. The change in scattered intensity as a function of the level of TEOS is due to increasing the mean square electron density fluctuation of the system. Huang et. al. showed that the electron density of SiO_2 was nearly twice that of TEOS, PTMO, or PDMS [24]. Thus as the amount of TEOS is increased, or as a higher percentage of alkoxides are condensed, the amount of SiO_2 rises. This would be revealed in the intensity of the

scattered intensity assuming of course that the level of mixing remains constant. This was deduced by Huang et. al. to be the case since the position of the SAXS profile maximum intensity did not shift significantly as a function of aging [24].

A morphological model was developed to account for the structure-property relationships of the TEOS/PDMS hybrid materials and the TEOS/PTMO CERAMERS [18,24,28]. The model is illustrated in Figure 2-3 for the TEOS/PTMO hybrid systems. There are three generalized regimes or phases which make-up the CERAMER morphology. The first regime identified in the upper left circle is intended to represent the PTMO rich regimes. The weight fraction of PTMO (assuming the functionalized oligomer number average molecular weight is 2600 g/mol) varies from a high of nearly 96% to a low of ca. 57% in the majority of the compositions evaluated by Huang [26]. Thus, as the weight fraction of TEOS is increased, the amount of three regimes just described would be expected to change accordingly. The changes in mechanical properties and scattering behavior of the CERAMERS can be adequately described by the appropriate modifications to the morphological model portrayed in Fig. 2-3. The characteristic spacing as determined from the reciprocal of the s value corresponding to the maxima in the SAXS intensity profile is symbolized by the distance between the silicate regimes (Fig. 2-3). Variation in the molecular weight of the oligomers would either shorten or lengthen the spacing and inversely effect the s value.

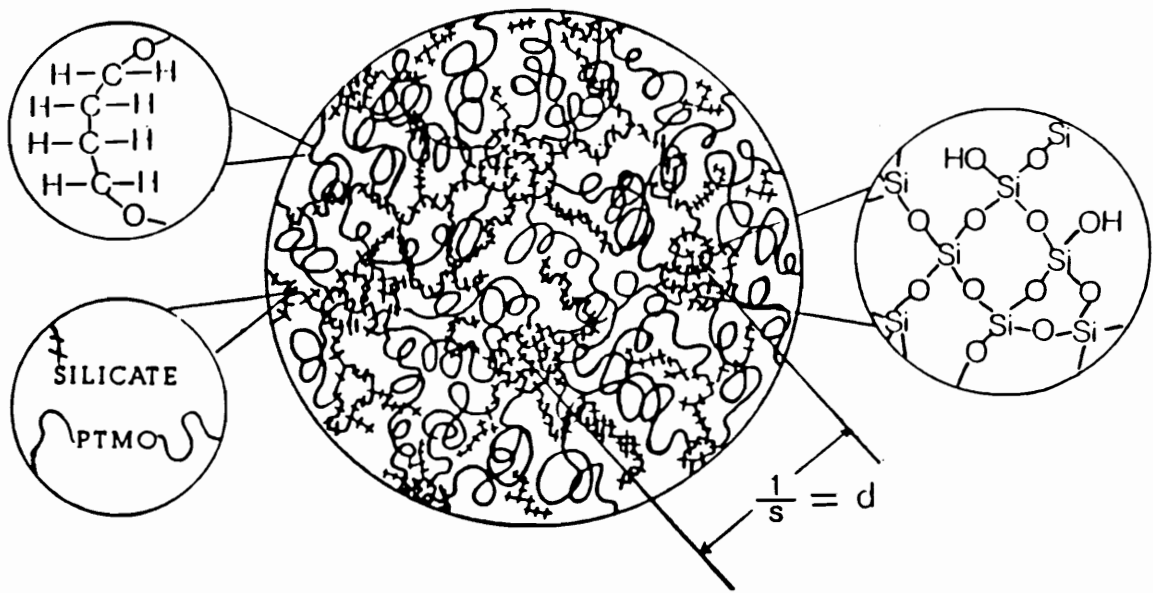


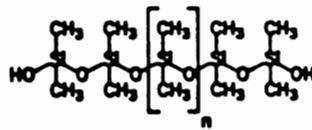
Figure 2-3 Morphological model for CERAMERS [24]

The properties of another series of CERAMERs, in which the oligomer was a functionalized poly(arylene ether) ketone, was reported by Noell et. al. [29]. The structure of the functionalized poly(arylene ether) ketone (PEK) oligomer (3900 g/mol) is illustrated in Figure 2-4 along with PDMS and PTMO oligomers for a comparison. The PEK oligomer has a number of major differences with respect to the other two (Fig. 2-4). The PEK backbone is mostly aromatic and thus would be much stiffer which would correlate with a higher T_g (ca. 150°C) compared with PTMO (-70°C) and PDMS (-120°C). The functionalization of the PEK oligomer generated a urea linkage rather than the urethane linkage produced by end capping the PTMO oligomers. The third difference is the molecular weight of the PEK which is slightly higher than the others. The general structure-property relationships of the TEOS/PDMS and TEOS/PTMO CERAMERs could be applied to the TEOS/PEK hybrid materials according to Noell et. al. [29]. The higher T_g of the PEK oligomer led to vitrification of the system which limited the extent of reaction and development of ultimate properties. Noell et. al. employed differential thermal analysis (DSC), dynamic mechanical analysis and FTIR to characterize the extent of reaction in the TEOS/PEK materials as a function of reaction temperature. The T_g of the TEOS/PEK CERAMER (ratio of TEOS to PEK is 3:1) was increased to a maximum of nearly 260°C by thermal cycling to 300°C in a DSC [29]. The $\tan \delta$ behavior of the TEOS/PEK materials gelled at ambient conditions was characterized by a broad loss dispersion peak from ca. 40°C to 100°C at which point it began to

rise. Curing the same composition at 100°C and 200°C caused the peak to shift to higher temperatures beyond the upper temperature limit of the instrument. The storage modulus of the TEOS/PEK material showed the onset of the glass transition temperature at 200°C by a drop from the glassy modulus of ca. 10^9 MPa. FTIR analysis of a TEOS/PEK CERAMER cured at 25°C and 200°C showed an increase, corresponding to the higher temperature cure, in relative intensity of an adsorption at 1100 to 1000 cm^{-1} which Noell et. al. attributed to a Si-O-Si stretching mode [29]. This qualitatively verified the authors claim that any change in properties as the cure temperature was raised was associated with condensation reactions resulting from increased mobility of the system [29]. Thus, the DSC, dynamic mechanical analysis and FTIR reflect the effects of vitrification on the extent of reaction as predicted by Ennis and Gillham's TTT phase diagram. The incorporation of PEK and TEOS in a hybrid network demonstrated that the structure-property relationships and the morphological model developed for the TEOS/PDMS and TEOS/PTMO materials could be useful in the design and evaluation of new materials that fit the category of CERAMERs.

2.5.3 SiO_2 Reinforced Networks

Professor James E. Mark has contributed a significant amount of knowledge in the area of hybrid materials derived from sol-gel processing. However, with

Polydimethylsiloxane**Poly(tetramethylene)oxide**

$n = 10 \text{ to } 40$

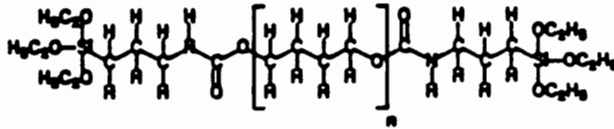
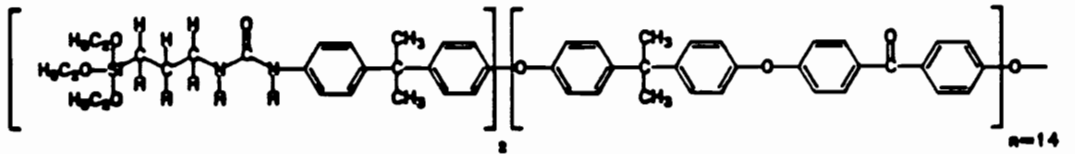
**Poly(ether ketone)**

Figure 2-4 Functionalized oligomers used in CERAMERs

respect to this review the work of Mark and his colleagues in the area of sol-gel derived hybrid systems will be addressed. The earliest report of sol-gel derived materials from Mark et. al. describes the formation of silica particles in situ within an elastomeric network of PDMS [20]. The first report of a hybrid system was the functionalization of poly(dimethyl siloxane) oligomers for the formation of elastomeric networks [20]. Sur and Mark reacted vinyl terminated poly(dimethyl siloxane) oligomers with triethoxysilane at 70°C for 24 hours with chloroplatinic acid. The functionalized oligomer tPDMS (the lower case t is meant to differentiate these oligomers from the silanol terminated PDMS oligomers). The tPDMS oligomers were used in three different ways, (1) reacted with silica (commercial grade fumed silica), (2) reacted with TEOS, and (3) reacted with titanium isopropoxide. The water necessary for hydrolysis was supplied via atmospheric moisture. The networks obtained from each method was extracted and then deswelled [20]. The mechanical properties of the tPDMS reacted with the fumed silica were insufficient for analysis. There was a rather large sol fraction of 0.4 which Sur and Mark assigned to insufficient silanols on the surface of the silica. The other two systems contained approximately 1.5 wt% metal oxide according to Sur and Mark [20]. The initial moduli of the TEOS/tPDMS material was on the order of 0.08 to 0.1 N mm⁻². These materials based upon the tPDMS oligomers (11,000 g/mol) represented "a stable elastomeric network structure" [20].

Mark et. al., using transmission electron microscopy, examined the morphology of silica particles formed in situ by the sol-gel process [74]. Two different networks were prepared with either a vinyl terminated PDMS or a silanol terminated PDMS cross linked by $\text{Si}(\text{OSi}(\text{CH}_3)_2)_4$ or TEOS, respectively [74]. The networks were then swollen with TEOS catalyzed by either ethylamine or an acid catalyst. The structures formed by base catalysis were well defined spherical particles with a reported diameter of approximately 20.0 nm. Aggregation occurred at high loadings of silica i.e. 85 wt %. The acid catalyzed structures were rather continuous and not as well defined as the base catalyzed particles. The reduction of the acid strength, i.e. changing from acetic acid to potassium dihydrogen orthophosphate, enhanced the formation of discrete particles [74]. The structures reported by Mark et. al. as related to the type of catalyst, i.e. acid versus base, are similar to those reported for sol-gel processes in solution [75]. The general morphology of the sol-gel derived structures as identified by SAXS analysis of fractal dimensions were also in agreement with the findings of Mark et. al. [42,76]. Brinker et. al. clearly demonstrated that the structures formed in acid catalyzed systems were swollen, linear structures in comparison to those formed by base catalysis [76].

More recently Clarson and Mark have formed titania particles within a poly(methyl phenyl siloxane) (PMPSX) elastomeric network by the sol-gel process [21]. The incorporation of silica in PDMS by the sol-gel process reduces the thermal stability of the elastomers possibly by attack on the PDMS chains by the surface

silanol groups of the silica according to Carlson and Mark [21]. The PDMS filled networks exhibited strain hardening behavior at high extensions which was speculated to be due to crystallization of the PDMS chains. The PMPSX used by Carlson and Mark had a molar mass of 186,000 g/mol, were atactic, and crosslinked by a free radical initiator. The titania particles were formed by a base catalyzed condensation of titanium tetraisopropoxide [21]. The stress-elongation response of the PMPSX/titania networks were linear upto the point of rupture. This was contrasted with a marked upturn in the stress-elongation response of silica filled PMPSX elastomers at high elongations. Carlson and Mark attributed the differences in the mechanical response of the two systems to contrasts in the nature of interactions between the filler particles and the PMPSX chains [21]. The other result of their studies was that the thermal stability of the PMPSX elastomer was not changed by the titania, but was with silica as the filler particle [21].

Numerous other reports in the literature describe systems similar to those studied by Mark et. al.. Mauritz et. al. used a sol-gel process to form silica particles in situ in Nafion membranes [22]. The Nafion membrane is a perfluorinated ionomer membrane. Mauritz used the sulfonated poly(tetrafluoroethylene) ionomer (Nafion 117). The membranes were pretreated to fully protonate the sulfonic acid groups. The pretreated membranes were then swollen in a solution of methanol and water for a prescribed period which was followed by the addition of a TEOS/methanol solution such that the ratio of TEOS to water was 1:4. The

methanol was replaced with ethanol and propanol to determine the influence of solvent on the structure. A second procedure used by Mauritz et. al. was the same as the first except the TEOS addition was a slow process. All the membranes were removed from the TEOS solution after a prescribed period of time, dried under vacuum and then heated for 2 hours at 110°C to effect the hydrolysis and condensation of the TEOS [22]. The weight gain of the membranes was regarded as the weight of silica in the membranes. The increase was uniform for the various immersion times of the membranes in the TEOS solution. FTIR and ^{29}Si NMR studies indicated that the first procedure generated silica structures that were linear with a large concentration of unreacted silanol groups which are typical of acid catalyzed sol-gel processes. The slow addition process allowed for higher loadings of the TEOS and by the two spectroscopic methods appeared to represent a more connected structure. The general mechanical behavior of the silica filled membranes were consistent with those reported by Wilkes [24] and Mark [21] for elastomeric networks filled with silica by the sol-gel process using acid catalysts and TEOS. The elastic modulus increased, the stress at break increased, and the elongation at break decreased as the ratio of TEOS to oligomer was raised. There was a sensitivity of the rate of TEOS uptake to the particular solvent used as well as the method i.e. rapid versus slow addition of TEOS [22].

Mauritz and Warren have further characterized the structure of the silica phase developed by the in-situ sol-gel conversion of TEOS in the Nafion membranes

by FTIR [77]. FTIR spectroscopic studies indicated that the structures, i.e. silicate "clusters", became more linear with time which correlated with a higher concentration of TEOS uptake [22]. The model that Mauritz and Warren proposed based upon the previous FTIR and ^{29}Si NMR spectroscopic studies [22] and their work [77] is characterized by a silicate network composed of bonded silicate ring structures which with time and more TEOS redistribute into more linear, slightly branched networks of silicates [77]. However, it would appear more reasonable that based upon the work of Kelts and Armstrong [9] as well as the other ^{29}Si NMR studies previously discussed (Section 2.4.3), the initial cyclic structures identified by Mauritz and Warren using FTIR are indeed trimers and tetramers of partially hydrolyzed TEOS. As time progresses, the cyclics undergo alcoholysis or hydrolysis and condensation with monomer to form the typical linear type silicate structure characteristic of an acid catalyzed sol-gel process.

2.5.4 Other Organic/Inorganic Hybrids

Pope, Asami and MacKenzie [78] prepared inorganic/organic hybrid materials by impregnating sol-gel derived silicate structures with methylmethacrylate monomer. TEOS was gelled in ethanol using hydrofluoric acid as the catalyst with a ratio of water to metal alkoxide of 4:1. The sol was heated to 40°C and following gelation heated to 600°C (The porosity of the gels was varied by thermal treatments

at 1000°C). The aerogels were then immersed in purified methyl methacrylate monomer with 2% benzoyl peroxide. The impregnated gels were cured at 60°C then heated to 90°C to complete the curing of the methyl methacrylate (PMMA). The properties of the PMMA impregnated silica gels varied as a function of the volume fraction polymer. The modulus of rupture (compressive mode) fell between the values of the unfilled silica and the PMMA. The density of the composite varied linearly with the volume fraction of PMMA as would be predicted by an ideal rule of mixtures. The refractive index of the composites varied according to the Clausius-Mossotti relationship:

$$(n^2-1)/(n^2+2)=(4\pi/3)\sum N_j\alpha_j \quad [1-2]$$

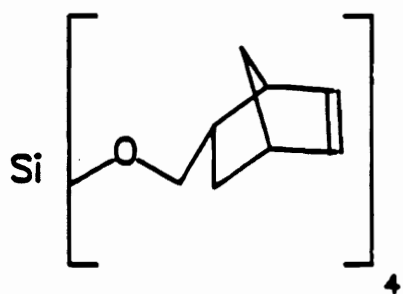
where n is the index of refraction, N_j is the concentration and α is the electronic polarizability [78]. The natural log of the elastic moduli of the samples, as determined from the compressive stress-strain curves, varied linearly with the volume fraction of the PMMA. The authors demonstrated that the behavior of the reduced elastic moduli of the composites as a function of volume fraction PMMA were similar to that of a PMMA filled Vycor-derived porous silica glass [78].

Other types of inorganic/organic hybrid materials have been reported in the literature. One example is a ring opening polymerization of 2-methyl-2-oxazoline (POZO) which is used to produce poly(n-acetylenimine) oligomers of various

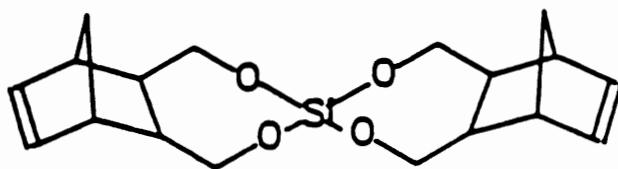
lengths [79]. The oligomers of POZO were then end capped with triethoxysilane and then coreacted with TEOS by a sol-gel process to produce an organic/inorganic hybrid material. The POZO/TEOS hybrids were transparent, monoliths with amphophilic properties according to the authors. Furthermore, porosity could be controlled in the materials by thermal treatments (600°C) which selectively degraded the POZO [79].

Another example involving a ring opening polymerization is the work of Novak et. al. [80]. Novak et. al. synthesized a series of alkoxysilane derivatives that were polymerizable by either a free radical polymerization or a ring opening metathesis polymerization (ROMP) in addition to the sol-gel process. Novak's objective apparently was to produce interpenetrating networks with polymers that are incompatible with silica [80]. The unique structure of the monomers synthesized is illustrated in Figure 2-5. The unique structure of both monomers 2 and 3 are such that upon hydrolysis the ring structure released is capable of polymerization by the a ring opening polymerization. The resultant composite gels (by the coreaction of the monomers and TEOS) were monolithic and transparent for most ratios of monomer to metal alkoxide. However, the authors did identify a number of limitations to the generation of transparent monoliths including ratio of monomer to metal alkoxide and relative rates of polymerization. The authors also reported the monoliths did not exhibit the normal shrinkage associated with the sol-gel derived structures due to both the ring-opening mechanism and a secondary ester-forming

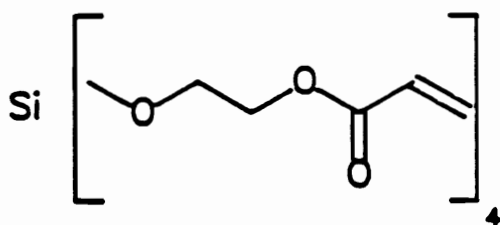
reaction with the anhydride. In some instances, the anhydride functionality formed an ester with the hydrolyzed alcohol, thus reducing the tremendous reduction of mass normally associated with sol-gel processes [80]. Wei et. al. have prepared organic/inorganic hybrid materials by the coreaction of poly(ally methacrylate) and poly(ally methacrylate-co-methacrylate), triethoxy silane functionalized, and TEOS under acid conditions [81]. The polymers were prepared by a group transfer polymerization which yielded molecular weight distributions (M_w/M_n) of on the order of 1.2 to 1.4. The gels produced from these materials were reportedly optically clear and monolithic structures. The thermal stability, in terms of thermal gravimetric analysis at a heating rate of ca. 20°C per minute, of the sol-gel derived hybrids was improved by approximately 30°C compared to the neat polymer.



I



II



III

Figure 2-5 Novel functionalized oligomers [80]

2.6 SUMMARY

There are a number of key features of the sol-gel process that directly influence the results to be presented in this dissertation. The sol-gel process can be summarized as follows:

1. The rates of hydrolysis and condensation vary as a function of the reaction system's pH. At low pH, the hydrolysis reaction is rapid and condensation is the rate determining step. At medium (neutral) pH, the rate of gelation approaches a maximum. At high pH, hydrolysis is the rate limiting reaction and time to gelation increases with pH.
2. The pH of the solution is a relative scale based upon the metal alkoxide, the solvent, the amount of water and the extent of reaction supplied. The comparative reaction rates of TEOS, titanium tetra-isopropoxide and zirconium tetra-n-propoxide are representative of the influence of metal alkoxide structure. The solvents can effectively change the pH of the solution by interactions with the catalyst as well as the sols. The amount of water of course can also influence the effective pK_a of a catalyst.

3. The structures that develop in a low pH reaction are distinctly less branched than those formed in neutral to high pH reactions. The level of condensation in a low pH reaction is less than that of a high pH system. Structures from a low pH sol-gel process will typically undergo more syneresis than those formed at a higher pH. The low pH structures have been described as a wispy structure compared to the cluster-like structures that form at high pH.
4. There have been three general approaches to the preparation of inorganic/organic hybrid materials. The first, by Schmidt, incorporated reactive organic functionalities into a sol-gel structure by use of silane coupling agents. The materials were typically thermally cured further to complete the sol-gel condensations as well as the polymerization of the organic functionality. The second process involves the functionalization of oligomers or polymers which could then coreact with metal alkoxides in a sol-gel process to produce a nanocomposite. The third approach involves the in-situ formation of either a sol-gel structure within a polymeric network or the formation of an organic phase within a sol-gel derived inorganic network. All three methods generate materials with structure-property relationships intermediate between a filled elastomer and a ceramic.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Introduction

A separate section of this thesis will be devoted to the materials, experimental procedures and characterization methods associated with the research described. The materials used in the preparation of the TEOS/PTMO CERAMERs are similar in most aspects to those described previously by Huang [26] and Glaser [27]. However, the method of end capping the PTMO oligomers with isocyanatopropyl triethoxysilane will be described in detail as it was practiced for the first time in our laboratory. The synthesis of polyimides studied in various CERAMER compositions will be described as performed by this author. A brief overview will be presented for those polyimides so graciously supplied by Prof. J. E. McGrath and co-workers. (The details of the synthetic methods and characterization will be published elsewhere.) [82]. Section 3.3 will detail the various sol-gel processes used to prepare the

CERAMERs prepared and characterized. Section 3.4 will be devoted to the methods of characterization and procedures for the operation of the equipment. The nomenclature of the various CERAMER materials as developed previously by Huang et. al. [17,18] has been modified slightly to accomodate the numerous changes in metal alkoxides, oligomers, catalysts, and solvents. The nomenclature will therefore be introduced for each type of material as it is described.

3.2 Materials

Table 3-1 lists the majority of the materials along with their common abbreviations which have been used for this project. The nomenclature does not necessarily follow any formal guidelines, but has provided continuity in the description of CERAMERs. The catalysts are listed first, followed by the metal alkoxides and then the oligomers/polymers. The PSS (70,000 g/mol) was supplied as a 30 wt% solution (Polysciences, Inc., Cat. No. 8770). This was used as is without further purification. There were 0.0026 equivalents/gram of the PSS solution as determined by titration with standardized NaOH. The density of the PSS solution was determined to be 1.2 gm/ml. The HCl (Fisher Scientific) was obtained as a 10N solution and used as received. The ethylamine (Aldrich, Inc.) was diluted to the appropriate concentration volumetrically and stored in a stoppered flask. The p-

toluene sulfonic acid (Aldrich Inc.) was obtained as a 30% aqueous solution and used as received.

3.2.1 Metal Oxides

Numerous metal alkoxides have been used in preparation of the CERAMER formulations described in this report. The materials were generally used as is without further purification unless stated otherwise in the text. The suppliers of the tetraethylorthosilicate were either Petrach Inc. or Fluka Inc.. The titanium tetraisopropoxide was purchased from either Aldrich, Inc. or obtained from Akzo, Inc.. The zirconium tetra-n-propoxide was obtained from Akzo, Inc.. The tetramethylorthosilicate was purchased from Fluka, Inc.. Typically the metal alkoxides were reagent grade with a purity of greater than 98%.

Two different titanium sols were used. The titanium tetraisopropoxide sols were prepared by a procedure developed by Wang [83]. A solution containing 20 ml. isopropyl alcohol (Aldrich, HPLC Grade), 0.6 gm. distilled deionized water and 0.10 ml. of 10N HCl was slowly added by a dropping funnel to 5.0 gm. of titanium tetraisopropoxide in a polypropylene Erlenmeyer flask (50 ml) (Fisher Scientific, Inc.) with vigorous stirring by a magnetic stir bar. The system was isolated from the atmosphere by Parafilm during the addition step. The resultant clear, titania sol was stored in a flask fitted with a septum (Aldrich). The sol was discarded

Table 3-1 Chemical Abbreviations

CHEMICAL REAGENT	ABBREVIATION
Tetraethylorthosilicate Tetramethylorthosilicate	TEOS TMOS
Aluminum tri-sec-butoxide Titanium tetra-iso-propoxide Zirconium tetra-n-propoxide Ethyl acetoacetate	AlOBu TiOPr ZrOPr EACAC
Poly(tetramethylene oxide)	PTMO
Isopropanol Tetrahydrofuran N-methyl pyrrolidinone Dimethylacetamide	IPA THF NMP DMAc
Hydrochloric Acid Poly(styrene sulfonic acid) Toluene sulfonic acid Ethylamine	HCl PSS TSA ETA

if any particulates were visible. Aliquots of the sol were removed by use of a disposable syringe (typically 3 ml volume Baxter Syringe) fitted with either a 16 gauge or 18 gauge hypodermic needle. This particular sol was used with the functionalized PTMO oligomers.

A second titanium sol was prepared by the slow addition of a solution containing 5.0 gm. of tetrahydrofuran (Aldrich, HPLC Grade) and 0.10 ml. of 10N HCl to a 25 ml. polypropylene Erlenmeyer flask containing a solution of 5.0 gm. of titanium tetraisopropoxide and 5.0 gm. of tetrahydrofuran. As before, the solution was stirred vigorously throughout the addition and it was isolated from the atmosphere by wrapping the junction between the dropping funnel and the flask with Parafilm. The sol was sensitive to the moisture content of the solvents as well as the atmospheric humidity. Thus care was taken to maintain dry solvents and isolate the system from the air. This sol was typically stable for three days as judged by the appearance of particles in it. The preparation of the zirconium sols which is quite different from the preparation of the titanium sols will be described in section 3.3.

3.2.2 Metal/Ethyl Acetoacetate Complexes

The procedure for preparation of the chelated metal alkoxides was reported by B. Wang elsewhere [84]. Typically 5.0 gm. of aluminum tri-sec-butoxide was weighed directly into a 50 ml polypropylene Erlenmeyer flask containing 12.2 gm.

isopropanol and a magnetic stir bar. Next, 5.28 gm. of ethylacetoacetate was weighed directly into the solution. The flask was stoppered with a septum plug and stirred vigorously for 30 minutes. At the end of 30 minutes, 0.36 gm. deionized water was added directly to the solution. The entire mixture was stirred continuously for an additional 60 minutes. A clear alumina/EACAC sol was formed by this procedure. The same procedure was followed for preparation of the titania/EACAC sols with the only difference being in the mole ratios of metal alkoxide to EACAC to solvent.

3.2.3 Functionalized PTMO Oligomers

The poly(tetramethylene oxide) oligomers were purchased from Polysciences, Inc. in molecular weights of 650 g/mol., 1000 g/mol., 2000 g/mol., and 2900 g/mol.. The oligomers were used as received. The hydroxyl equivalent of the oligomers was provided by Polysciences Inc. for most lots. However, in the absence of a determined value, the lowest representative value was used for calculating the stoichiometry. The isocyanatopropyltriethoxy silane was purchased from Petrarch Inc. and used as received.

A typical procedure was to heat the PTMO oligomer to approximately 60°C and weigh it into a pretared 500 ml. three neck (standard taper ground glass joints 19/24) round bottom Pyrex flask (Fisher Scientific). The flask was then equipped with a glass stirring bar fitted with a Teflon blade (Aldrich Inc.), a mercury

thermometer inserted through a nitrogen inlet, and a 125 ml. dropping funnel (Aldrich Inc.). The entire system was heated to approximately 80°C and purged for 30 minutes with pre-purified N₂ gas, which was passed through a drier tube filled with silica gel (Fisher Scientific). The isocyanatopropyltriethoxy silane was weighed directly into the dropping funnel which was then fitted to the flask. The stoichiometry used was typically 1.02 to 1, isocyanatopropyltriethoxy silane to PTMO hydroxyl groups. The isocyanatopropyltriethoxy silane was added dropwise to the PTMO. The entire mixture was stirred constantly with an overhead air driven mixer and kept under a constant N₂ purge. The end-capping reaction was monitored by FTIR for disappearance of the hydroxyl group (3400 cm⁻¹) and the NCO functional group (2200 cm⁻¹). Typically the reaction required three to four days for completion. The product identified as PTMO was stored in a dessicator prior to use in preparation of the CERAMERs. The FTIR of the 2000 g/mol endcapped PTMO oligomer was compared to that of the original endcapped PTMO supplied by 3M Corporation [26].

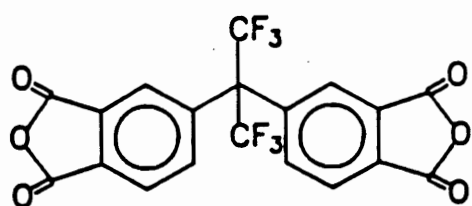
3.2.4 Preparation of Functionalized Polyimides

There are a number of different polyimides with the alkoxide functionality which have been evaluated. Both the chemistry of the polyimides and the silane functionality have been varied in the course of this research. Therefore, the

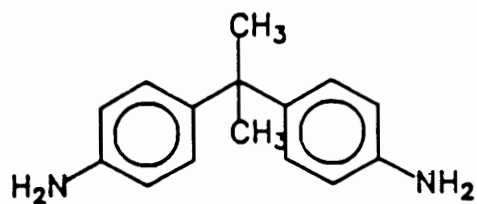
following sections will be organized according to the polyimide chemistry and the particular endcapping used will be described for each polyimide oligomer. The chemical structure of the various dianhydrides, diamines, siloxanes, and silanes used are given in Figure 3-1. The abbreviations used in this dissertation for the monomers is given below each structure.

3.2.4.1 BTDA/Siloxane Polyimides

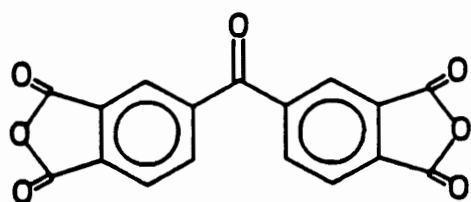
The following procedures were developed during a summer internship at Dow-Corning Corporation [85]. The stoichiometry of the monomers was based upon the Flory distribution for number average molecular weight for a step growth polymerization with A-A, B-B, and A monomers [35]. A conversion of 100% was assumed and an excess of the benzophenone tetracarboxylic acid dianhydride (BTDA) was added to obtain anhydride end groups. The stoichiometry is given in Table 3-2 for the disiloxane polyamic acid. The number average molecular weight of the imide based upon 100% conversion of the polyamic acid oligomer is included in Table 3-2. The final theoretical weight of both the polyamic acid and the polyimide based 100% condensation of the alkoxide groups was also calculated and included in Table 3-2. The BTDA was used as received at a reported purity of 99.8% min anhydride. The 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethylene-1,3-disiloxane (AmDSX) was distilled under vacuum and stored in a glass stoppered flask



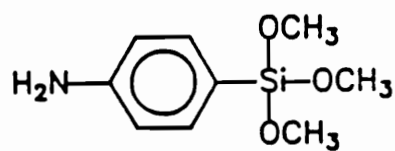
6F-BTDA



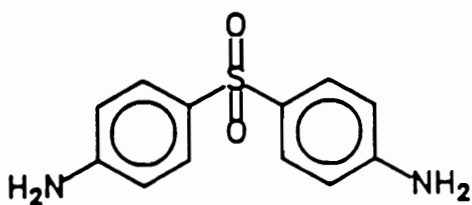
Bis A



BTDA



AMP



DDS

Figure 3-1 Chemical structures of polyimide precursor

by R. King [86]. The 4-trimethoxysilylaniline (AmPTMOS) was synthesized and purified by R. King. The dimethylacetamide (DMAc) was refluxed over calcium hydride in a single neck 500 ml round bottom flask (SNRBF) and then vacuum distilled at approximately 26" Hg prior to use. The distillate was at a temperature of 132°C. The distillate was collected in a 250 ml SNRBF which was closed with a rubber septum. This was then secured with a brass wire.

The reaction scheme for preparation of the siloxane containing polyimide is shown in Figure 3-2. The BTDA was weighed into a 3 NRBF (250 ml) inside a glove box. A Mettler 3600 electronic balance was used which provides a measurement accurate to the nearest 0.001 gm and a precision of 0.002 gm. The 3NRBF was equipped with a ground glass joint stirrer with a TEFLON paddle and a N₂ gas inlet and outlet. N₂ inlet was via a U-tube filled with CaCO₃ dessicant and the outlet was connected to a bubbler to monitor the flow rate. The N₂ flow was started immediately along with the stirrer at a medium speed. Approximately 70 mls of the required distilled DMAc was transferred with a 5 or 30 ml ground glass bore syringe equipped with a Luer-Lok type 6 inch long, 22 gauge needle. The first 5 to 10 mls were used to carefully wash any of the BTDA collected on the sides into the flask. The flow was approximately 100 to 120 bubbles per minute. The resulting mixture looks slightly yellowish and was more of a suspension than a true solution. The AmDSX was weighed (using a Mettler H30 Analytical Balance, which is readable to the nearest 0.0001 gm.) into a 10 dram sample bottle and immediately capped. This

Table 3-2 Stoichiometry for BTDA/DMSX/AmPTMOS polyimide

Target M_n : 5000 g/mol.

	BTDA	DMSX	AmPTMOS
F.W.	322.23	248.52	213.31
Mole Ratio	1.1331	1.000	0.2662
Weight (gms)	10.8923	7.4137	1.6940
Solvent: DMAC		Volume: 85.56 ml.	

was performed at room conditions, but would be advised in a glove box to reduce exposure to atmospheric moisture. The material was checked for water content using CaH_2 . The weighed sample was transferred to a 250 ml addition funnel equipped with a Teflon stopcock, attached to the outlet side of the flask. Transfer was accomplished using a powder funnel followed by adding two to three mls of the DMAc to the vial and then using an additional 5 mls to wash it into the addition funnel. Addition to the reaction mixture was at a rate of approximately 30 drops per minute. The reaction mixture became a clear amber colored solution after the first few mls of the AmDSX was added. If the AmDSX was added too fast condensation builds up on the inside of the flask which will react with the BTDA and effectively reduces the stoichiometry, so addition must be slow. The complete addition of the AmDSX was completed within one hour at which time a drop was removed, using a long Pasteur pipet; for analysis by FTIR to verify the presence of the anhydride end group by the peak at 1857 cm^{-1} . The AmPTMOS was then weighed and added in a similar manner to the reaction mixture. The remaining portion of the required DMAc was added with the final reactant, using it to wash the sides of the addition funnel. The reaction mixture was stirred continuously for an additional 2 to 3 hours to equilibrate prior to storing at approximately 5°C . The best method was to pre-weigh an 8 oz bottle and tilt the entire assembly minus the dropping funnel so the solution was transferred under a N_2 atmosphere. The final solution was analyzed by FTIR as a neat solution, after curing at 110°C for 15 minutes and finally curing at

180°C for 15 minutes. The polyamic acid peaks (Figure 3-3) are at 1651, 1549, and 3200 cm^{-1} . The anhydride peak is at 1857 cm^{-1} . The imide peaks at 1735 cm^{-1} and the carbonyl bands at 1635 cm^{-1} disappear along with the hydroxy absorption at 3300 cm^{-1} . This particular spectrum was obtained by spreading a drop on the surface of a salt plate and then curing at 110°C for 15 minutes followed by a 15 minute cure at 180°C in a gas chromatograph oven which is equipped with a blower for accelerated solvent evaporation.

3.2.4.2 6F-BTDA/Bis A Polyimides

This series of polyimides were prepared by either M. Spinu [87] or M. Rogers [88] of Prof. J. E. McGrath's laboratory. The details of the synthetic procedures have been reported elsewhere [89]. The process flowchart is given in Figure 3-4 for preparation of the 6F-BTDA/BisA polyimide oligomers. The polyimides prepared by the process outlined in Figure 3-4 were then functionalized by a hydrosilylation of a norbornene end group according to the scheme given in Figure 3-5 [87].

The 6F-BTDA/BisP polyimides were prepared using basically the same process as outlined in Figure 3-4, except 2-aminopyridine was used as an end blocker to control molecular weight and as the leaving group in the transimidization reaction. The 6F-BTDA/BisP polyimides, prepared according to the process illustrated in

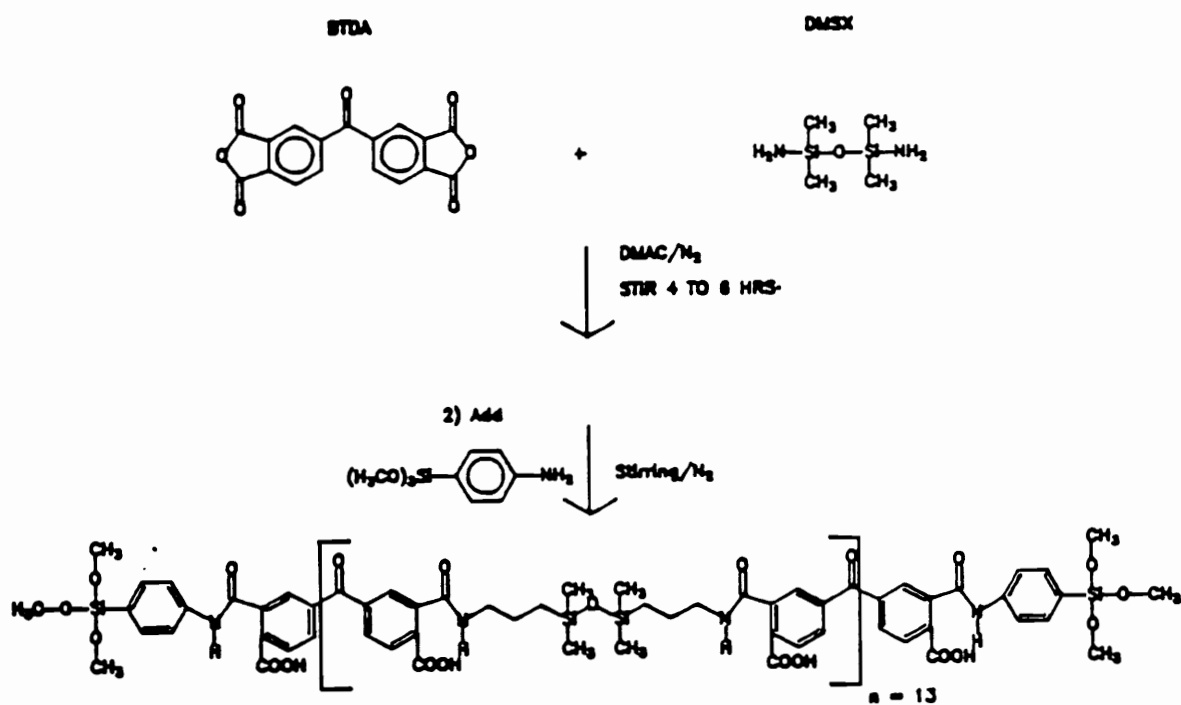


Figure 3-2 Reaction scheme for BTDA/DMSX/AmPTMOS polyimide

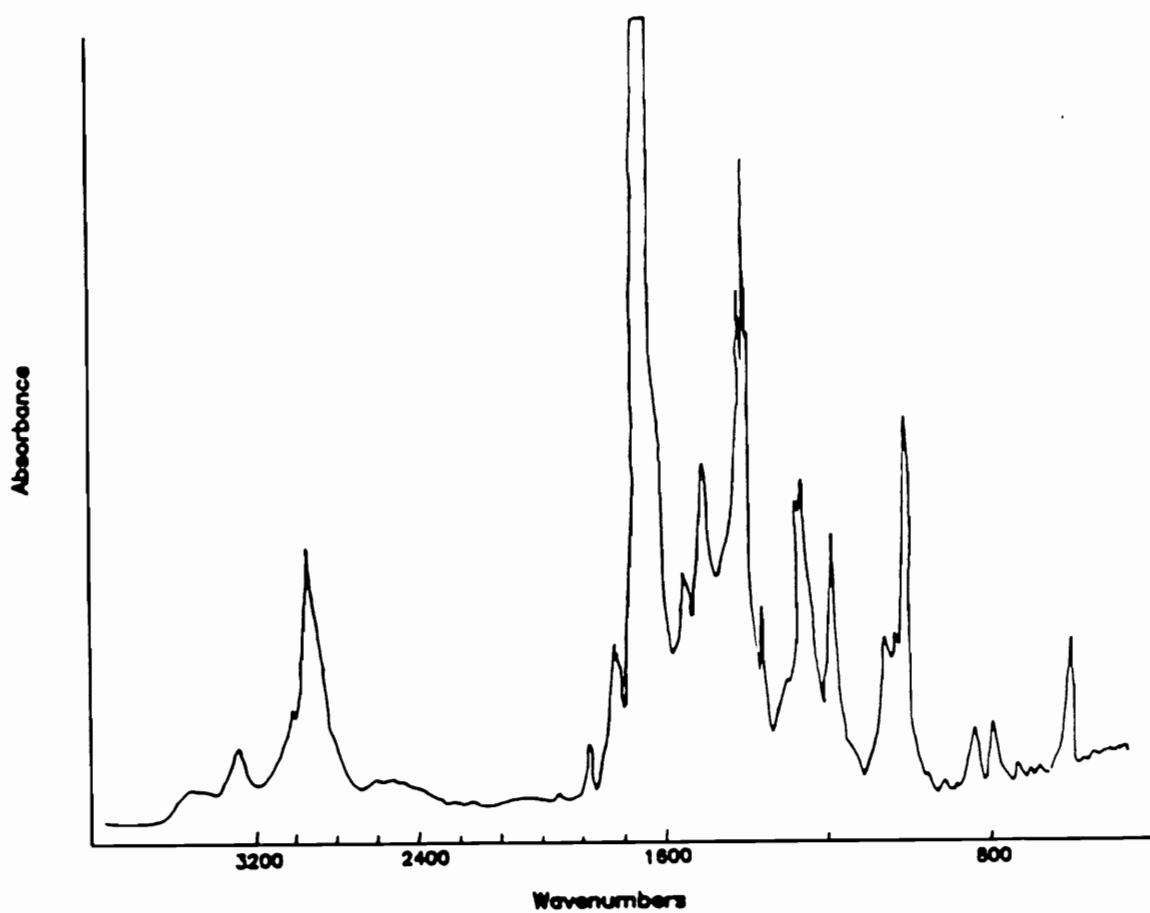


Figure 3-3 FTIR spectra of cured BTDA/DMSX/AmPTMOS polyimide

Figure 3-6, were then functionalized with AmPTMOS isomers by a transimidization process [88]. The AmPTMOS was used as obtained from Petrarch, Inc. in the form of a mixture of isomers. Another method of endcapping the 6F-BTDA/BisP oligomers was to react AmPTMOS directly with anhydride end groups of the polyimide oligomers (As predicted by the Flory distribution for step-growth polymerizations). An appropriate amount of AmPTMOS isomers was added directly to the polyimide oligomers in a stoichiometric ratio of 1.1 to 1.0, silane to imide, respectively (Figure 3-7). The resultant functionalized oligomers which are actually polyimide-amic acids, were then used directly in a sol-gel process. Three different molecular weights were functionalized with AmPTMOS by the transimidization process [88]: (1) MR57 = 10,300 g/mol.; (2) MR89 = 5,800 g/mol.; and (3) MR90 = 13,000 g/mol. The molecular weight of all oligomers is defined by the nomenclature.

3.3 SOL-GEL PROCESSES

The following sections describe the methods of preparation used to generate the various CERAMERs that were characterized. The sections are separated by oligomer first and metal alkoxide second.

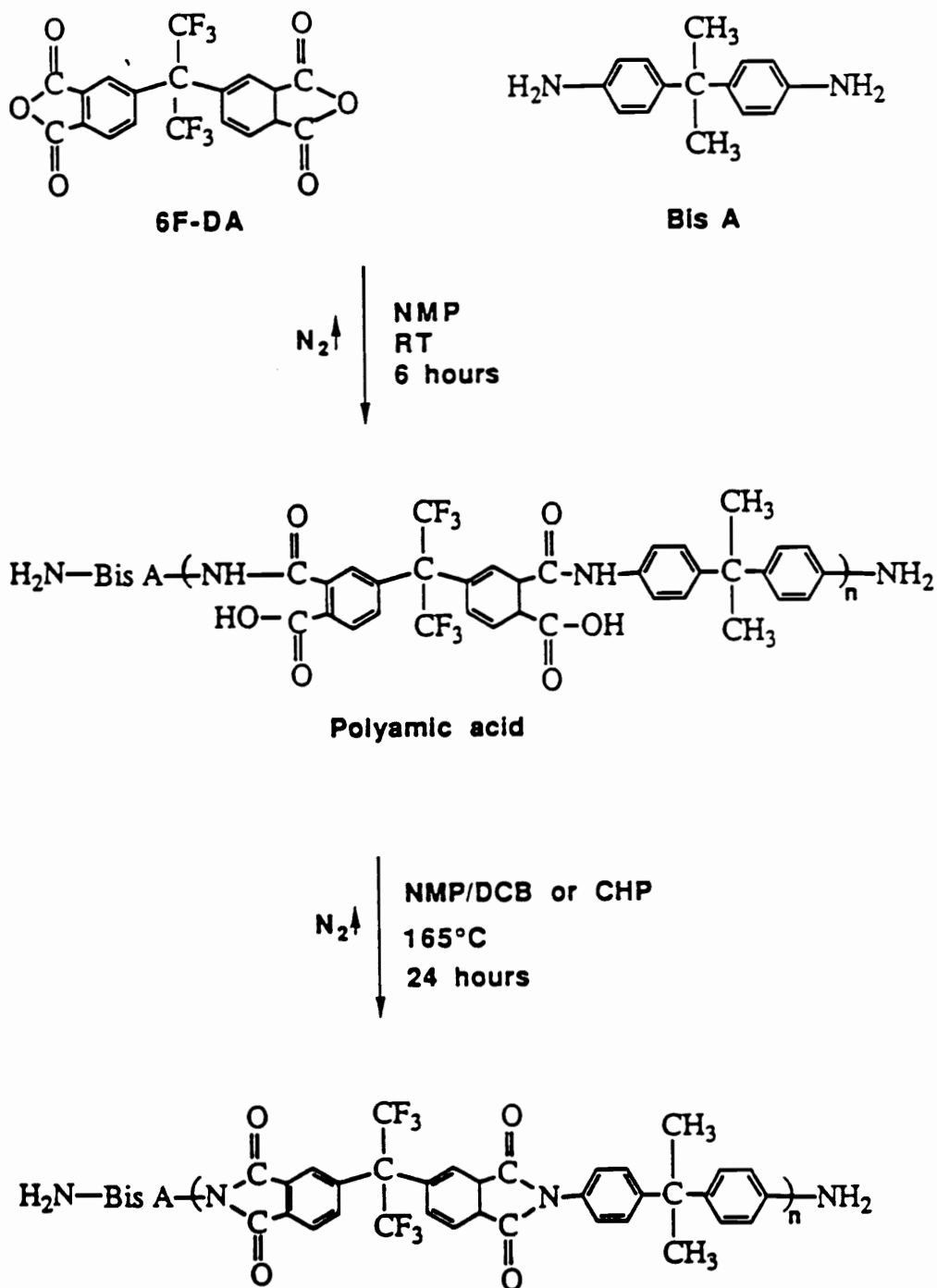
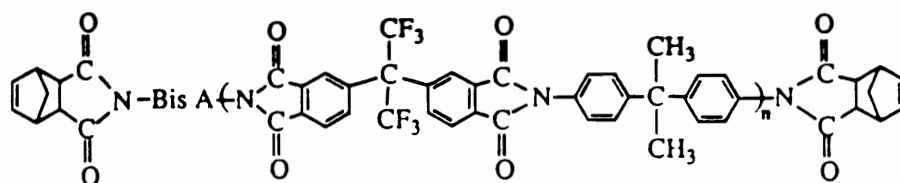


Figure 3-4 Reaction scheme for 6F-BTDA/BisA Polyimides



Nadimide terminated polyimides

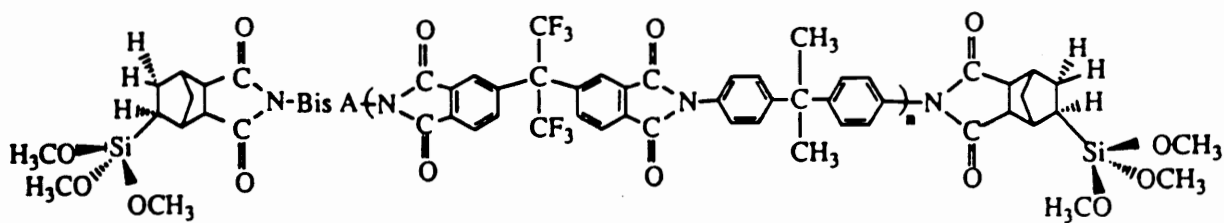
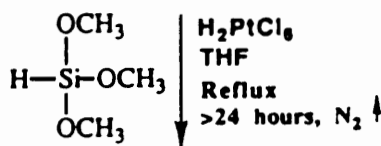


Figure 3-5 Hydrosilylation end-capping reaction

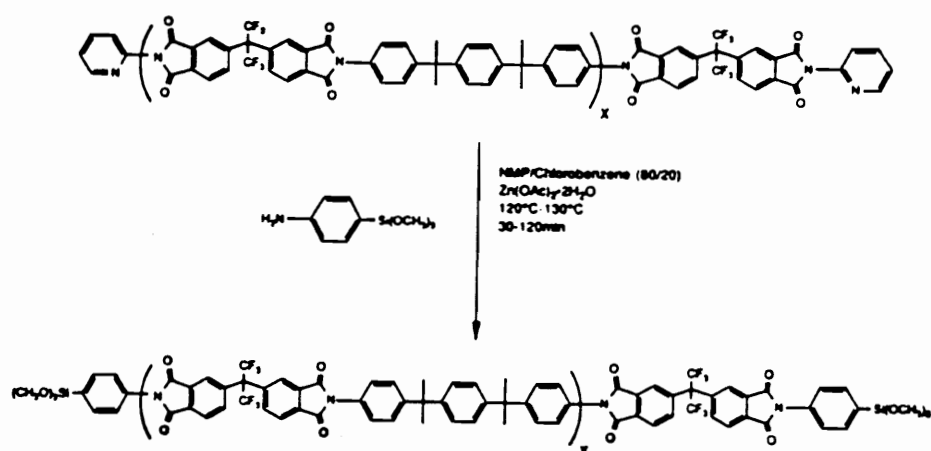


Figure 3-6 Transimidization end-capping reaction

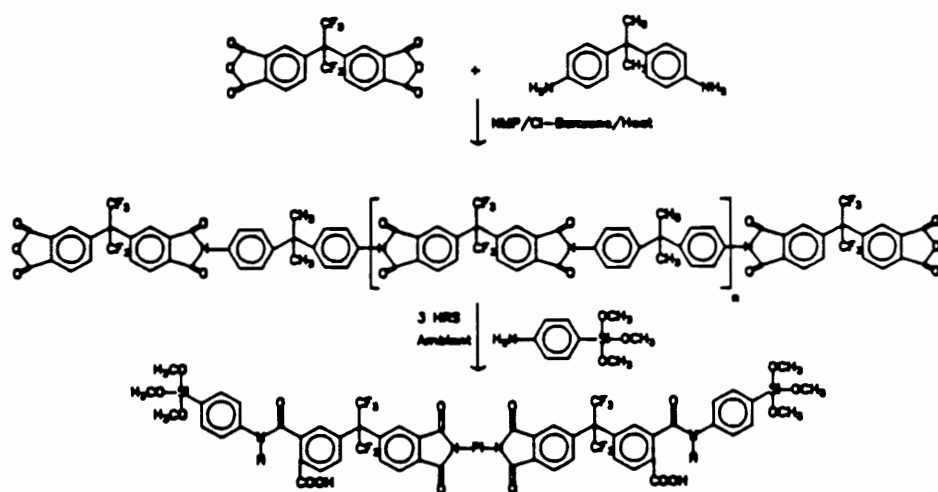


Figure 3-7 End capping of anhydride terminated 6F-BTDA/BisP

3.3.1 TEOS/PTMO CERAMERS

The nomenclature which was developed for the TEOS/PTMO CERAMER systems, is shown in Table 3-3. The number in the parenthesis immediately following TEOS refers to the initial weight fraction of TEOS with respect to the oligomer. The value in the parenthesis following PTMO, in this case 2K for 2000 g/mol, is the number average molecular weight of the uncapped oligomer. The value 100 refers to the water added which will hydrolyze 100 percent of the alkoxide groups in the solution. The final value, 0.014 refers to the acid to alkoxide ratio in equivalents. The specific catalyst will be designated.

A typical procedure is as follows: 6.0 ml. of isopropanol (IPA) and four ml. of tetrahydrofuran (THF) are mixed in a 50 ml flask at ambient conditions. A 5 gram portion of TEOS and 5 grams of the silane endcapped oligomer are weighed into the IPA/THF solvent and stirred for approximately 10 to 15 minutes. The distilled-deionized water is then added volumetrically with stirring. One milliliter of the PSS solution (ca. 0.9 gm of PSS) is then added dropwise to the solution with vigorous stirring. Upon addition of the PSS solution, the viscosity appears to increase significantly as indicated a reduction of the magnetic stir bar speed. The mixture (sol) is stirred for 1 to 2 minutes after addition of the acid and then cast into a Teflon coated petri dish and covered to reduce evaporation. The high viscosity of the solution necessitated extra care in casting to remove bubbles generated by the

Table 3-3 Nomenclature for TEOS/PTMO CERAMERs

TEOS(50)-PTMO(2K)-100-0.06 HCl	
NOTATION	DESCRIPTION
TEOS	TEOS REFERS TO TETRAETHYL ORTHOSILICATE
(50)	WEIGHT FRACTION METAL ALKOXIDE WITH RESPECT TO OLIGOMER (wt%)
PTMO	PTMO REFERS TO POLY(TETRAMETHYLENE OXIDE) OLIGOMER, END CAPPED WITH ALKOXIDE
(2K)	MOLECULAR WEIGHT OF OLIGOMER PRIOR TO END CAPPING WITH ALKOXIDE FUNCTIONALITY (2K = 2000 g/mol.)
100	MOLAR RATIO OF WATER TO ALKOXIDE (mol%)
0.06	RATIO OF ACID TO ALKOXIDE (equivalents)

stirring. This is not required for a system catalyzed with an equivalent amount of HCl. The sol is then allowed to gel undisturbed at ambient conditions for approximately 4 days and then opened to the air to remove excess solvent. The age of a gel is designated as the elapsed time from the date of preparation of the sol.

3.3.2 Metal-Ethyl Acetoacetate/PTMO CERAMERS

The metal-EACAC/PTMO CERAMERS nomenclature (Table 3-4) is slightly different from that of the TEOS/PTMO CERAMERS (Table 3-3). The first number listed in the brackets is the mole ratio of the EACAC to the metal alkoxide. The number immediately following the abbreviation of the metal alkoxide in the parentheses is the weight fraction of metal alkoxide with respect to the combined weight of the metal alkoxide and the oligomer. The molecular weight of the unfunctionalized oligomer is listed in the parentheses following the designation for the oligomer used. The next number, in order from left to right, is the mole ratio of water to metal alkoxide used. The final number is the mole ratio of catalyst to metal alkoxide, which is not typically used in the metal/EACAC compositions. The procedures for preparation of the aluminum-ethylacetylacetate/PTMO and titanium-ethyl acetoacetate/PTMO CERAMERS were developed by B. Wang and have been reported elsewhere [84]. Typically the functionalized PTMO oligomer (2000 g/mol) was heated to 60°C to melt the crystalline phase which formed after 24 to 48 hours

at ambient temperatures. The functionalized PTMO oligomer was then weighed directly into the alumina/EACAC sol. The resultant mixture was stirred vigorously for 3 to 5 minutes and then cast into a polystyrene petri dish (Fisher Scientific, Inc.) which was covered immediately and allowed to gel undisturbed for 3 days. The resultant gel was allowed to dry open to the air at ambient conditions for 3 more days. The Al/EACAC/PTMO and Ti/EACAC/PTMO formulations evaluated are listed in Table 3-5.

3.3.3 Metal Alkoxide/PTMO CERAMERS

The nomenclature developed for the TEOS/PTMO CERAMERS was adapted directly for the titanium tetra-iso-propoxide/PTMO CERAMERS and the zirconium tetra-n-propoxide/PTMO CERAMERS. The endcapped PTMO oligomer was dissolved in 10 ml. of isopropanol. Next, the titania sol was added directly to the PTMO solution and then the mixture was stirred for 1 to 2 minutes. The mixture was transferred to polystyrene petri dishes, which were covered immediately and allowed to gel undisturbed at ambient conditions for 2 days. The covers were then removed to eliminate residual solvent at ambient laboratory conditions for 2 to 3 days prior to testing.

The zirconium tetra-n-propoxide sols were prepared in a similar fashion to the titanium sols with two exceptions. The first step was to blend 5.0 gm. zirconium

Table 3-4 Nomenclature for Metal-EACAC/PTMO CERAMERs [84]

[2] M/EACAC(50)-PTMO(2K)-33-0	
NOTATION	DESCRIPTION
[2]	MOLAR RATIO OF METAL ALKOXIDE TO EACAC (MOLES)
M/EACAC	M REFERS TO METAL ALKOXIDE, EACAC REFERS TO ETHYL ACETOACETATE
(50)	WEIGHT FRACTION METAL ALKOXIDE WITH RESPECT TO OLIGOMER (WT%)
PTMO	PTMO REFERS TO POLY(TETRAMETHYLENE OXIDE) OLIGOMER, END CAPPED WITH ALKOXIDE
(2K)	MOLECULAR WEIGHT OF OLIGOMER PRIOR TO END CAPPING WITH ALKOXIDE FUNCTIONALITY (2K = 2000 g/mol.)
33	PERCENTAGE OF WATER ADDED WHICH IS REQUIRED TO HYDROLYZE ALL ALKOXIDE PRESENT (%)

Table 3-5 M/EACAC/PTMO CERAMERS

M/EACAC	Al(Bu) ₃	EACAC	PTMO(2K)	WATER	IPA
[2]	5.0 gm	5.28 gm.	2.5 gm.	0.12 gm.	12.2 gm.
[1.33]	5.0 gm.	3.51 gm.	2.5 gm.	0.12 gm.	12.2 gm.
[1]	5.0 gm.	2.64 gm.	2.5 gm.	0.12 gm.	12.2 gm.

M/EACAC	Ti(OPr) ₄	EACAC	PTMO(2K)	WATER	IPA
[0.8]	5.0 gm	1.82 gm.	2.5 gm.	0.12 gm.	12.2 gm.
[0.5]	5.0 gm.	1.13 gm.	2.5 gm.	0.12 gm.	12.2 gm.

tetra-n-propoxide with 5.0 gm. of functionalized PTMO ($M_n = 2000$ g/mol) and 10.0 ml. of tetrahydrofuran for 30 minutes. A solution containing 20.0 ml. of isopropanol and 0.10 ml. 10N HCl was added very slowly to the zirconium tetra-n-propoxide/PTMO/tetrahydrofuran solution. Vigorous stirring was required to maintain a homogeneous solution and thus prevent precipitation of the zirconium sol. The solution was then typically poured into several (3 to 4) polystyrene petri dish, which were covered immediately and left undisturbed for one day. The covers were then removed and the gels were allowed to dry in the hood for 2 to 3 days prior to testing.

3.3.4 Polyimide CERAMERS

There are many different formulations of metal alkoxide/polyimide blends in terms of the metal alkoxide and the polyimide which have been evaluated. The following sections are organized according to the major polyimide studied. There are basically three different polyimides: (1) 6F-BTDA/BisA(P)/AmPTMOS; (2) 6F-BTDA/BisA/Nadic/TMOS and (3) BTDA/DMSX/AmPTMOS. The procedures for incorporation of the different metal alkoxides will be described in the sections of each polyimide.

3.3.4.1 TiOPr/6F-BTDA/BisP/AmPTMOS CERAMERs

The polyimide oligomer was received in solution (usually NMP, however, residual chlorobenzene was possible as well as catalyst associated with the transimidization reaction) at a concentration of approximately 15% solids. Normally it was necessary to dilute this to 8% solids with THF. However, the final series of oligomers received were denoted as MR57, MR89, and MR90 (Descriptions of all polyimide oligomers are included in Table 3-8) were all used as received, i.e. 15% solids. A titania sol was prepared as described in Section 3.2.1 using dry THF. The THF must be extremely dry as the sols are quite sensitive to moisture at ambient conditions. The polyimide solution was poured quickly into a 25 ml. polypropylene flask containing the required amount of titania sol and a magnetic stir bar. The solution was stirred vigorously to reduce premature gelation. Normally only 1 to 2 minutes of mixing was possible. Thus, the sols were cast rapidly into poly (4-methyl 1-pentene) petri dishes (VWR Scientific) and covered. The dishes were typically placed directly into a circulating oven. The temperature in the oven was maintained at 60°C or 100°C. The normal time to gelation was 1 to 2 days. However, as the concentration of the titania sol was raised, the time to gelation increased. The gels were removed from the 100°C oven and sectioned into pieces which were post cured at elevated temperatures in a Fisher High Temperature Furnace. The gels were

normally quite flexible following the initial cure at 100°C. However, with time at ambient the gels became more brittle possibly due to loss of solvent.

3.3.4.2 TEOS/6F-BTDA/BisA/Nadic/TMOS CERAMERs

The nomenclature for this group of CERAMERs is included in Table 3-7. The procedures followed for these materials was quite similar to those described in Section 3.3.4.2. The solvents, however, used were THF and NMP. THF was not acceptable as the gels were non-transparent after initial gelation at 60°C. The gels produced with TEOS, TMOS, or TiOPr as the metal alkoxide were not monolithic. The TEOS was pre-hydrolyzed prior to use. Less than stoichiometric quantities of water were used due to incompatibility with the sols. The post cure at elevated temperatures of the gels was done in the Fisher High Temperature Furnace. The schedules for the heating cycles are described in the results and discussion sections.

3.3.4.3 TEOS/Siloxane Copolyimide CERAMERs

The nomenclature developed for these hybrid systems is closely related to that of the TEOS/PTMO CERAMERs (Table 3-6). The typical reaction scheme for preparation of the TEOS/Polyimide CERAMERs is depicted in Figure 3-8. The TEOS was pre-hydrolyzed prior to the addition of the polymeric species to prevent

Table 3-6 Nomenclature for 6F-BTDA polyimide CERAMERs

TEOS(50)-6F/NAD(8K)-25-0.06 HCl TiOPr(18)-6F/AMP(8K)-0-0.06 HCl	
NOTATION	DESCRIPTION
TEOS TiOPr	TEOS REFERS TO TETRAETHYL ORTHOSILICATE TiOPr REFERS TO TITANIUM TETRA ISOPROPOXIDE
(50) (18)	WEIGHT FRACTION METAL ALKOXIDE WITH RESPECT TO OLIGOMER (wt%)
6F/NAD 6F/AMP	PTMO REFERS TO POLY(6F-BTDA-BisA) END CAPPED BY HYDROSILYLATION (NAD) OR TRANSIMIDIZATION (TI)
(8K)	ESTIMATE OF MOL. WT. OF POLYIMIDE PRIOR TO END CAPPING WITH ALKOXIDE FUNCTIONALITY (8K = 8000 g/mol.)
25 0	MOLAR RATIO OF WATER TO ALKOXIDE (mol%) NO WATER ADDED TO TiOPr/PI SYSTEMS
0.06	RATIO OF ACID TO ALKOXIDE (equivalents)

INCORPORATION OF ENDCAPPED POLYAMIC ACID

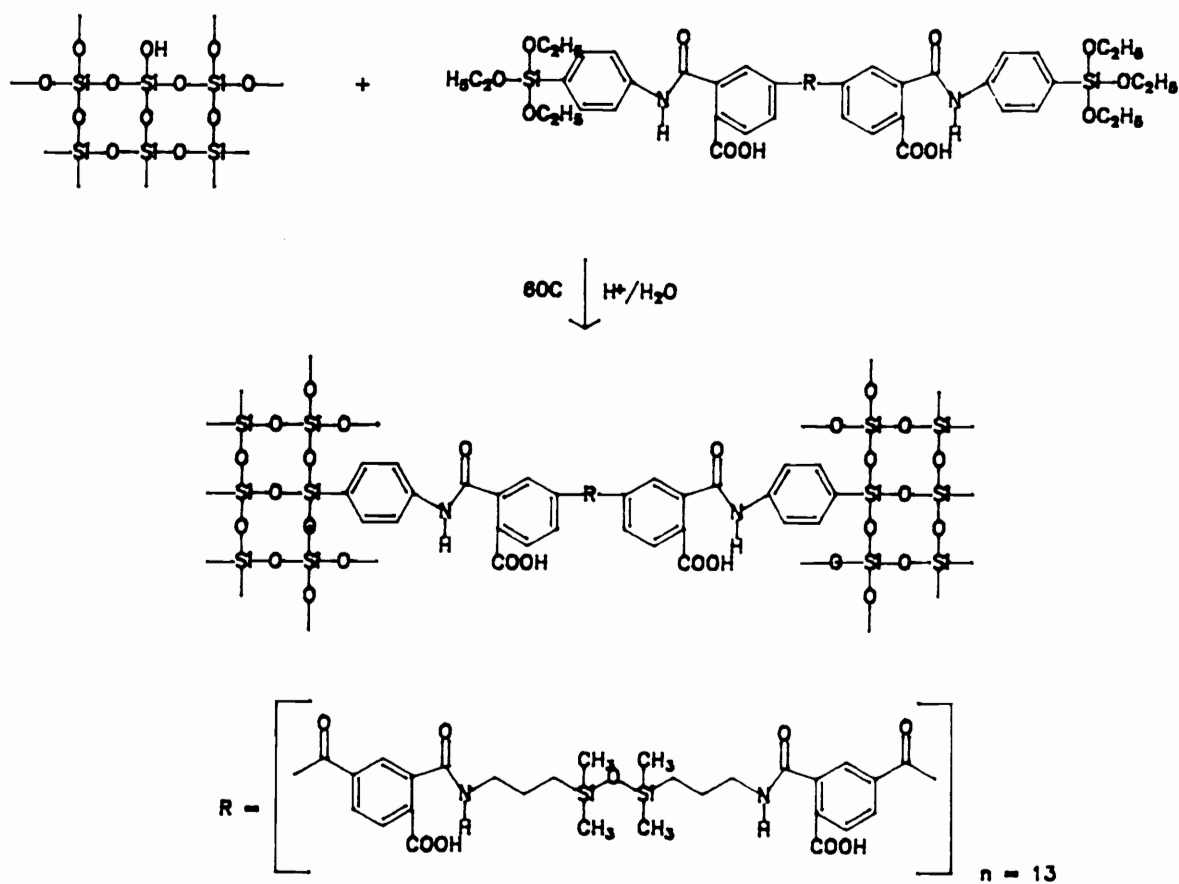


Figure 3-8 Typical reaction scheme for preparation of TEOS/DMSX/AMP CERAMERS.

macrophase separation in the sol. A 5.0 gm. mass of TEOS was weighed into a pre-tared 100 ml round bottom flask equipped with a Teflon stir bar. The water was then weighed into the flask followed by the HCL. At the higher concentrations of TEOS a precipitate appears. The solution was stirred for 5 minutes at room conditions and then the desired weight of the polyamic acid was weighed directly into the flask. The mixture was stirred for 5 minutes at a high speed to effect a homogeneous solution. The solution was then poured into a Teflon coated glass petri dish (100x15mm). The petri dish was covered immediately and placed in an oven (vacuum) pressurized with N_2 . The oven temperature was maintained at 60°C. After 12 hours the petri dish covers were removed and the gels allowed to cure more fully for an additional 72 hours under the same conditions. The system typically gelled after 24 hours. The gels were removed from the petri dishes and cut with scissors while still warm to remove the edge formed around the perimeter. The gels were placed on a sheet of woven Teflon cloth which was on a sheet of Kapton film on an aluminum plate (1/4"x3"x6"). Then a second piece of the woven Teflon material and the Kapton were placed on the gel followed by a second piece of aluminum. The assembly was held together by Kapton tape. This assembly was placed in a gas chromatograph oven (Hewlett Packard) at 110°C for 24 hours at which time the temperature was increased to 180°C at a rate of approximately 10°C per minute. The samples were left for an additional 24 hours at these conditions. The cured samples were then sectioned on a small cut off saw (Buehler Isomet) with

a diamond wafering blade with water cooling. These pieces were then used for Dynamic Mechanical Analysis, density measurements and weight loss measurements.

3.4 CHARACTERIZATION

The instruments and methodology of each is briefly described in the following sections. Details as to sample conditioning are given in the section of Results and Discussion of each of the following chapters.

3.4.1 Dynamic Mechanical Analysis

Thermal dynamic mechanical analysis (DMA) was performed on the CERAMERs using an automated Rheovibron Model DDV-IIC Dynamic Viscoelastometer or a Rheometrics Model 800 Viscoelastometer. The Rheovibron operates in a tensile mode. The Rheometrics operates in a torsional shear mode. The Rheovibron is capable of measuring the viscoelastic response of a sample from approximately -150°C to ca. 200°C at three frequencies (1.1 hz, 11.0 hz, and 110.0 hz). The typical heating rate employed was 1 to 2°C/min. A nitrogen purge (pre-purified N₂) was maintained in the sample compartment for the entire time of each analysis. Typical sample dimensions were 0.01 to 0.10 cm. x 0.3 cm x 3.0 cm. The dynamic mechanical spectra presented in the following chapters represent the typical

Table 3-7 Nomenclature for TEOS/DMSX CERAMER compositions

TEOS(50)-DMSX(5000)-100-0.043-60C	
NOTATION	DESCRIPTION
TEOS	TEOS REFERS TO TETRAETHYL ORTHOSILICATE
(50)	WEIGHT FRACTION METAL ALKOXIDE WITH RESPECT TO OLIGOMER (wt%)
PTMO	PTMO REFERS TO POLY(TETRAMETHYLENE OXIDE) OLIGOMER, END CAPPED WITH ALKOXIDE
(2K)	MOLECULAR WEIGHT OF OLIGOMER PRIOR TO END CAPPING WITH ALKOXIDE FUNCTIONALITY (2K = 2000 g/mol.)
100	MOLAR RATIO OF WATER TO ALKOXIDE (mol%)
0.06	RATIO OF ACID TO ALKOXIDE (equivalents)
60C	MAXIMUM CURE TEMPERATURE

behavior of each material. The information provided by the various thermo-mechanical spectra is corrected (to account for non-uniformity in sample dimensions and instrumental artifacts) in some cases such that the glassy storage modulus is of the order of 10^9 MPa. Therefore, only the transitions and relative response of two materials will be considered important. The Rheometrics RMS8 applied a sinusoidal strain of 0.1% at three frequencies (0.1 hz, 1.0 hz, and 10 hz.) The temperature was ramped at 5°C per minute and held for 3 minutes prior to application of the strain. Sample dimensions were approximately 0.5 cm. x 1.5 cm. x 5.0 cm.. Most samples required finishing with 400 grit sand paper for insertion into the gripping device.

3.4.2 Mechanical Properties

The stress-elongation response of the CERAMERs was determined by measurement with an Instron Model 1122 tensile testing machine. A dogbone specimen was obtained from a conditioned gel by the use of a "dinking die". The dimensions of the specimens conformed with the ASTM procedure D638. Samples were conditioned at ambient for a specified period of time, normally 6 to 8 days. Any special treatments are identified along with the stress-elongation response of the samples. The crosshead speed of the Instron was 2.0 mm/min. All data was obtained by either a strip-chart recorder or by an A to D converter using a software package marketed under the name Q-tek. A program in basic language converted

the data into stress-elongation data, which was then plotted by other software with graphics capability. The stress was determined by dividing the load by the initial cross-section of the specimen. The elongation at break was calculated as the percent difference between the final length and the initial divided by the initial gauge length of the dogbone specimen (1.0 cm.). The elastic (Young's) modulus was calculated using the initial slope of the linear portion of the stress-elongation curve. The average of typically 4 to 6 specimens was determined for each sample and reported along with the standard deviation. All testing was performed at ambient conditions, i.e. 22°C.

3.4.3 Small Angle x-Ray Scattering

Small angle x-ray scattering (SAXS) behavior was determined with a Siemens Kratky camera system. The angular dependence of the scattered intensity was determined with a Braun position sensitive detector from Innovative Technologies, Inc. The incident x-ray source was from a Siemens Cu-W x-ray tube powered by a Siemens Model 1726 Generator. All data was converted and analyzed with a software package developed by D. Tyagi and modified by H.-H. Huang [90].

3.4.4 Thermal Analysis

Thermal analysis of the CERAMERs was typically performed with the SEIKO Thermal Analysis System. The main components are the SEIKO Data Station Model 5040, the Differential Scanning Calorimeter Model 210 (DSC), the Thermal Mechanical Analyzer Model 100 (TMA), and the Thermogravimetric/Differential Thermal Analyzer Model 200 (TG/DTA). The DSC and TG/DTA modules were calibrated with indium, tin and zinc standards prior to use. The standard operating procedures of each module were followed according to the manufacturer's manual. Samples were obtained for DSC and TG/DTA experiments using a #2 cork borer to assure uniformity in size and surface area. The exceptions to this were the polyimide materials which were too brittle. The mass of samples was typically 10 to 15 mg for the DSC analyses and 4 to 8 mg for the TG/DTA analyses. The other conditions, i.e. purge gas, heating rate, and cycling, are provided along with the results in the following chapters.

3.4.5 Electron Microscopy

Scanning electron micrographs were obtained with a Cambridge Instruments Stereoscan 200 electron microscope. Samples were prepared by conditioning for 24 hours under a vacuum followed by fracturing at cryogenic temperatures (immersed

in liquid N₂ for approximately 10 to 15 minutes). The fractured specimens were mounted on double faced adhesive tape on aluminum stubs. The entire assembly was then sputter coated with approximately 10 nm to 20 nm of gold using either a Surface Probe Inc. sputter coater under an argon atmosphere. The samples were then spot coated with either carbon or silver conducting paint to assure good conductivity between the specimen and stub.

3.4.6 Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectra were obtained with either a Nicolet Model 5DXB FTIR Spectrometer or a Perkin-Elmer Model 1710 FTIR Spectrometer [84]. Polyamic acid solutions were coated onto KBr plates which were then heated to and held at the appropriate cure temperature. The KBr plates were transferred to a dessicator to cool and then analyzed between 4000 cm⁻¹ and 600 cm⁻¹. The PTMO samples were heated to 60°C and then one to two drops were spread between two KBr plates and analyzed in the same fashion.

CHAPTER 4

THE INFLUENCE OF POLY(STYRENE SULFONIC ACID) ON THE STRUCTURE/PROPERTY RELATIONSHIPS OF THE TEOS/PTMO HYBRID SYSTEMS

4.1 INTRODUCTION

The properties of sol-gel derived structures are dependent upon the type and quantity of the catalyst employed (1,4,37). The use of a polymeric supported catalyst, such as poly(styrene sulfonic acid), was viewed as a means of varying a number of properties previously reported by Huang et. al. (18). Huang et. al. determined that the physical and mechanical properties of CERAMERs prepared under standard laboratory conditions (ca. 20°C and 50+/-10 % relative humidity) underwent significant changes after extended time periods under the same conditions. The Young's modulus and stress at break increased along with a decrease in the elongation at break as a function of age for CERAMERs based upon TEOS and

hydroxyl terminated PTMO oligomers which were reacted with isocyanatotriethoxy silane (18). Similar changes in the mechanical properties were reported for the TEOS/PTMO CERAMERs following post cures at temperatures, ca. 80°C, above the initial processing temperature, ca. 20°C. The changes in the mechanical properties were attributed to a "chemical aging process", for which a mechanism has not been determined, but is believed to be related to a higher extent of reaction of the silicon alkoxides. This would result in densification of the silicate structure by the elimination of alcohol and water as the by-products of the formation of a Si-O-Si linkage (NOTE: The hydrolysis/condensation reaction products of TEOS will be referred to as 'silicate structure' in this text even though it is not completely accurate in describing the actual structure.). The elimination of the solvents, which would behave as plasticizers, would also contribute to the observed changes in the properties with time. The aging effect was also reported, but to a lesser extent for a hybrid composition incorporating titanium isopropoxide which is considered a catalyst for the sol gel reaction (8,10,11).

One explanation of the time dependent behavior of the TEOS/PTMO systems, as well as other CERAMERs i.e. those prepared with TEOS and functionalized poly(arylene ether ketone) oligomers, is based upon the Time Temperature Transformation (TTT) model developed by Gilham for network forming systems (11). As the sol-gel process proceeds, the viscosity of the system continues to increase until at the gel point where it rapidly approaches infinity.

However, as the extent of conversion increases, T_g also increases until it reaches the reaction temperature, at which point the system vitrifies. Vitrification effectively stops the diffusion of the reacting species and thus stops the reaction. Time and thermal treatments at a temperature higher than the initial reaction temperature will further the process (one will recognize this must be below the degradation temperature of the oligomeric component). It is postulated that these changes with time in the CERAMERs are related to an increase in the connectivity of the network, which would support higher stresses as has been demonstrated for numerous CERAMERs (10,11). Another possible explanation for these time dependent changes in the CERAMERs is diffusion of low molecular weight species out of the network. The low molecular weight species of concern would of course be the acid catalyst and the solvents used for dilution of reactants as well as those generated by the reaction.

The selection of an acid catalyst for these hybrid materials was prompted by the desire to produce well mixed systems on a molecular level. Brinker demonstrated lightly branched linear-like silicate structures are formed for the acid catalyzed sol-gel conversion of TEOS (12). Basic catalysts, on the other hand, tend to promote the formation of highly branched, dense silicate particles from TEOS. The acid catalyzed gels also develop a higher density than base catalyzed systems. Thus, acid catalyzed gels have a more continuous silicate structure that should promote mixing with the oligomers assuming of course the thermodynamics of mixing are favorable. HCl and

glacial acetic acid are two catalysts that have been used effectively to produce CERAMERs based upon PDMS and TEOS as well as the PTMO/TEOS forms.

The low molecular weight of both HCl and glacial acid would more than likely lead to diffusion of the ions within the gel structure of a CERAMER, especially prior to the elimination of the solvents. A polymeric catalyst as suggested by Prof. G. L. Wilkes might reduce the observed chemical aging of the CERAMERs compared to low molecular weight mineral or organic acids by reducing the mobility of the ionic species. In view of Sakka's work in which fibers were drawn from sols composed of silicon based metal alkoxides (13), a high molecular weight catalyst might also be useful as a rheological modifier to enhance spinnability. The ability to draw fibers from sols is quite sensitive to the viscosity. At low extents of reaction the viscosity is too low in contrast to the viscosity of a gel which are not suitable for fiber spinning. Thus, it would be desirable for these applications to increase the sol viscosity.

This chapter details the successful application of poly(styrene sulfonic acid) (PSS) as a catalyst for preparation of these novel of inorganic/organic hybrids based upon TEOS and the silane end-capped oligomers of PTMO. Poly(styrene sulfonic acid) is readily available in various molecular weights and degrees of sulfonation, so it was selected for this study. In attempt to determine the effect of the polymer support for the catalyst, p-toluene sulfonic acid (TSA) catalyst was evaluated in the TEOS/PTMO formulations. The mechanical and morphological features of

CERAMERs produced with PSS will be compared with equivalent compositions catalyzed with HCl and the TSA. In addition, the thermogravimetric behavior will be discussed in terms of retained solvent effects and general degradation behavior of the CERAMERs.

The experimental conditions and procedures for the preparation and characterization of these materials were given in Chapter 3.

4.2 RESULTS AND DISCUSSION

4.2.1 Dynamic Mechanical Behavior

4.2.1.1 Effect of Polymeric Acid Catalyst

The storage moduli, E' , and $\tan \delta$ behavior are represented in Figure 4-1 for two TEOS(50)-PTMO(2K)-100-0.014 CERAMERs aged for 12 days. One sample was catalyzed with HCl and the other with PSS. The storage modulus in the glassy state is similar for the two systems. Indeed, the storage moduli behavior below -100°C is what one would expect for a glassy polymer, ca. 2 GPa. The onset of the T_g occurs at nearly the same temperature, approximately -70°C , for both the HCl and PSS catalyzed CERAMERs as indicated by the drop in the storage modulus. However, the rubbery plateau above T_g is distinctly higher for the PSS catalyzed CERAMER than for the HCl catalyzed CERAMER. The observed difference is believed to be related to a higher extent of reaction for the PSS system which will be discussed later.

The loss behavior of these two materials provides more information as to the nature of the structural differences that account for the higher storage modulus of

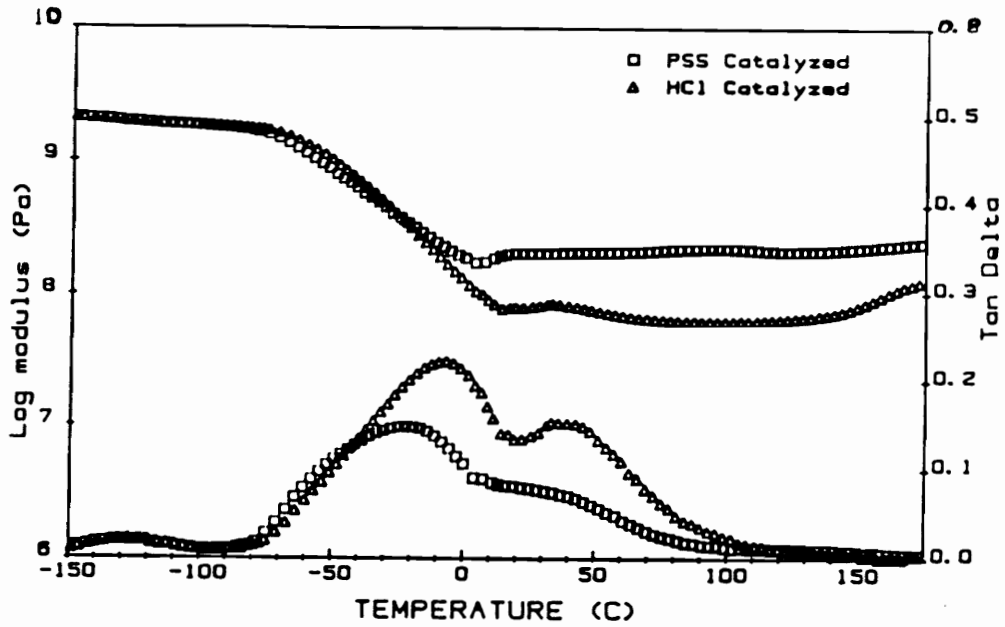


Figure 4-1 Dynamic mechanical behavior of PSS and HCl catalyzed CERAMERs:TEOS(50)-PTMO(2K)-100-0.014 X. Frequency = 11 hz.

the PSS catalyzed CERAMER in the rubbery region. The broadness of the loss dispersion peak is representative of the distribution of relaxation times of the PTMO segments associated with the different environments. The bimodal nature of the loss behavior in Fig. 4-1 is most likely related to some partial microphase separation. The broad $\tan \delta$ peak indicates by its maximum that the T_g (-15°C) of the PSS CERAMER is slightly lower than the T_g (0°C) of the HCl catalyzed CERAMER. This is contrary to the expected $\tan \delta$ behavior for a network forming system where the T_g increases with higher conversions of the functional species. A model, proposed for a related system by Huang et al. (as referred to in Chapter 2.0, Section 2.3.2), describes two types of segmental restrictions imposed on the PTMO oligomers that influence the $\tan \delta$ T_g peak (6). A TYPE 1 restriction, according to this model, is due to the PTMO segments that are reacted at both ends into the silicate network. This TYPE 1 restriction of the PTMO segments limits backbone mobility and thus increases the thermal energy requirement necessary for long range segmental motion associated with the glass transition. The second restriction, referred to as a TYPE 2, occurs when the PTMO oligomer is "encapsulated" by a partially condensed TEOS network. It has been reported that sol gel derived silicate structures similar to those formed in the CERAMERs under acidic conditions, are a combination of linear and cyclic polymers (13, 14). The formation of cyclic silicates could conceivably contribute to the loss dispersion curve in two different modes. One mode, as suggested by FTIR studies, is a ring bending and/or a bond rocking mode associated

with the cyclic silicate structures (15). The other mode, in terms of loss dispersion, is the restriction of the chain segments passing through the cyclic structures. It was reported by Mauritz that the relative concentration of the cyclic silicate structures with respect to linear silicates formed by the condensation of TEOS within Nafion membranes decreased with time (15). Thus, it is conceivable that in the early stages of gel formation in the CERAMERs, PTMO segments could become encapsulated by some of these cyclic silicate structures. The density and thus rigidity of these silicate structures, as well as restrictions on the PTMO segments encapsulated within them, increase as the condensation of the reactive species proceeds. The structural changes associated with the higher extent of reaction lead to a decrease in the magnitude of the $\tan \delta$ peak toward the higher temperature range of the broad dispersion and thus cause an apparent shift of the $\tan \delta$ maxima to a lower temperature. This, in conjunction with the higher rubbery modulus, is indirect evidence that the PSS catalyzed CERAMERs convert a higher percentage of TEOS for an equivalent composition catalyzed with the same concentration of HCl.

The apparent higher extent of condensation catalyzed by the PSS compared to HCl was assumed to be due to the difference in the strength of the sulfonic acid versus HCl. A gel was synthesized using p-toluene sulfonic acid (TSA) as the catalyst to compare a monomeric catalyst with a polymeric catalyst which has the same acid functionality. The storage moduli and the $\tan \delta$ of the TSA catalyzed CERAMER of composition TEOS(50)-PTMO(2K)-100-0.014 are depicted as a function of

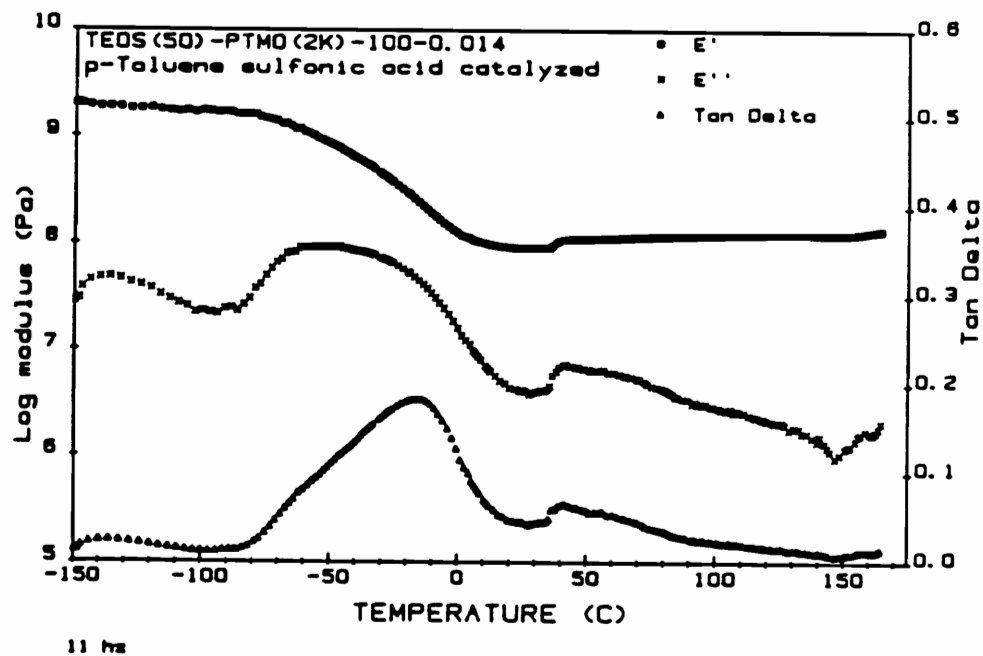


Figure 4-2 Dynamic mechanical behavior TSA catalyzed CERAMER: TEOS(50)-PTMO(2K)-100-0.014. Frequency = 11 hz.

temperature in Figure 4-2. The differences between the two CERAMERs, i.e. the PSS catalyzed sample depicted in Fig. 4-1 and the TSA catalyzed sample depicted in Fig. 4-2; are rather insignificant in terms of both the storage moduli and the $\tan \delta$ behavior. The magnitude of the storage moduli is equivalent for both the PSS catalyzed CERAMER and the gel produced with the TSA catalyst. The large loss dispersion which starts at near ca. -80°C reaches a maxima for both materials at near -15°C . Thus, it would appear that the differences between the PSS catalyzed CERAMER and the HCl CERAMER (Fig. 4-1) may indeed be related to the strength of the acid catalyst.

4.2.1.2 Effect of TEOS

The molecular environments that give rise to the TYPE 1 and TYPE 2 restrictions should depend upon the volume fraction and compatibility of TEOS and PTMO for a given set of reaction conditions. The influence of the silicate phase on the dynamic mechanical behavior is illustrated in Figures 4-3 and 4-4. The storage moduli are plotted in Fig. 4-3 for a series of PSS catalyzed CERAMERs, TEOS(X)-PTMO(2K)-100-0.014, where the initial weight fraction of TEOS was varied from 0% to 70%. At temperatures below -100°C all five of the CERAMERs (Fig. 4 3)-

behave as a glassy polymer in terms of the storage moduli as seen for the two in Figure 4-1. The storage modulus of the CERAMER composition TEOS(0)-PTMO(2K)-100-0.014 begins a sharp decline near ca. -80°C , followed by a very distinct rise at ca. -70°C . This behavior as reported previously for these materials is attributed to crystallization of the PTMO chains. The addition of 40% TEOS to the CERAMER eliminates any evidence of crystallization. The storage moduli (Fig. 4-3) in the rubbery region increases from ca. 10^7 to 10^8 Pa as the weight fraction of TEOS is raised from 40 to 70 wt%, respectively.

The loss dispersion peaks show both a temperature shift to a higher range and a decrease in the area with higher volume fraction of TEOS (Fig. 4-4). All the $\tan \delta$ peaks appear to begin near -80°C , then broaden significantly as the TEOS level is increased. The composition TEOS(0)-PTMO(2K)-100-0.014 displays a very large loss dispersion near ca. -80°C associated with long range motion of the PTMO chains. The rather broad loss dispersion extending from ca. -60°C to ca. 10°C is due to melting of the crystalline portion of the PTMO phase. The $\tan \delta$ maxima (0.3) peak for the CERAMER containing 40% TEOS is nearly twice the maxima (0.16) of the $\tan \delta$ peak of the 70% TEOS hybrid. This reduction in the loss dispersion is attributed to the entrapment of PTMO segments within the silicate network which limits their contribution to the molecular motions that give rise to the peak. The decrease in the magnitude of $\tan \delta$ along with the shift of the peak maxima to a higher temperature for this series, is similar to reported trends for previous studies

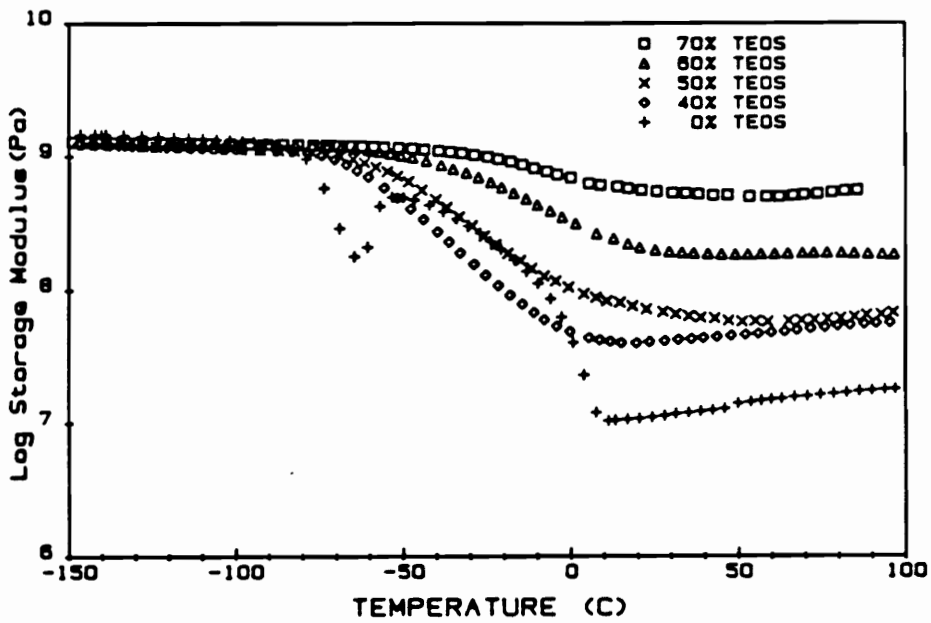


Figure 4-3 Storage modulus as a function of weight fraction TEOS: TEOS(X)-PTMO(2K)-100-0.014 PSS. Frequency = 11 hz.

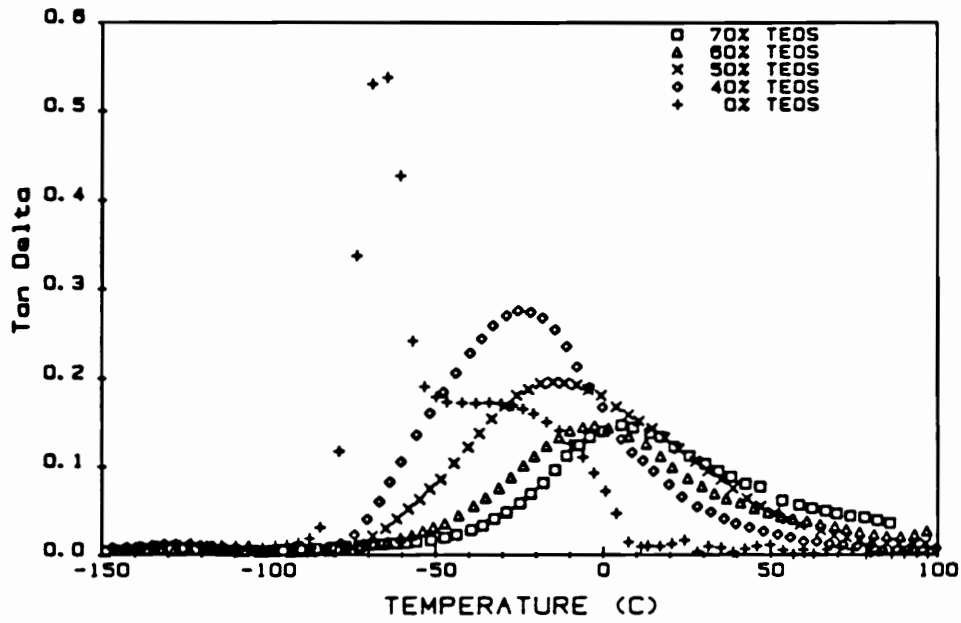


Figure 4-4 Tan δ behavior as a function of weight fraction TEOS:TEOS(X)-PTMO(2K)-100-0.014 PSS. Frequency = 11 hz.

in this laboratory on formulations catalyzed with HCl (6,8,10).

4.2.1.3 Effect of TEOS:Water Ratio

The ratio of TEOS to water has been adequately characterized in sol-gel processes in terms of the final structure and extent of condensation in the silicate network [1,9,38,43,50]. The effect on the dynamic mechanical behavior of PSS catalyzed CERAMERs is illustrated in Figures 4-5 and 4-6. The storage modulus of the hybrid system TEOS(50)-PTMO(2K)-X-0.014, where X varies from 50% to 200%, changed very little when the water was increased by a factor of 2 from 50% to 100% (Fig. 4-5). There was a significant rise in the magnitude of the storage modulus in the rubbery regime with a quadrupling of the water added, i.e. 50% to 200% (Fig. 4-6). Additional insight into the influence of these two types of environments on the damping behavior of the CERAMERs was provided by Figure 4-6. Three different levels of water, 50%, 100% and 200%, were evaluated in a CERAMER based upon the same 2000 g/mol oligomer of silane end capped PTMO. Each CERAMER contains 50% TEOS and 0.014 equivalents of PSS catalyst. The bimodal nature of the damping curve diminishes as the level of water is increased. This trend correlates well with previous reports in the literature which indicate that the sol gel reaction proceeds further as the mole ratio of water to alkoxide is increased. It is interesting that the change to higher levels of water shifts the overall maxima of each peak to

a higher temperature, but the range of the overall loss dispersion does not change significantly. The interpretation might be that at this level of TEOS, i.e. 50%, TYPE 1 restrictions predominate the environment of the PTMO chains, however, there is no direct evidence for this. However, in consideration of the work of Kelts and Armstrong [9], as well as Coltrain et. al. [37,50] this appears reasonable. The higher level of water does effectively dilute the acid concentration and effectively increase the pH, though maybe only slightly, it maybe postulated that such an increase decreases the time to gelation. The CERAMER with the highest level of water may gel faster and therefore there is less time for it to achieve the lowest energy state. Thus, more mixing between the phases would be predicted (TYPE 2 interactions). The loss dispersions in Fig. 4-6 predict such a trend.

4.2.1.4 Effect of Oligomer Molecular Weight

The extent of mixing in these novel hybrid materials on their dynamic mechanical behavior was examined by substitution of the 2000 g/mol oligomer of PTMO with two different oligomers, one of 650 g/mol and the other 1000 g/mol. The values for the molecular weight are, of course, prior to functionalization with the isocyanatopropyltriethoxysilane. The storage moduli and damping characteristics are plotted as a function of temperature in Figure 4-7 for three CERAMER compositions, TEOS(50)-PTMO(X)-100-0.0.14, where X, the molecular weight of the

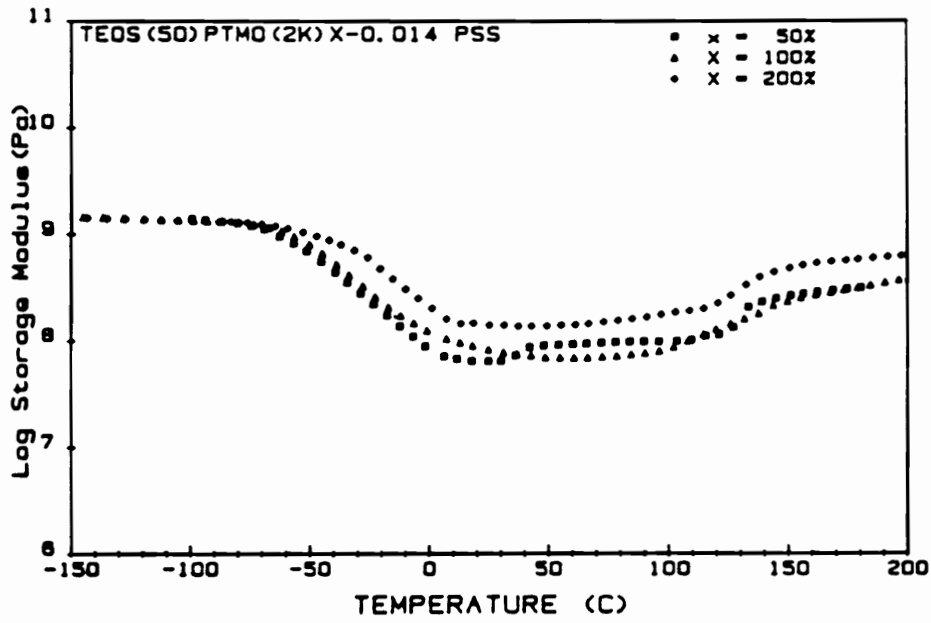


Figure 4-5 Storage modulus as a function of TEOS:water ratio: TEOS(50)-PTMO(2K)-X-0.014 PSS. Frequency = 11 hz.

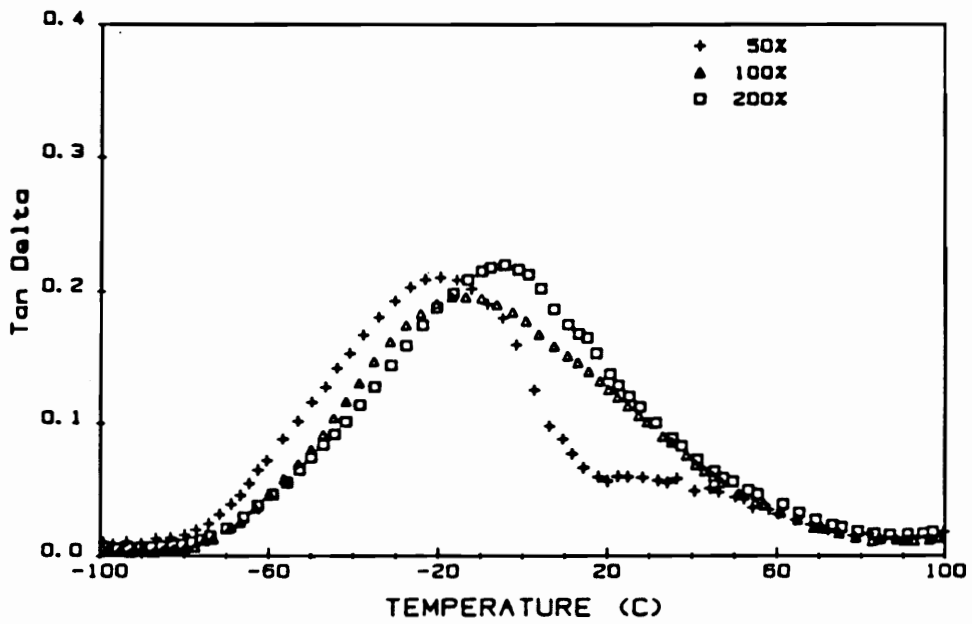


Figure 4-6 Damping behavior as a function of TEOS:water ratio: TEOS(50)-PTMO(2K)-X-0.014 PSS. Frequency = 11 hz.

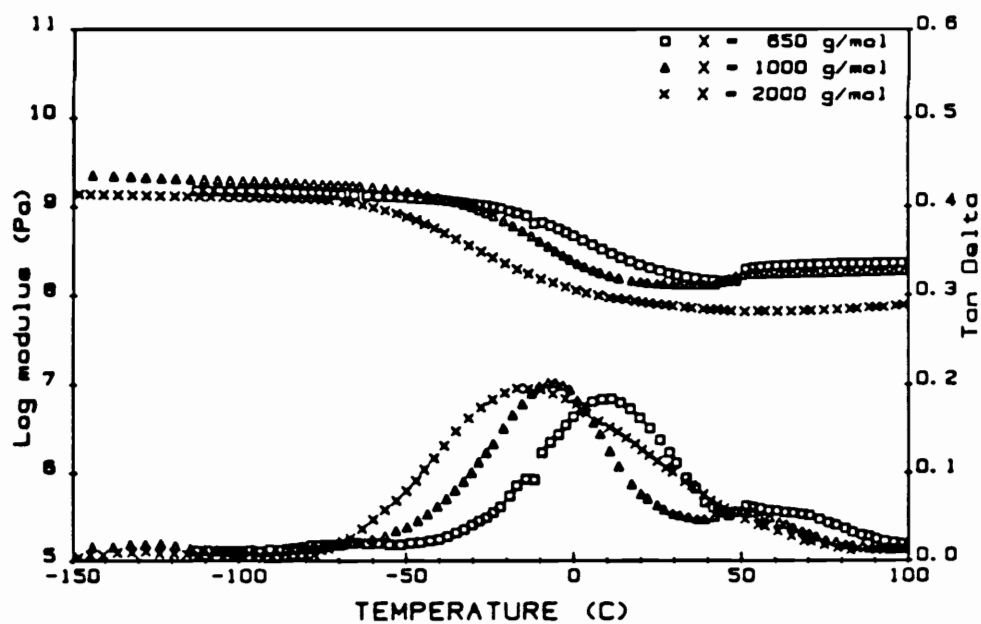


Figure 4-7 Dynamic mechanical behavior as a function of PTMO M_n : TEOS(50)-PTMO(X)-100-0.014 PSS. Frequency = 11 Hz.

oligomer is either 650 g/mol, 1000 g/mol or 2000 g/mol. The onset of the glass transition temperature as reflected in the decrease in the storage modulus or the onset of the loss behavior by the $\tan \delta$ peak, shifts to higher temperatures as the molecular weight of the oligomer is decreased. Again this behavior reflects the same trends as reported by Huang et. al. It further supports the concept of TYPE 1 and TYPE 2 interactions in these novel materials. The maxima of the loss dispersion for the CERAMER prepared with the 650 g/mol oligomer is approximately 30°C higher than that of the hybrid network prepared with the 2000 g/mol oligomer (Fig. 4-7).

The use of a low molecular weight PTMO oligomer, i.e. 650 g/mol, shifts the T_g to a higher temperature and raises the rubbery modulus of the CERAMER as indicated in Figure 4-7. The level of TEOS in the CERAMER composition TEOS(X)-PTMO(650)-50-0.014 PSS, where X varies from 20% to 60% (Figure 4-8), determines the magnitude of the storage modulus in the same manner as previously shown for the gels prepared with TEOS and the 2K g/mol end capped PTMO oligomer (Fig. 4-3). The rise in the storage modulus with heating to temperatures above ambient has been ascribed to further curing of the system as will be discussed in the following section on aging. The loss dispersion behavior of the compositions TEOS(X)-PTMO(650)-50-0.014 PSS (Figure 4-9) shows a systematic shift to a higher temperature with increasing levels of TEOS. A significant decrease in the overall loss dispersion occurs simultaneously with the rising T_g . The maximum T_g of ca. 15°C associated with the CERAMER TEOS(60)-PTMO(650)-50-0.014 PSS, is just

below ambient, ca. 20°C. The reader will note that the TEOS to water ratio is higher in the compositions whose dynamic mechanical response are given in Figs. 4-8 and 4-9 compared with those of Figs. 4-3 and 4-4. The differences in storage modulus and $\tan \delta$ behavior between CERAMERs prepared with a TEOS to water ratio of 2:1 versus 1:1 was subtle (Fig. 4-5) and therefore not significant for fresh gels (ca. 8 to 14 days).

4.2.1.5 Effect of Aging

Aging in CERAMER hybrid materials was first reported by Huang, Glaser and Wilkes [24]. The influence on dynamic mechanical behavior can be quite significant as reported by Huang et. al. [24] for TEOS/PTMO inorganic/organic hybrid materials. There is a strong correlation between the trends observed in the dynamic mechanical behavior of the CERAMER TEOS(50)-PTMO(2K)-X-0.014 as a function of water (Fig. 4-5 and Fig. 4-6) and the aging behavior of the PSS catalyzed formulation TEOS(50)-PTMO(2K)-50-0.014 CERAMER (Figure 4-10). The storage modulus increases only slightly with aging of approximately 105 days compared to 14 days (Fig. 4-10). The loss dispersions of the CERAMER composition TEOS(50)-PTMO(2K)-50-0.014 PSS (Fig. 4-10) decrease in magnitude with increasing age from 7 days to 14 days to 104 days. The maximum $\tan \delta$ value of each loss dispersion shifted to a lower temperature as the time at ambient

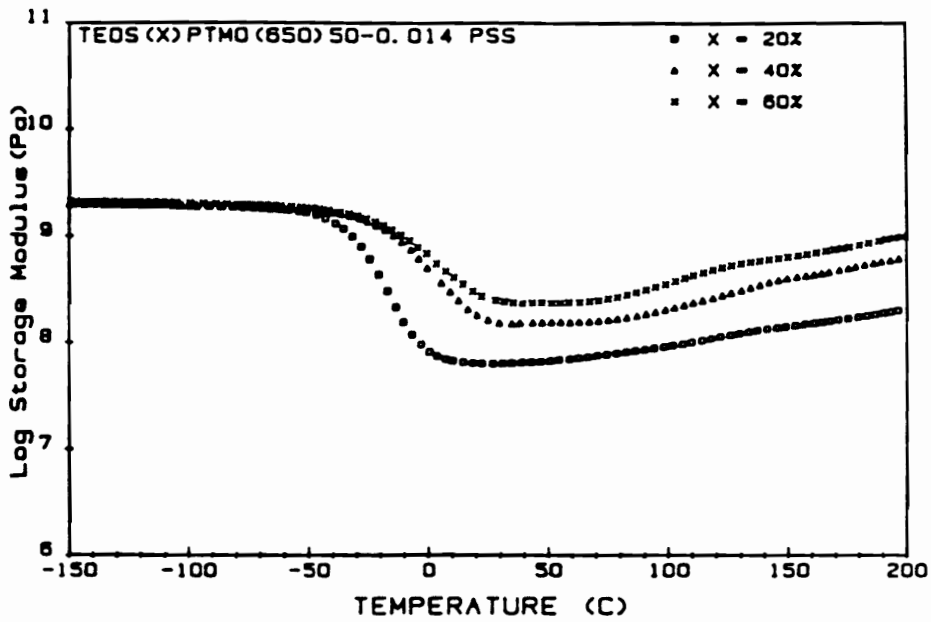


Figure 4-8 Storage moduli as a function of weight of TEOS: TEOS(X)-PTMO(650)-50-0.014 PSS. Frequency = 11 Hz.

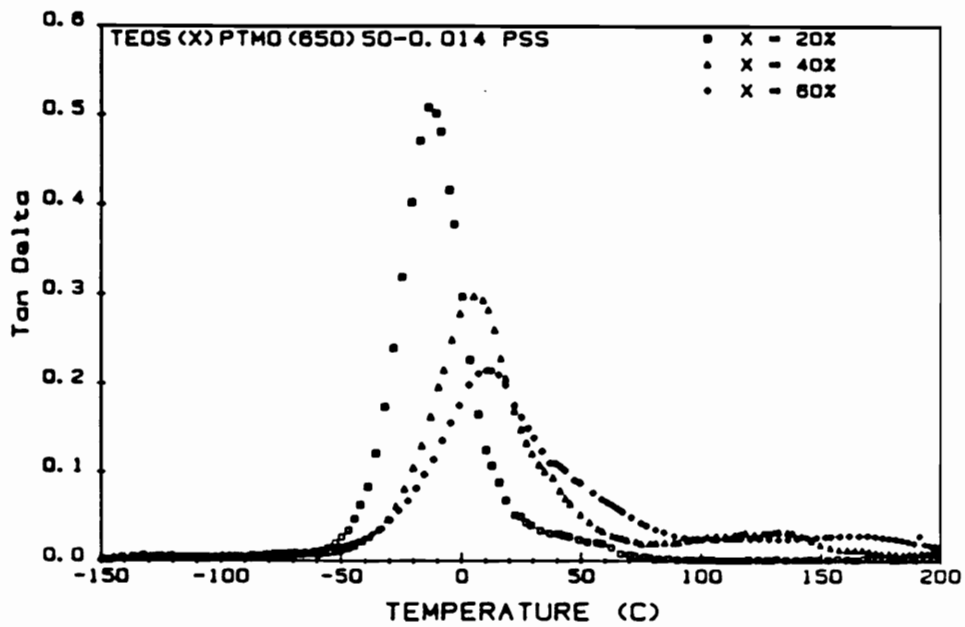


Figure 4-9 Damping behavior of CERAMER: TEOS(X)-PTMO(650)-50-0.014 PSS. Frequency = 11 hz.

conditions was increased. The overall damping behavior (Fig. 4-10), which is broad (ranging from ca. -80°C to 100°C), also decreased as the material aged at ambient conditions. These changes resemble the effect of decreasing the TEOS to water ratio (Fig. 4-6). The $\tan \delta$ behavior of TEOS/PDMS CERAMERs and TEOS/PTMO CERAMERs changed in a similar manner in response to variations in the TEOS to water ratio and aging according to the results of Huang et. al. [24]. Huang et. al. ascribed the changes to the nature of the interactions between the PTMO and the silicate phase as well as the extent of reaction in the network. The similarity between the CERAMER systems studied to this point would support the conclusions of Huang et. al. [24]. The effect of aging on the materials damping characteristics, as suggested by Huang et. al., could also be attributed to the slow process of equilibration of the gels which is believed best described as by a microphase separation mechanism.

There is a marked difference in the dynamic mechanical behavior of aged samples when the molecular weight of the PTMO oligomer is decreased from 2000 g/mol to 650 g/mol. The storage modulus in the rubbery regime (ca. 20°C to 100°C) was higher for a CERAMER, composition TEOS(60)-PTMO(2K)-50-0.014, which was aged 18 days and 108 days at ambient conditions (Figure 4-11). The $\tan \delta$ dispersions decreased rather markedly over the same temperature range (Fig. 4-11) and the maxima of the broad peak shifted approximately 5°C to a lower temperature. These trends are in line with the observed changes in Fig. 4-10.

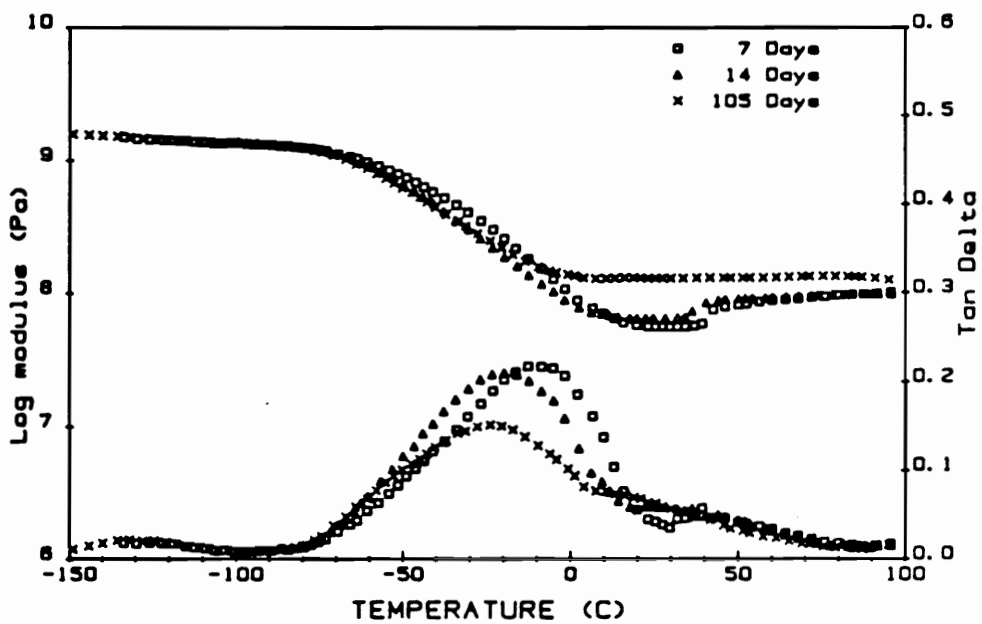


Figure 4-10 Dynamic mechanical behavior of PSS catalyzed CERAMERS as a function of age: TEOS(50)-PTMO(2K)-50-0.014 PSS. Frequency = 11 hz.

However, when the molecular weight of the oligomer was lowered, significant changes in the dynamic mechanical behavior were recorded as a function of aging. The storage moduli and the $\tan \delta$ behavior as a function of temperature for a CERAMER, TEOS(60)-PTMO(650)-50-0.014, which was aged for 7 days and 31 days are portrayed in Figure 4-12. The storage modulus of the CERAMER aged 31 days increases significantly in the rubbery regime such that the characteristic decrease at the T_g is practically non-existent. Rather than resembling a filled rubber as the system in Fig. 4-11 does, the dynamic mechanical response of the composition TEOS(60)-PTMO(650)-50-0.014 PSS (Fig. 4-12) after aging for 31 days is more like that of a highly crosslinked epoxy network. The maxima of the $\tan \delta$ peak of the CERAMER with the 650 g/mol PTMO oligomer shifted to a higher temperature after aging 31 days compared with aging for 7 days (Fig. 4-12). Indeed, the maximum $\tan \delta$ value is very close to room temperature which strongly suggests the material has vitrified based upon the TTT Model proposed by Gillham [72] and applied to the TEOS/PEK CERAMERs by Noell et. al. [29]. This is quite different from the changes observed in the CERAMERs with the 2000 g/mol PTMO oligomer (Fig. 4-9 and Fig. 4-10) and occurs over a much shorter time span. Huang suggested that with aging the maximum of the loss dispersion shifted to a lower temperature due to the thermodynamic process, as mentioned earlier, of microphase separation [26]. The $\tan \delta$ behavior of the samples prepared with the higher molecular weight oligomer upon aging may support Huang's hypothesis. The incorporation of the

lower molecular weight oligomers in the TEOS/PTMO gels appeared to significantly alter the morphology as best one can predict morphological features from dynamic mechanical behavior alone.

Closer examination of the final value of the storage modulus after heating the CERAMER (Fig. 4-12) to 200°C in the DMA revealed that it was very close to the value of the sample aged for 31 days. The samples were typically quite brittle and very dark after heating in the DMA to 200°C and usually crack upon cooling under tension. The high modulus of the gels made with the low molecular weight PTMO oligomer (650 g/mol) also made it difficult to handle the samples after aging. The lower modulus of the CERAMERs prepared with the 2000 g/mol PTMO oligomer made these materials better candidates for post cures at elevated temperature. Therefore, a CERAMER based upon the 2000 g/mol PTMO oligomer was thermally aged at 120°C for 3 hours under vacuum. The dynamic mechanical behavior of the sample, TEOS(50)-PTMO(2K)-100-0.014 PSS, was plotted along with the sample in the as gelled condition (age was 16 days) as a function of temperature which is given in Figure 4-13. The storage modulus of the gelled sample typically exhibited an upturn at temperatures of 100° to 120°C and thus the higher temperature was selected for the post-cure. The final value of the storage modulus of the 16 day old gel at the end of the DMA run to 200°C is approximately 8.5 Pa on a logarithmic scale. The final value of the post cured sample was practically the same at the end of the DMA analysis to 175°C (Fig. 4-13). The T_g shifted up approximately 45°C

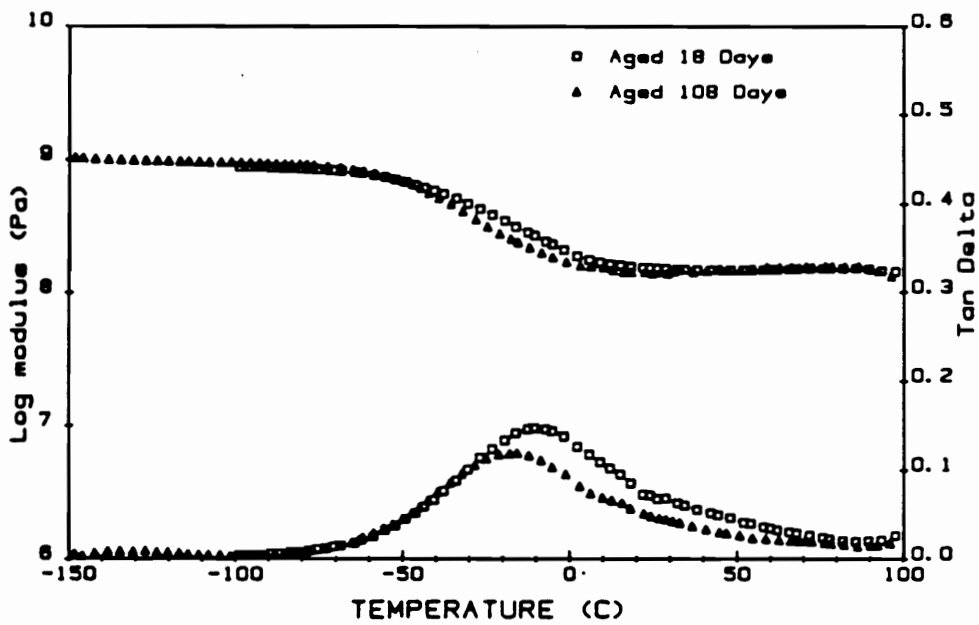


Figure 4-11 Dynamic mechanical behavior of CERAMERs as a function of age: TEOS(60)-PTMO(2K)-50-0.014 PSS. Frequency = 11 hz.

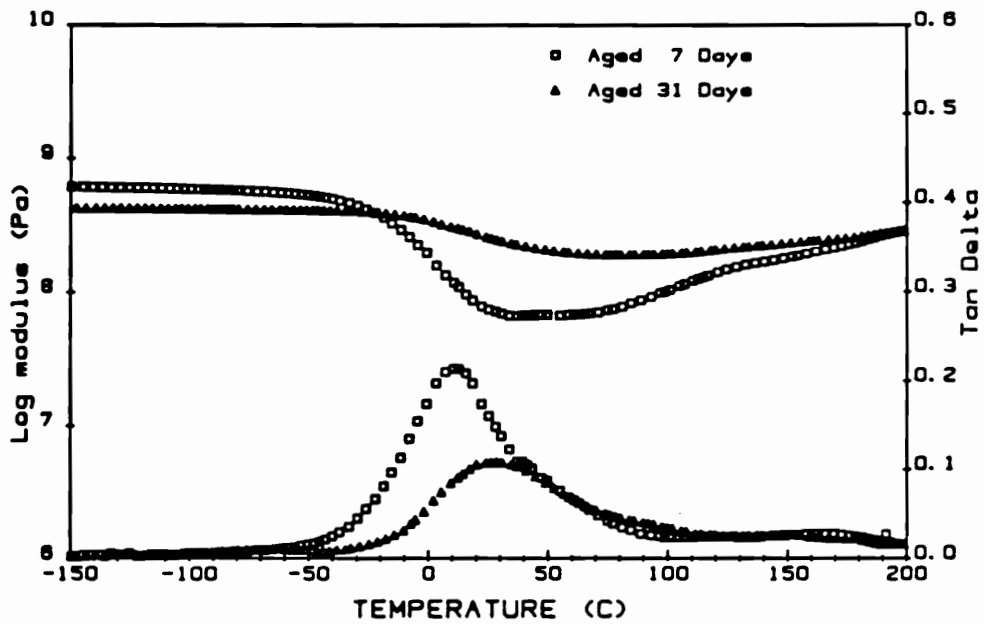


Figure 4-12 Dynamic mechanical behavior of CERAMERs as a function of age: TEOS(60)-PTMO(650)-50-0.014 PSS. Frequency = 11 hz.

due to the post cure at 120°C as indicated by the maximum of the $\tan \delta$ peak. This is as one would predict for a network which had vitrified prior to achieving its full extent of reaction. The T_g of this particular CERAMER (Fig. 4-11) does not, however, reflect the predicted trend of increasing to the temperature at which it was aged. Furthermore, the loss dispersions of the annealed sample (to 120°C) are broader than prior to the post cure. The temperature range extended from ca. -70°C to ca. 90°C for the loss dispersions of the 16 day old sample compared to a range from -70°C to nearly 150°C for the annealed sample. The low temperature molecular relaxations were practically eliminated by the annealing at 120°C as reflected in the low $\tan \delta$ values below ca. -40°C (Fig. 4-13). The breadth of the loss dispersions suggests that if there were two separate phases, albeit on a molecular scale since the samples are optically clear, that the annealing enhanced mixing. Yet, there is a slight step in the $\tan \delta$ peak at near 50°C which may indicate there are two distinctly different relaxation processes that together were responsible for the damping characteristics. The morphology of these materials will be addressed in more detail in the Section 4.4 by the use of small angle x-ray scattering.

4.2.1.6 Effect of TEOS to Catalyst Ratio

The ratio of the metal alkoxide to catalyst was shown to be critical in terms of the effective pH of the sol-gel process which appears to be the key variable in

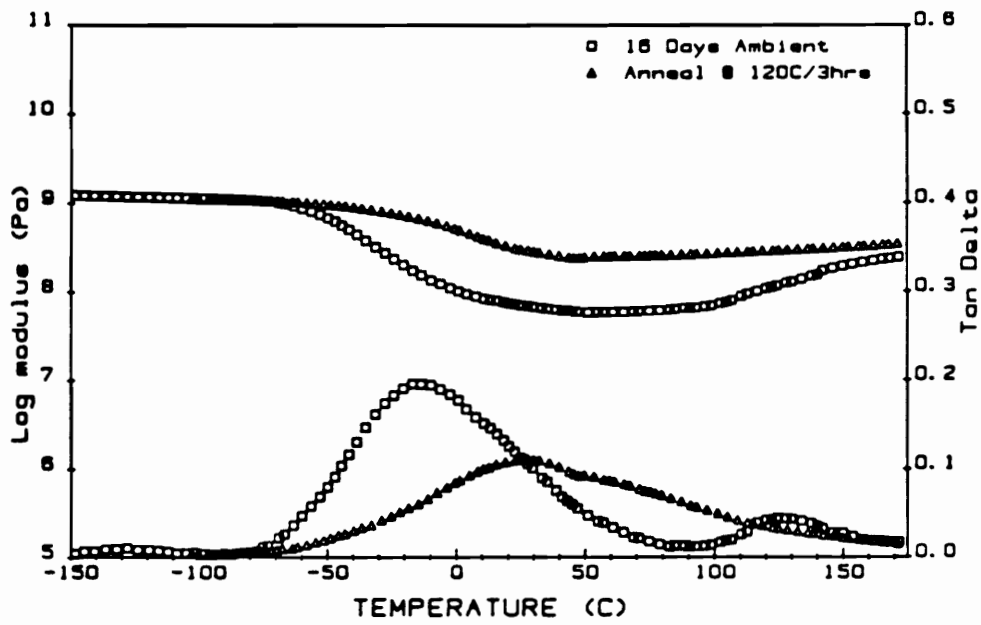


Figure 4-13 Dynamic mechanical behavior as a function of aging temperature: TEOS(50)-PTMO(2K)-100-0.014 PSS. Frequency = 11 hz.

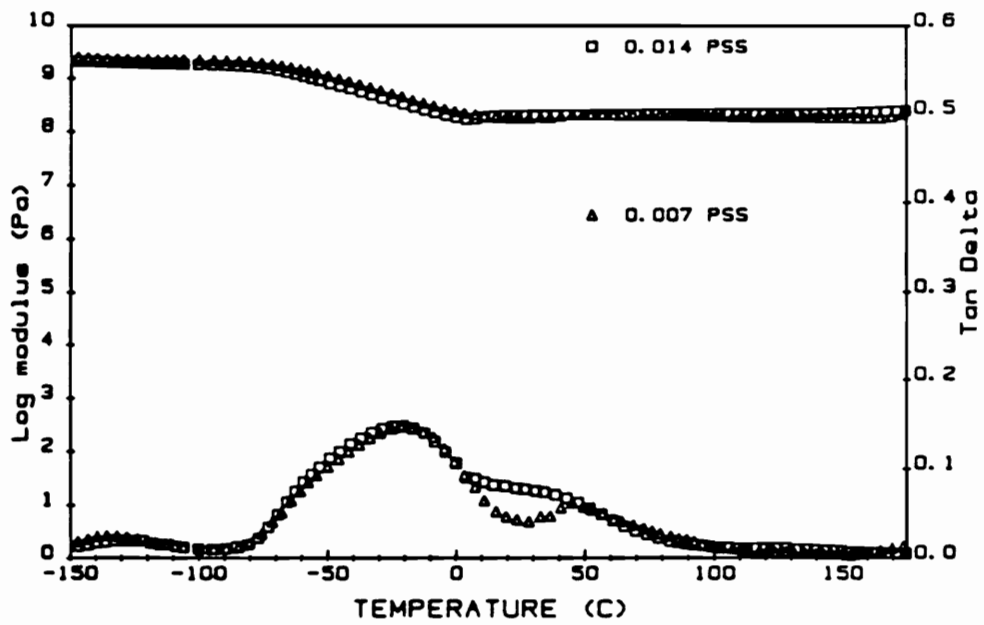


Figure 4-14 Dynamic mechanical behavior as a function of TEOS:acid ratio:
TEOS(50)-PTMO(2K)-100-X

catalyzed hybrid. Both samples were 14 days old when tested, which is the reason for the slightly higher modulus value of the PSS catalyzed sample. The higher Young's modulus of the PSS catalyzed CERAMER compared with the HCl catalyzed sample supports the earlier statement that the PSS catalyzed network is more complete. This was verified by swelling experiments on samples prepared at the same time which were previously extracted in a Soxhlet apparatus for 48 hours using THF as the solvent. Both the PSS and HCl catalyzed CERAMERs (TEOS(50)-PTMO(2K)-100-0.014), contained less than 1% extractables by this method which indicates that the networks contained insignificant sol fractions. The equilibrium volume increase for the PSS catalyzed ceramer was 33% after swelling for 24 hours in THF compared to 46% for the HCl ceramer. This behavior, in conjunction with the DMA and stress-strain data, is strong evidence that the PSS catalyzed ceramer has a more fully cross-linked or interconnected network than the HCl catalyzed CERAMERs of equivalent composition.

4.2.2.2 Effect of TEOS

The corresponding stress-elongation reponse of PSS catalyzed CERAMERS as a function of TEOS levels (Figure 4-16) clearly demonstrates an increase in the modulus at 25°C with an increase in the level of TEOS. The Young's modulus, stress at break and elongation (%) at break are listed in Table 4-1 corresponding to

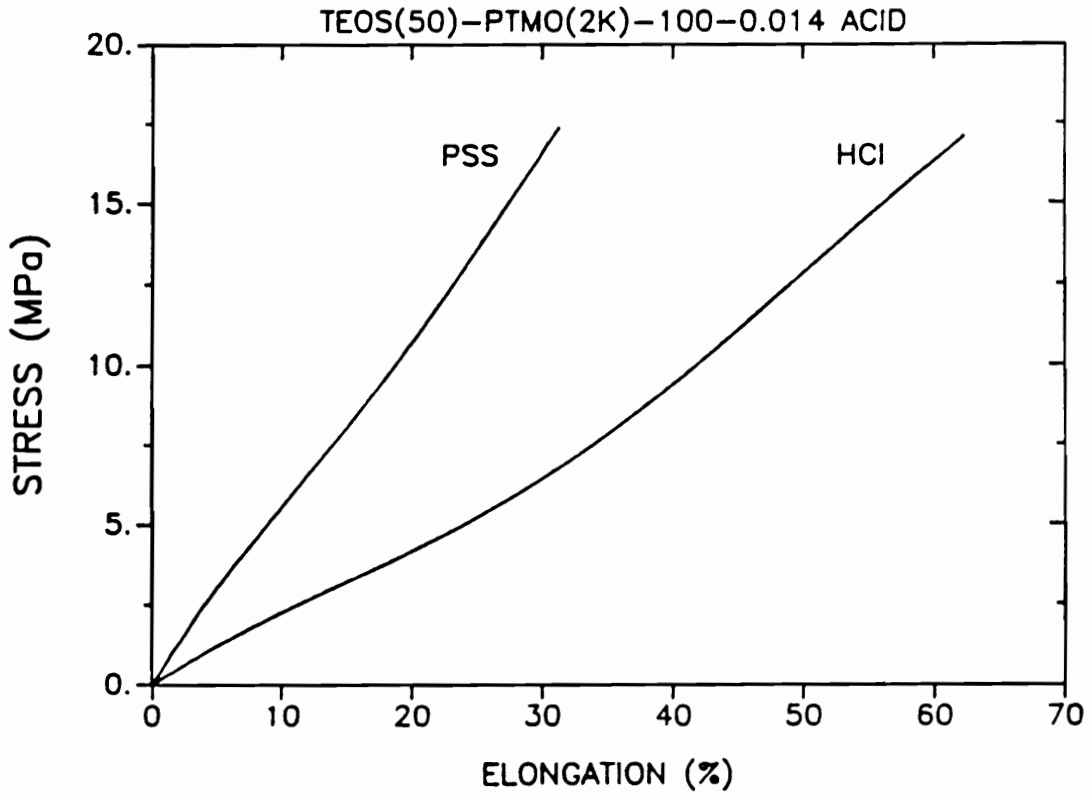


Figure 4-15 Mechanical behavior of PSS versus HCl catalyzed CERAMERs:
TEOS(50)-PTMO(2K)-100-0.014 X.

the stress-elongation behavior represented in Fig. 4-16. The modulus for the 40 wt% TEOS CERAMER is 25 MPa compared to 250 MPa for the modulus of the 70 wt% TEOS sample. These values, measured 10 days after casting, compare to equivalent compositions of the HCl CERAMERs which were tested 30 days after casting [24]. There is no evidence of yield behavior in the compositions presented in Figure 4-16 and in fact most show nearly 100% recovery at elongations of less than 50% of the elongation at break. The sharp increase of Young's modulus with increasing TEOS in the PSS catalyzed ceramer also can be interpreted in terms of the TYPE 1 and TYPE 2 restrictions. The lower modulus of the 40% TEOS ceramer reflects an environment in which there is sufficient freedom from restrictions for PTMO chains to alter conformations in response to the strain applied during the experiment. Eventually the inorganic phase will become the continuous phase and support the bulk of the applied load. Similar trends were observed for HCl catalyzed CERAMERs of equivalent compositions [24,26].

4.2.1.3 Effect of TEOS:Water Ratio

The effect of TEOS to water ratio was relatively insignificant in terms of the mechanical properties of the PSS catalyzed CERAMER compositions evaluated. The Young's modulus, stress at break and elongation (%) at break did not increase by a significant amount with the ratio of TEOS to water varied from 1:2 to 1:4 as

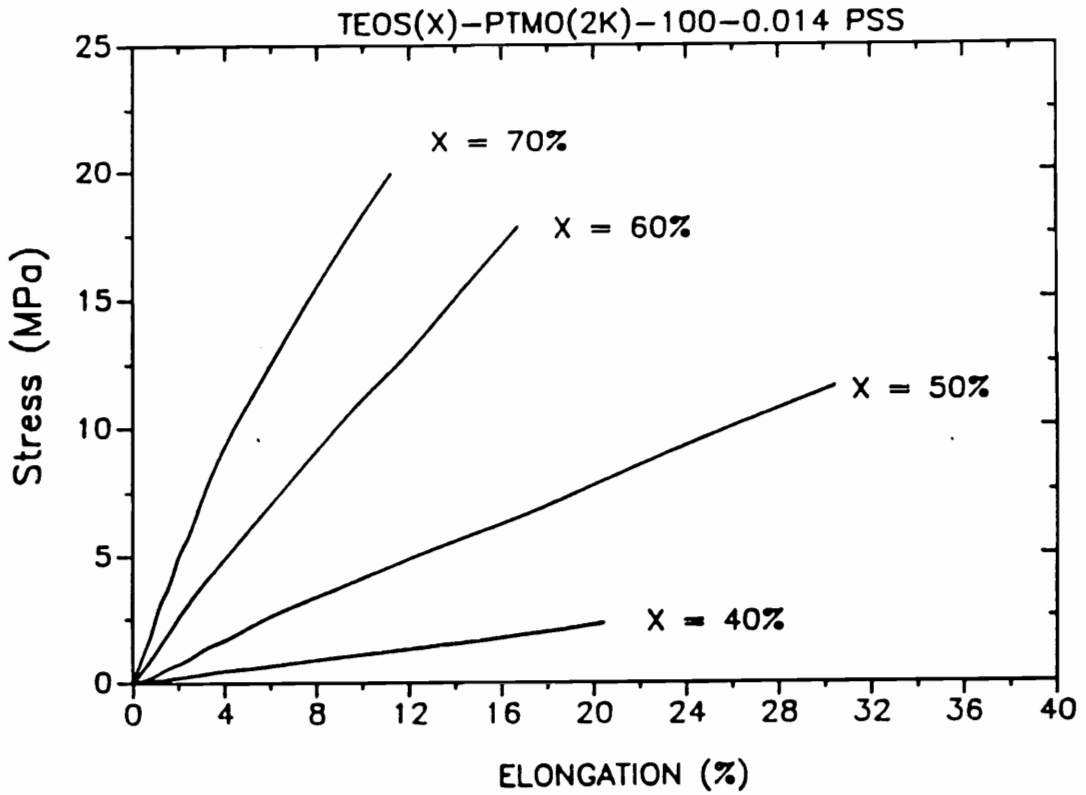


Figure 4-16 Mechanical behavior of PSS catalyzed CERAMERs (TEOS(X)-PTMO(2K)-100-0.014 where X varies from 40% to 70%)

Table 4-1 Mechanical properties of PSS catalyzed CERAMERs

TEOS(X)-PTMO(2K)-100-0.014 PSS			
TEOS (wt%)	YOUNG'S MODULUS (MPa)	STRESS AT BREAK (MPa)	ELONGATION AT BREAK (%)
40	25	5	23
50	45	11	29
60	89	15	22
70	243	19	11

seen in Table 4-2 for the CERAMER composition TEOS(50)-PTMO(2K)-X-0.007 PSS, where X was either 50 or 100%. There was, however, a significant increase in the Young's modulus when the ratio of the water to TEOS was raised from 4:1 to 8:1 (Table 4-2). The change in modulus would indicate the network was more highly cross-linked, i.e. a higher percent of the functional groups were condensed in the sol-gel process. Yet, the stress at break actually decreased slightly. This could be accounted for in terms of sample defects. But, another possible explanation may be that the higher water increased the condensation rate such that the TEOS and alkoxides attached to the PTMO oligomers were hydrolyzed rapidly. Then, due to the difference in reactivity between the two alkoxides, i.e. TEOS vs. organo substituted triethoxy silane, the two phases self condensed at a higher rate than a "cross" condensation. This type of mechanism would create a filled elastomer with less chemical bonding between the TEOS generated species and the PTMO oligomers. This is only a hypothesis for which a reasonable analysis for verification was not determined.

4.2.2.4 Effect of Oligomer Molecular Weight

A reduction in the molecular weight of the PTMO oligomer used resulted in a higher storage modulus in the rubbery regime of the CERAMER composition TEOS(50)-PTMO(650)-100-0.014 PSS compared with a gel prepared with the 2000

Table 4-2 Mechanical properties as a function of TEOS:Water ratio

TEOS(50)-PTMO(2K)-X-0.007 PSS			
WATER (wt%)	YOUNG'S MODULUS (MPa)	STRESS AT BREAK (MPa)	ELONGATION AT BREAK (%)
50	63	11	21
100	61	9	18

TEOS(50)-PTMO(2K)-X-0.014 PSS			
WATER (wt%)	YOUNG'S MODULUS (MPa)	STRESS AT BREAK (MPa)	ELONGATION AT BREAK (%)
100	45	11	29
200	75	9	16

g/mol PTMO oligomer (Fig 4-7). The mechanical properties of a series PSS catalyzed compositions based upon the general formula TEOS(X)-PTMO(650)-100-0.014 PSS, where X varies from 40 to 60%; are listed in Table 4-3. The gel of composition TEOS(50)-PTMO(650)-100-0.014 PSS has a Young's modulus of 56 MPa compared with a gel of the same formula, except for the PTMO oligomer which was 2000 g/mol, which had a modulus of 45 MPa (Both the gels were prepared the same day and aged 8 days prior to testing). The stress at break was lower, as was the elongation at break for the CERAMER based upon the 650 g/mol oligomer. The lower stress at break would indicate the network was not sufficiently developed to support the load in the 650 g/mol containing CERAMER compared to the gel prepared with the higher molecular weight oligomer.

The higher modulus with a lower stress at break might also be associated with the relative weight fraction of the inorganic component with respect to the PTMO oligomer. The relative weight fraction of the TEOS to PTMO is nearly 50% higher in the gels prepared with the 650 g/mol oligomer compared to those formed with TEOS and the 2000 g/mol PTMO oligomer. This is based upon the assumption that the alkoxide groups are completely hydrolyzed and the resulting silanols are exhausted completely by condensation reactions. The combination of shorter PTMO chains and the higher weight fraction of inorganic would most likely lead to more mixing between the two phases. It also would lead to a more continuous silicate network. Thus, the elastic modulus would be much higher for a gel with a silicate

Table 4-3 Mechanical properties of PSS catalyzed CERAMERs based on 650 g/mol PTMO

TEOS(X)-PTMO(650)-100-0.014 PSS			
TEOS (wt%)	YOUNG'S MODULUS (MPa)	STRESS AT BREAK (MPa)	ELONGATION AT BREAK (%)
40	37	4	12
50	56	5	11
60	194	10	7

structure, albeit not a well defined one, as the supporting structure. This is in contrast to the gel, TEOS(50)-PTMO(2K)-100-0.014 PSS, which distributes the load during the stress-elongation test over a continuous PTMO structure. Indeed, the modulus decreases significantly with increasing molecular weight of the oligomer as depicted in Figure 4-17. The three stress/elongation plots in Fig. 4-17 represent the average response of the CERAMER composition TEOS(50)-PTMO(X)-100-0.014 PSS, where X was either the 650 g/mol, 1000 g/mol, or 2000 g/mol oligomer of PTMO. Note that the "ultimate" properties of the three materials (as prepared) also increased with the molecular weight of the PTMO oligomer. This correlates with the trends in the modulus described in Section 4.2.1.4. Again the weight fraction of TEOS (in the form of TEOS or various degrees of hydrolysis and condensation) was different for each of the three CERAMERs whose mechanical behavior is depicted in Fig. 4-17.

4.2.2.5 Effect of Aging

The mechanical properties of the PSS catalyzed CERAMER composition TEOS(50)-PTMO(2K)-100-0.014 were notably different after the thermal post curing (3 hrs. at 120°C) of a sample previously aged 16 days at ambient conditions (Table 4-4). The Young's modulus was increased by a factor of 5, from 45 MPa to 218 MPa. The stress at break was raised from 11 MPa to a value of 37 MPa while the percent

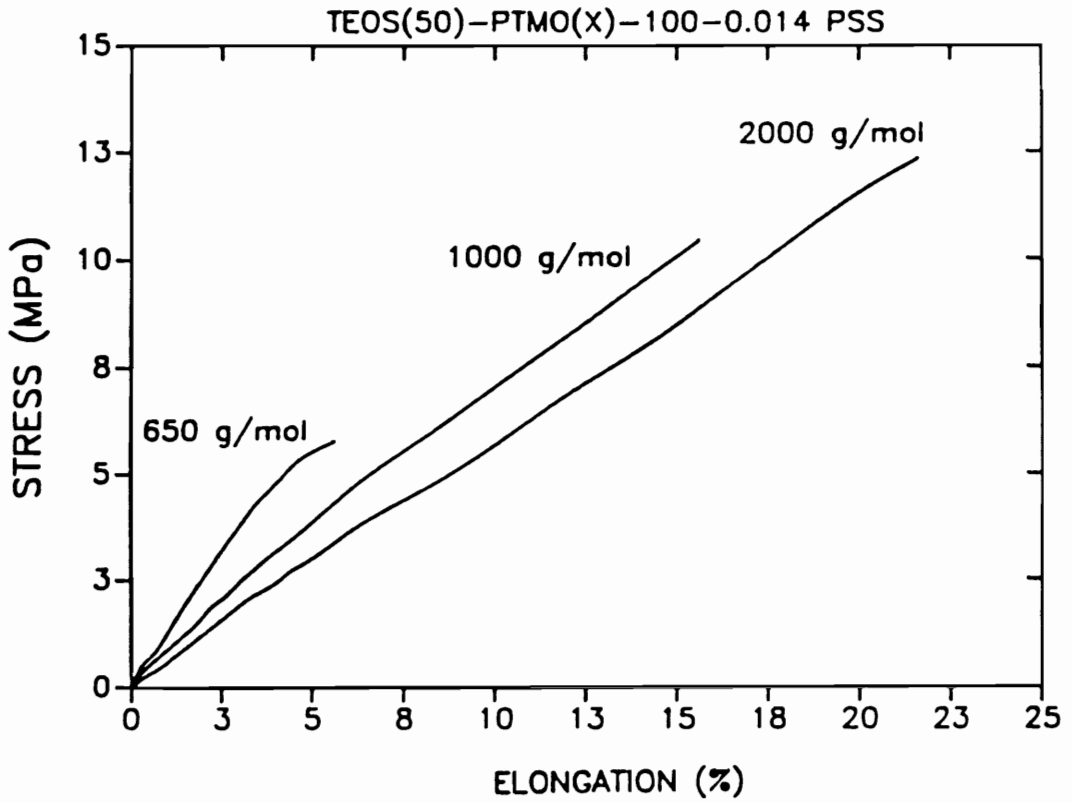


Figure 4-17 Mechanical response as a function of Oligomer M_n :TEOS(50)-PTMO(X)-100-0.014

elongation at break decreased from 30% to 5%. The results indicate that the extent of reaction was increased by the thermal processing at 120°C. However, the amount of solvent in the CERAMER gels was another consideration and thus, samples were dried in a vacuum chamber to reduce the adsorbed solvent. The elastic modulus was increased by the vacuum treatment (Table 4-4). The stress at break and elongation at break, however, were reduced significantly by the vacuum treatment of the CERAMER. This suggests that the thermal treatment at 120°C did increase the number of bonds in the gel such as the silicate structure derived from the sol-gel processing of TEOS [68]. The vacuum treatment of the gel may have disrupted the fragile structure by increasing the capillary pressure through rapid transport of the solvent out of the pores [31]. This would in turn be expected to create voids within the gel structure which would act as stress concentrators and thus lead to premature failure. Another possible explanation is that the vacuum treatment does remove the solvent which may act as a plasticizer. The mechanical properties of the gel would change as observed in this case. The actual reasons for this behavior are not understood at this time.

4.2.2.6 Effect of TEOS to Acid Ratio

The Young's modulus increased by 20% as a result of a higher ratio of TEOS to catalyst. The mechanical properties of two CERAMER formulations catalyzed

Table 4-4 Mechanical properties as a function of post gelation treatments of CERAMERs

TEOS(50)-PTMO(2K)-100-0.014 PSS			
TREATMENT BEYOND 16 DAYS AMBIENT	YOUNG'S MODULUS (MPa)	STRESS AT BREAK (MPa)	ELONGATION AT BREAK (%)
CONTROL	45	11	29
3 HR @ 120°C	218	37	5
VACUUM	69	7	7

with either 0.014 equivalents of PSS or 0.007 equivalents of PSS are compiled in Table 4-5. The stress at break, however, actually decreased from 11 MPa to 9 MPa. The lower stress at break is nearly the same as that determined for the lower ratio of TEOS to water for the CERAMER composition TEOS(50)-PTMO(2K)-200-0.014 (Table 4-2). This supports the premise that a rapid rate of hydrolysis forms the silicate phases rather fast, but that the overall network does not have sufficient continuity to withstand the large loads.

4.2.3 Small Angle X-ray Scattering Behavior

4.2.3.1 Effect of Polymeric Acid Catalyst

The morphological features of these materials were investigated by small angle x-ray scattering (SAXS) to gain further insight regarding the local structure. The results presented up to this point indicate that structural differences between the HCl catalyzed and PSS catalyzed CERAMERs are mainly related to the extent of condensation of the silicate component. The bimodal nature of the loss dispersion behavior (Fig. 4-1) indicates some microphase separation which has been described in terms of TYPE 1 and TYPE 2 environments. The SAXS behavior of the HCl catalyzed hybrid materials has been well characterized in this laboratory and supports this observation [17,18,19,22,24]. The SAXS profiles are presented in Fig.

Table 4-5 Mechanical properties as a function of TEOS:Acid ratio

TEOS(50)-PTMO(2K)-100-X PSS			
ACID (eqs)	YOUNG'S MODULUS (MPa)	STRESS AT BREAK (MPa)	ELONGATION AT BREAK (%)
0.014	45	11	29
0.007	61	9	18

4-18 for three CERAMERs (TEOS(50)-PTMO(2K)-100-0.014) as a plot of the scattering intensity versus s an angular factor related to the scattering vector. The angular factor s is defined as $(2\sin \Theta/\lambda)$ where Θ is one-half the radial scattering angle and λ is the wavelength. The reciprocal of s can be used as an estimate of the correlation length, as discussed earlier, but is only an approximation due to the smearing effect [63]. The presence of a maximum in the profile is indicative of a characteristic length in the scattering source which is due to a periodic fluctuation of the electron density similar to what one would measure for a two phase system which has undergone phase separation. Recall that the HCl catalyzed CERAMERs are optically clear and thus there is no evidence of any macrophase separation capable of scattering in the visible range (Chapter 2, Section 2.5.2) which leads one to conclude the maxima of the SAXS profile is due to microphase separation within the hybrid network. The PSS catalyzed CERAMERs which do scatter a small amount of light as a consequence of surface roughness (application of a silicone oil to the surface eliminates the scattering). The SAXS behavior of a PSS CERAMER and a TSA gel (Fig. 4-18) illustrates the similarity in morphology with the same composition of a HCl catalyzed hybrid. The position of the maxima of the three scattering profiles implies the same average spacing for the domains. The somewhat higher scattering intensity for the PSS and TSA CERAMERs compared to the HCl catalyzed material is further support of a denser silicate phase in the PSS CERAMER and the TSA CERAMER. A higher silicate density increases the

average electron density fluctuation for the system and thus raises the scattering intensity. This is supported by other more complete studies from our laboratory on HCl catalyzed CERAMERs [18].

4.2.3.2 Effect of TEOS

The intensity of scattered radiation of the CERAMERs catalyzed with HCl increases as a function of the weight fraction of TEOS added initially to the materials for the compositions TEOS(X)-PTMO(2K)-100-0.014 where X varied from 0 to 50%. However, as illustrated in Figure 4-19, as a plot of the smeared scattered intensity versus s , the maximum scattered intensity drops off sharply with the composition TEOS(60)-PTMO(2K)-100-0.014 PSS. A larger drop occurs in the scattered intensity as the level of TEOS is increased by an additional 10% TEOS, i.e. from 60% to 70%. The corresponding scattering factor s decreases, however, with the addition of more silicon alkoxide to the CERAMER which indicates the characteristic length has increased. The relative interdomain spacings for this series are listed in Table 4-6 along with the relative weight fraction of TEOS and mole fraction of silica in the form $\text{SiO}_{3/2}$ which is calculated with the assumption that the TEOS and silane endgroups of the PTMO oligomers will undergo complete hydrolysis and condensation.

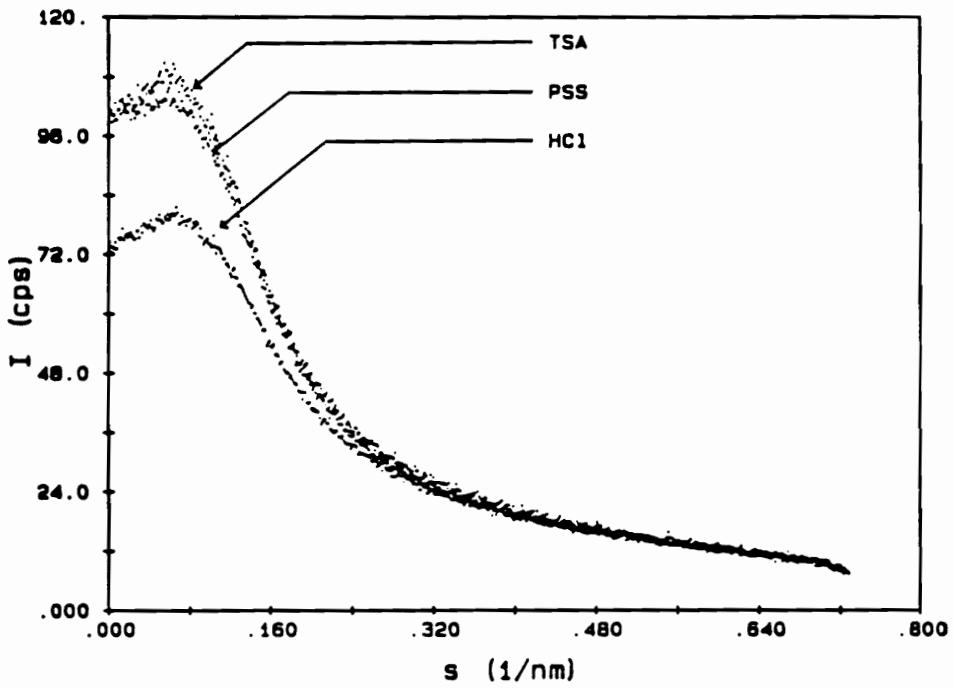


Figure 4-18 Effect of catalyst type on SAXS behavior: TEOS(50)-PTMO(2K)-100-0.014 ACID

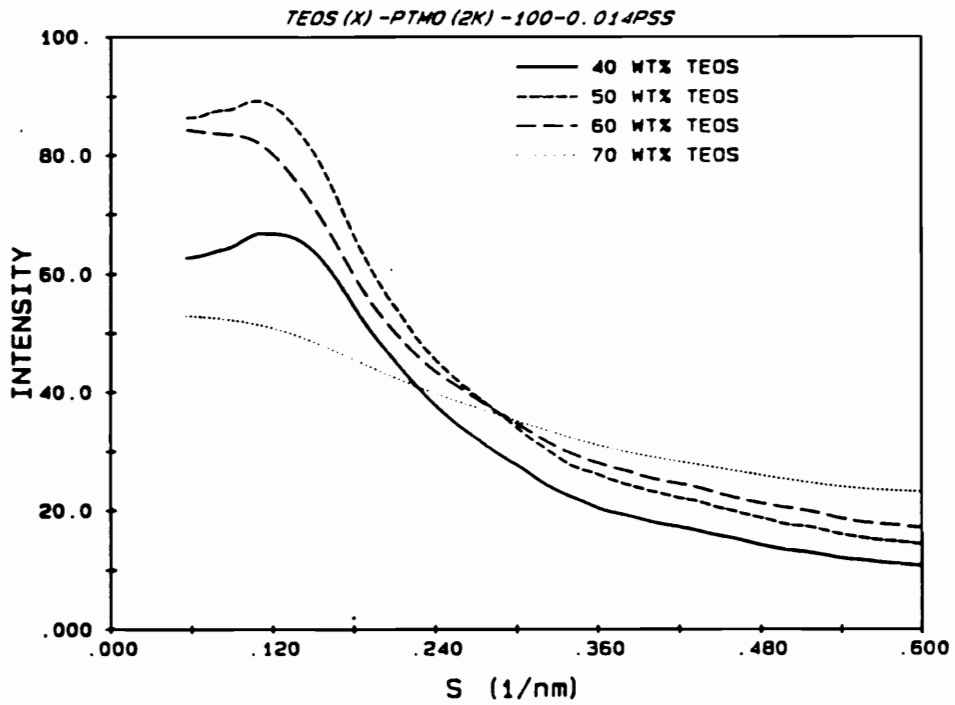


Figure 4-19 SAXS behavior as a function of TEOS level:TEOS(X)-PTMO(2K)-100-0.014 PSS

Table 4-6 SAXS characteristic lengths as a function of TEOS weight fraction:TEOS(X)-PTMO(2K)-100-0.014 PSS

TEOS(X)-PTMO(2K)-100-0.014 PSS		
TEOS (wt.%)	SiO _{3/2} (wt.%)	d _{SAXS} (nm)
0	0	6.4
40	22.8	8.5
50	29.3	9.2
60	37.3	11.0
70	47.2	11.4

An explanation of this SAXS behavior in terms of the morphology that generates the profiles in Figs. 4-18 and 4-19, is facilitated by a more detailed examination of certain aspects of the theory of SAXS. The reader will recall that the small angle x-ray scattering intensity is directly proportional to the mean square electron-density fluctuation of the scattering volume. This relationship, which was derived by Debye and Bueche [63] for a system with spherical symmetry, is given by Equation 4-1:

$$I(s) = 4\pi i_e \langle \rho^2 \rangle V \int_0^{\infty} \gamma(r) \frac{\sin(2\pi sr)}{(2\pi sr)} r^2 dr \quad [4-1]$$

where $\langle \rho^2 \rangle$ represents the mean square electron density fluctuation, V is the illuminated volume, $\gamma(r)$ is a probability density function which is a measure of the inhomogeneity in the electron density, and s is the angular vector previously described. The term i_e is the Thomson scattering coefficient and r is a length scale. The angular intensity of the scattered irradiation varies with the mean square electron density fluctuation, the scattering volume, and is a function of the integral in Equation 4-1. The mean square electron density fluctuation for a sharp two phase system is related to the product of the volume fraction for each phase and the square of the difference in electron densities between the two phases. As a probability function, $\gamma(r)$ represents the probability that a rod of a given length will have both

its ends in phases (PTMO chains define one phase and the silicate structure defines the second phase) with the same electron densities. This function defines the correlation length, which, in this thesis is estimated by the reciprocal of the angular vector s at the maximum peak position in the scattering profile. The CERAMERs whose SAXS profiles are illustrated in Figure 4-19 are assumed to be represented by a two phase system with spherical symmetry. The increase in the d-spacing with increasing levels of TEOS added is believed to be related to an increase in the size of the inorganic phase. The rise in the maximum scattered intensity corresponds to an increase in the difference between the average electron densities of the two phases. Thus, the rise in the maximum scattering intensity with increasing levels of TEOS, suggests that the inorganic phase density is increasing. It could also suggest that there is less mixing between the two phases. However, this seems unlikely in light of the dynamic mechanical behavior described earlier. It is believed that higher intensity of the SAXS profile of the PSS catalyzed CERAMER compared to the equivalent composition catalyzed with HCl, along with the mechanical properties of both materials, demonstrates that the PSS catalyzed CERAMER is more highly cross-linked, i.e. more highly condensed.

The reason for a decrease in the scattering intensity at low s values and an increase at higher s values as the TEOS level was increased from 50% to 60% and then 60% to 70% indicates that a structural change occurred. In the CERAMERs the two phases are most likely defined by the environments that would generate the

TYPE 1 and TYPE 2 restrictions previously described by Huang et. al. [24] which were correlated with the mechanical properties of the PSS catalyzed CERAMERS in this chapter. A gradual change in the amount of mixing between the silicate structure and the PTMO phase (as reflected in the rising intensity at high values of s , i.e. the tail region of Fig. 4-19) is one possible explanation for the change in the overall SAXS profiles. The effect of extensive mixing would be a reduction of the electron density in the inorganic phase and a corresponding increase in the PTMO regimes. The result would be a decrease in the mean square electron density fluctuation. In terms of the scattering profile, the maxima would decrease such that the overall profile would become relatively flat.

The morphological model (Fig. 4-20) developed by Huang et al. [18,19,24] provides an illustration which is useful in understanding the SAXS behavior of these CERAMERS. The PTMO oligomers are represented as lines and the inorganic rich structures are denoted by cross-hatching in Figure 4-20. The correlation distance, expressed as the reciprocal of the value of s where the intensity displays a maximum, is depicted as the spacing between the inorganic phases made up largely of the silicate structure (assuming TYPE 1 environments predominate). The SAXS behavior clearly supports the morphology defined by this model in terms of the behavior of the d-spacing. The apparent structural change that occurs at the higher levels of TEOS, could be depicted as a shift in the relative volume fractions of PTMO and the silicate structure. That is, at some point, the inorganic phase would

become the dominant volume fraction which in conjunction with mixing, would reduce the overall maxima in the scattering profile. This morphological model also helps to explain the broad nature of both the loss dispersion behavior of the dynamic mechanical studies. The influence of varying the volume fraction of the silicate phase has been discussed and visually one can relate the observed changes in the dynamic mechanical behavior with the model i.e., increase the silicate phase and the modulus will increase due the higher glass content.

4.2.3.3 Effect of TEOS to Water Ratio

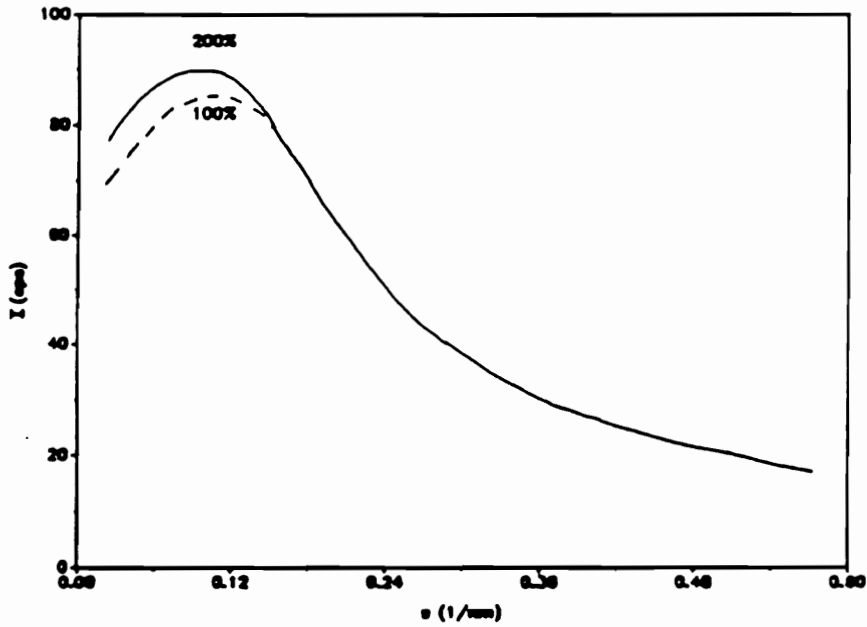
The effect of the TEOS to water ratio was to increase the modulus in these systems with little change and in some cases a decrease in the stress at break. The morphological model just described predicts that the SAXS intensity should increase if the silicate structure forms more bonds by condensation reactions and eliminates the solvent by products. The SAXS profiles in Fig. 4-21 were generated by the CERAMER compositions TEOS(50)-PTMO(2K)-X-0.014 PSS where X was either 100 or 200 mole percent and a third formulation TEOS(50)-PTMO(2K)-50-0.007 PSS. The higher the amount of water provided to the system at the beginning of the reaction the greater the maximum scattering intensity (The effect of TEOS:Acid ratio will be discussed in Section 4.2.3.6). The profiles in Fig. 4-21 most likely reflect an increased extent of condensation in the silicate phase with higher levels of water

added. There was also a slight shift in the maximum intensity of the profile to a smaller value of s as the water level was increased. The interdomain spacing would increase if the PTMO chains were extended somewhat by the densification and concomitant shrinkage associated with a higher extent of condensation in the silicate structures.

4.2.3.4 Effect of Oligomer Molecular Weight

Another variable one can evaluate to test the model in terms of the scattering behavior is the molecular weight of the oligomer separating the silicate regions. The expectation is that as the molecular weight of the oligomer is decreased the spacing between these regions would decrease. This should shift the maximum in the scattering profile to a higher s value if the dimensions represent an interdomain spacing, i.e. correlated to the molecular weight of the PTMO oligomer. A corresponding decrease in the intensity would also be expected to occur since the volume fraction of the PTMO will decrease at a given level of TEOS as the molecular weight of the PTMO is decreased. This is clearly demonstrated in Figure 4-21, which is a comparison of the SAXS behavior for three CERAMERs catalyzed by PSS using silane end capped PTMO oligomers of 650 g/mol, 1000 g/mol and 2000 g/mol. All three were formulated with 50% TEOS, 100% water and 0.014 equivalents of PSS. The maxima of the scattering profile is shifted to a higher s value

a) TEOS(50)-PTMO(2K)-X-0.014 PSS



b) TEOS(50)-PTMO(2K)-X-0.007 PSS

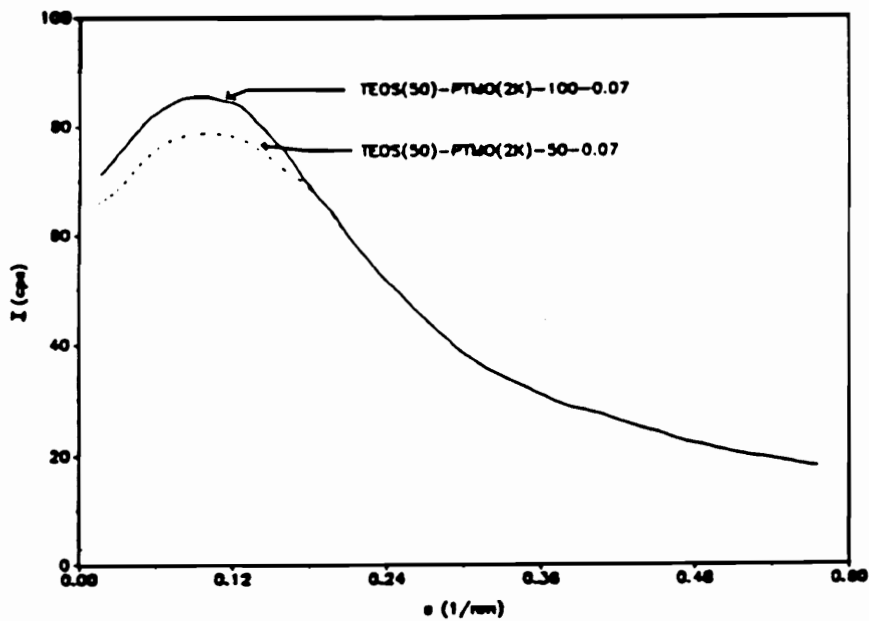


Figure 4-20 SAXS behavior as a function of TEOS:Water ratio.

with decreasing molecular weight of the oligomer as predicted. As noted, the maxima for the 650 g/mol oligomer is very broad but a maximum value still exists. It is also evident that the intensity is higher at larger s values for the CERAMER based upon the 650 g/mol PTMO oligomer compared with the CERAMERs made with 1000 g/mol and 2000 g/mol, which indicates more mixing. This trend also follows those observed for the HCl catalyzed materials and demonstrates the similarity in morphologies for these CERAMERs based upon PTMO and TEOS [18,22].

The morphological model (Fig. 2-3) described previously for CERAMERs based upon TEOS/PTMO and applied to the other CERAMER hybrid materials developed in this laboratory [24,28,29,30] predicted that the interdomain spacing, given by d , should increase with the molecular weight as shown in Fig. 4-21. There are a number of ways one could evaluate the relationship between the SAXS d -spacings and the molecular weight of the PTMO oligomers for these materials. Of course, it is important to recognize the shortcomings of any attempt to relate the d -spacings from the SAXS profiles provided in this thesis directly with the dimensions of the PTMO chains. The d -spacing dimensions are correlated to an average distance between two phases of the same density and as such include the dimensions of the silicate phase as well as the PTMO chains. In addition to this, the effect of the slit configuration on the dimensions has already been stated, i.e. the SAXS profiles presented throughout this thesis represent smeared data which means the

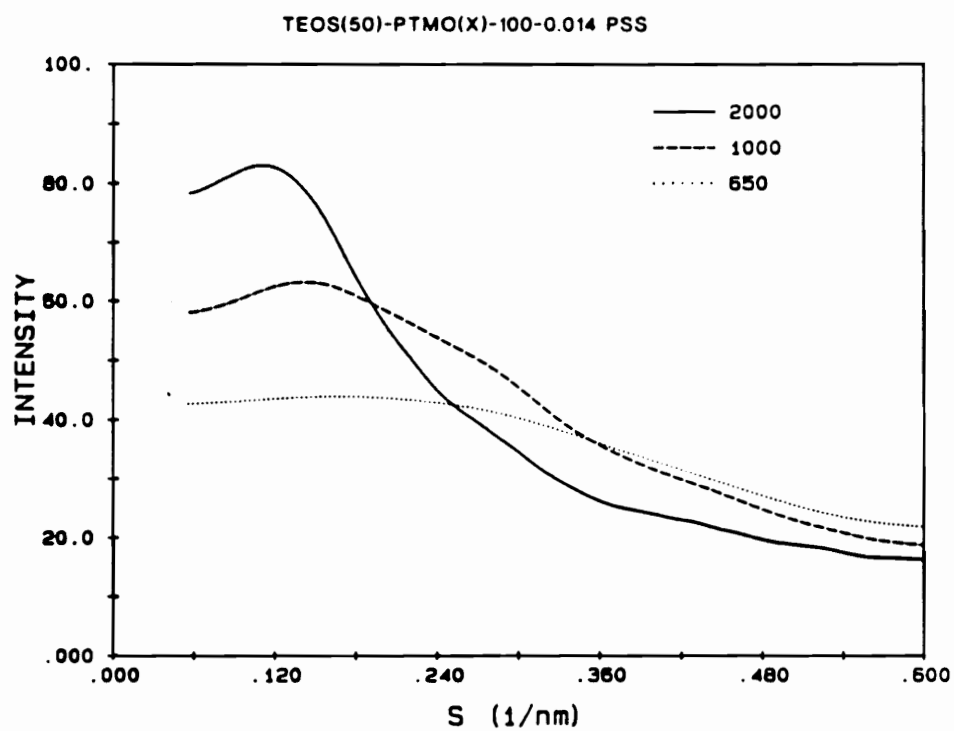


Figure 4-21 SAXS behavior as a function of PTMO molecular weight:TEOS(50)-PTMO(X)-100-0.014 PSS

d_{SAXS} values are typically larger than values obtained using a pin-hole collimation. However, even with these restrictions and limitations an attempt was made to at least evaluate the nature of the relationship between the SAXS d-spacings and the predicted dimensions of the PTMO chains. The method that was selected for this is based upon the root mean square end-to-end distance of a Gaussian chain which can be expressed as follows:

$$rms = \langle r^2 \rangle^{\frac{1}{2}} = \sqrt{c_{\infty} n l^2} \quad [4-2]$$

where n is the number of bonds of the chain, l is the length of the bond and c_{∞} is the characteristic ratio. The relationship given by Eqn. 4-2 assumes that the number of repeat units in the chain is large enough that the chain conformations can be described by Gaussian statistics. This is a further limitation in consideration of the low molecular weight of the PTMO oligomers which may not display Gaussian behavior. The fact that the chain ends are not free within the context of the CERAMER network would be expected to cause a perturbation of the chain dimensions. This is not addressed by Equation 4-2. Another method of obtaining the rms of the PTMO chains uses the steric factor, σ (which is 1.64 for PTMO in a theta solvent, ethylacetate/n-hexane (1:3.4) [91]. This factor is related to the characteristic ratio by the following relationship:

$$c_{\theta} = \frac{(1 + \overline{\cos\theta})}{(1 - \overline{\cos\theta})} \sigma^2 \quad [4-3]$$

where θ is the bond angle and the other terms are as previously described. The steric factor was selected for calculating the rms of the PTMO oligomers. The d spacings calculated from the SAXS profiles of the scattering behavior of four CERAMERs of the composition TEOS(0)-PTMO(X)-100-0.014 PSS, where X was either 650 g/mol, 1000 g/mol, 2000 g/mol, or 2900 g/mol; are compiled in Table 4-7. Two values for the theoretical (rms) of the PTMO oligomer (calculated using Eqn. 4-3 and $\sigma = 1.64$) are included in Table 4-7. The two separate rms values given are: rms_0 which was calculated using the hydroxyl terminated oligomers molecular weight; and second, rms_E which was calculated with the mass contribution of the isocyanatopropyltriethoxysilane end group included. Examination of the tabulated values (Table 4-7) reveals the d_{SAXS} values are typically larger than the calculated values of the rms as one would predict based upon the factors listed above which contribute to the magnitude of the d_{SAXS} values.

The d_{SAXS} values can be shown to scale with the square root of the molecular weight as the rms does, except for the CERAMER based upon the 2900 g/mol PTMO oligomer. The numbers listed in Table 4-8, clearly illustrate the effect of relatively small changes in the magnitude of the steric factor on the rms. A plot of the molecular weight of the triethoxysilane end capped PTMO oligomers versus the characteristic dimensions of the chains as measured from SAXS data and as

Table 4-7 Characteristic dimensions (Calculated and Measured) of PTMO Oligomers

OLIGOMER (g/mol)	rms_o (nm)	rms_E (nm)	d_{SAXS} (nm)	factor (d/rms_E)
650	2.4	2.75	3.87	1.41
1000	2.98	3.26	4.73	1.45
2000	4.21	4.42	6.39	1.45
2900	5.08	5.26	6.17	1.17

Steric factor = 1.64 [91]

d_{SAXS} : determined from smeared $I(s)$

Table 4-8 PTMO dimensions as a function of the steric factor.

OLIGOMER (g/mol)	STERIC FACTOR					
	1.64	1.85	2.05	2.25	2.45	2.31 [‡]
	rms _E (nm)					d _{SAXS}
650	2.75 [†]	3.10	3.44	3.77	4.11	3.87
1000	3.26	3.71	4.15	4.61	4.85	4.73
2000	4.42	5.03	5.62	6.25	6.57	6.39
2900	5.26	5.99	6.69	7.44	7.82	6.17

[†] Represents theta condition for high mol. wt. PTMO [91]

[‡] Factor calculated from d_{SAXS} spacing

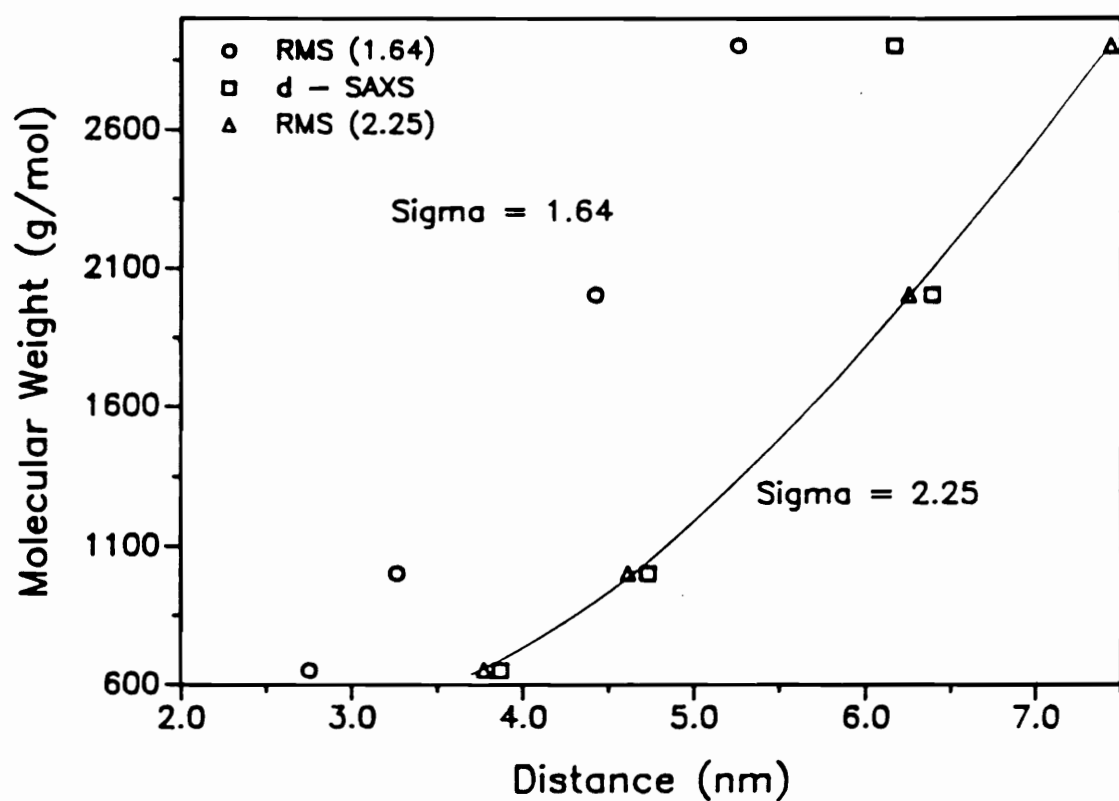


Figure 4-22 Comparison of the calculated rms_E for CERAMERS as a function of PTMO molecular weight versus the d_{SAXS} characteristic length.

calculated (Table 4-8) illustrates the effect of increasing the steric factor from 1.64 to 2.25 (Fig. 4-22). The trends are quite clear from the data points included in the plot. The solid line in Fig. 4-22 represents the function given by Eqn. 4-3. This is a rather crude analysis, yet, the numbers do indicate that there is a relationship between the SAXS spacings and the molecular weight which is similar to that between the rms of a Gaussian chain and the square root of the molecular weight of the PTMO oligomers.

4.2.3.5 Effect of Aging

The SAXS profiles of the HCl catalyzed TEOS/PTMO CERAMERS tended to increase in intensity as a function of time at ambient conditions [24]. However, the PSS catalyzed CERAMERS showed little to no change with time. This behavior suggested that the PSS catalyzed CERAMERS were reacted to a higher extent, i.e. conversion of the alkoxy groups to siloxane bonds. The scattered intensity of the HCl catalyzed CERAMERS tended to increase with aging [26] indicating that the electron density of the silicate phase was raised by elimination of the alkoxy group and formation of a Si-O-Si bond.

4.2.3.6 Effect of TEOS:Acid Ratio

Figure 4-20 illustrated the effect of varying the TEOS:water ratio for two different TEOS:acid ratios 1:0.06 and 1:0.03 identified by the nomenclature as 0.014 PSS and 0.007 PSS, respectively. There was no significant difference in the overall scattering profile or the maximum scattered intensity between the SAXS behavior of the two TEOS:acid ratios given in Fig. 4-20. Figure 4-23 illustrates the effect of four different TEOS:acid ratios. The differences are quite small overall between the maximum scattered intensity from CERAMER compositions TEOS(50)-PTMO(2K)-100-X, where X is 0.014, 0.007, or 0.004, but a general trend of decreasing intensities was observed.

4.2.4 Scanning Electron Microscopy

The differences between the PSS catalyzed and HCl catalyzed CERAMERs have not been on a scale that normally one would expect to determine by examination with scanning electron microscopy (SEM), i.e. ca. from 0.1 μm to 1000 μm . However, it was quite astonishing to note that there were significant differences between the microstructure of the CERAMERs prepared with HCl and PSS. Figure 4-24 contains four micrographs of the two different materials at two different magnifications. The lower magnification (approximately 200x) reveals a smooth

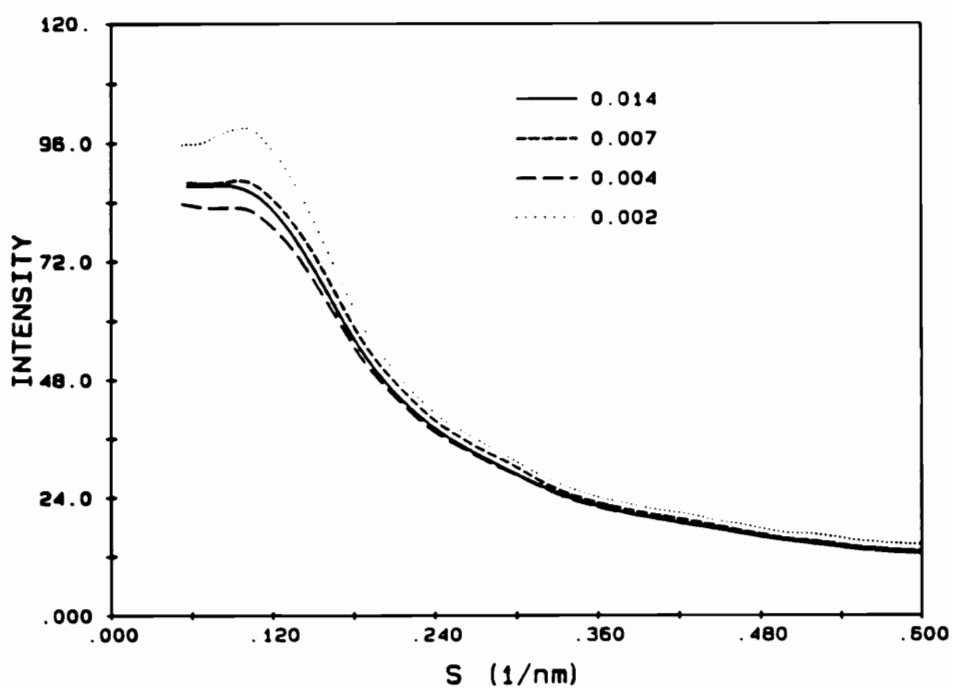


Figure 4-23 SAXS behavior as a function of TEOS to Acid ratio: TEOS(50)-PTMO(2K)-100-X.

surface for the PSS catalyzed CERAMER and a rather irregular globule like surface of the HCl catalyzed CERAMER. Both micrographs are of fractured surfaces (liq. N₂) of the composition TEOS(50)-PTMO(2K)-100-0.014 X where the acid used was identified on the micrograph. The surfaces appear to have failed in a plastic manner as the stress lines would indicate. The PSS catalyzed sample have rather large bubbles dispersed through the bulk of the sample which were not present prior to examination in the SEM. The higher magnifications of the two samples revealed a rather unusual surface for the PSS catalyzed hybrid material. Note that the small domes on the surface are not solid. Indeed, constant exposure of the surface to the beam, resulted in the destruction of the bubbles and generation of new ones. The surface of the HCl catalyzed CERAMER did not exhibit the same behavior upon exposure to the beam. The samples were approximately 10 days old when evaluated by SEM. The PSS samples were subjected to a vacuum for 48 hours in an attempt to eliminate the outgassing observed in the SEM. The scanning electron micrograph of the vacuum treated sample compared to the gel not treated is given as Figure 4-25. There was a reduction of the amount of material outgassing, however, it was not eliminated totally. The remnants of the bubbles are easily identified in the micrograph by the "striated" appearance. The instability of the PSS catalyzed CERAMER in the electron beam was attributed to the PSS catalyst, since the HCl catalyzed hybrids appeared to be quite stable. There appeared to be no significant difference as a function of TEOS, acid, water, or molecular weight in the PSS

catalyzed materials. The lowest level of acid examined was 1/8 that of the composition whose micrograph was given as Fig. 4-24.

4.2.5 Thermogravimetric Behavior

4.2.5.1 Effect of Polymeric Acid Catalyst

The main distinction between CERAMERs catalyzed with PSS and HCl appears to be a small but significant difference in the extent of reaction. Yet, the difference was reproducible and significant with respect to measured properties. It is reasonable that a higher extent of condensation should result in a higher residue on ignition, i.e. thermogravimetric analysis to 800°C, for the PSS catalyzed materials which corresponds to lower weight loss due to ethanol or water by-products. As stated earlier, samples that were extracted and dried prior to swelling experiments demonstrated significantly more swelling for the HCl catalyzed CERAMER than the PSS catalyzed CERAMER, which supports other data indicating a higher conversion for the PSS CERAMERs. There is, as illustrated in Fig. 4-26, a slightly lower weight loss for the PSS CERAMER compared to the HCl CERAMER as measured between 30°C and 800°C. The difference of 1 to 2% is reproducible. However, the initial weight loss of nearly 16% in the PSS CERAMER between 100°C and 160°C does not occur with the HCl system.

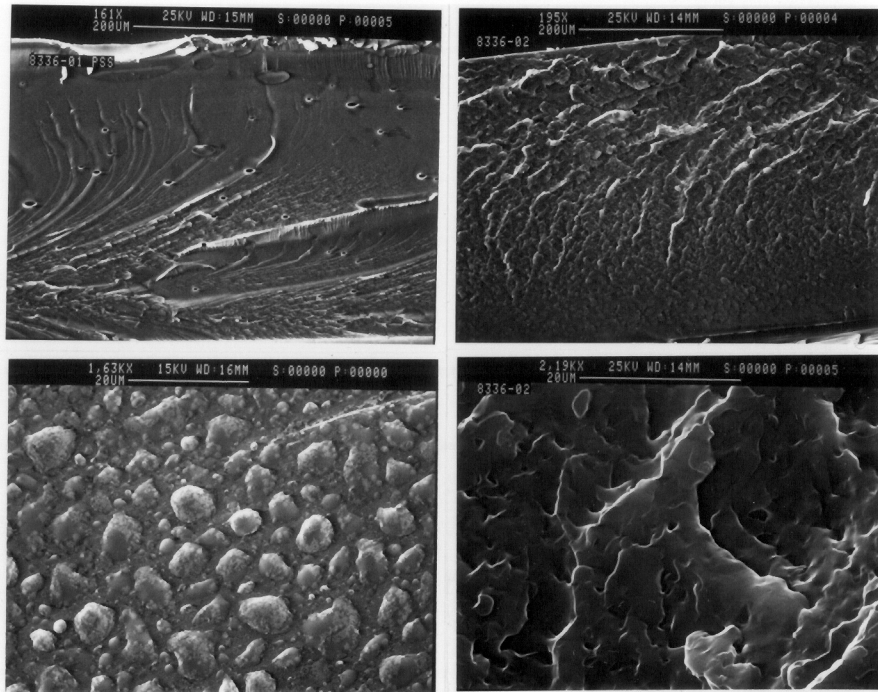


Figure 4-24. Scanning Electron Micrographs of PSS and HCl CERAMERs: TEOS(50)-PTMO(2K)-100-0.014 X

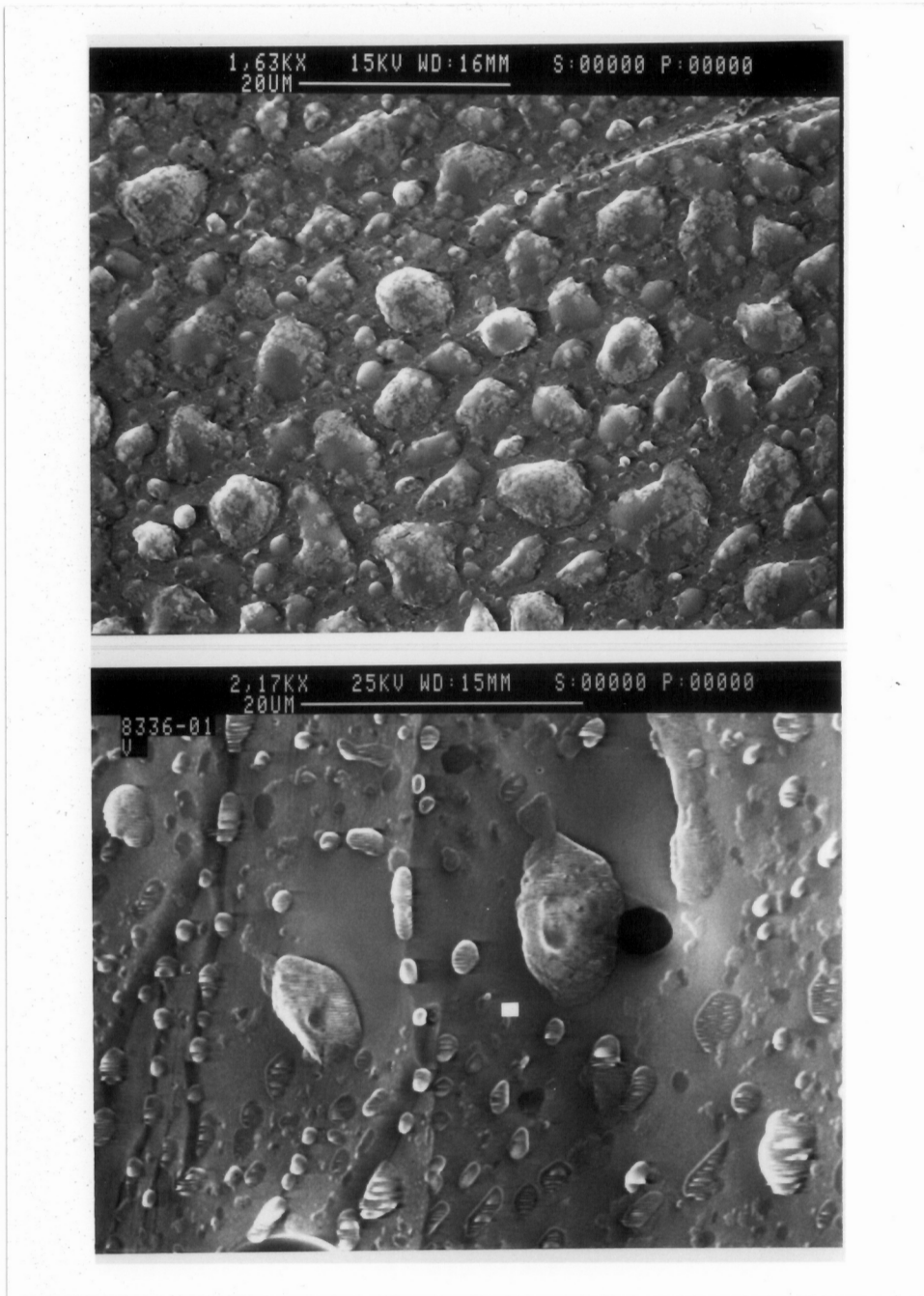


Figure 4-25 Effect of Vacuum Drying PSS catalyzed CERAMER on morphology:
TEOS(50)-PTMO(2K)-100-0.014 PSS

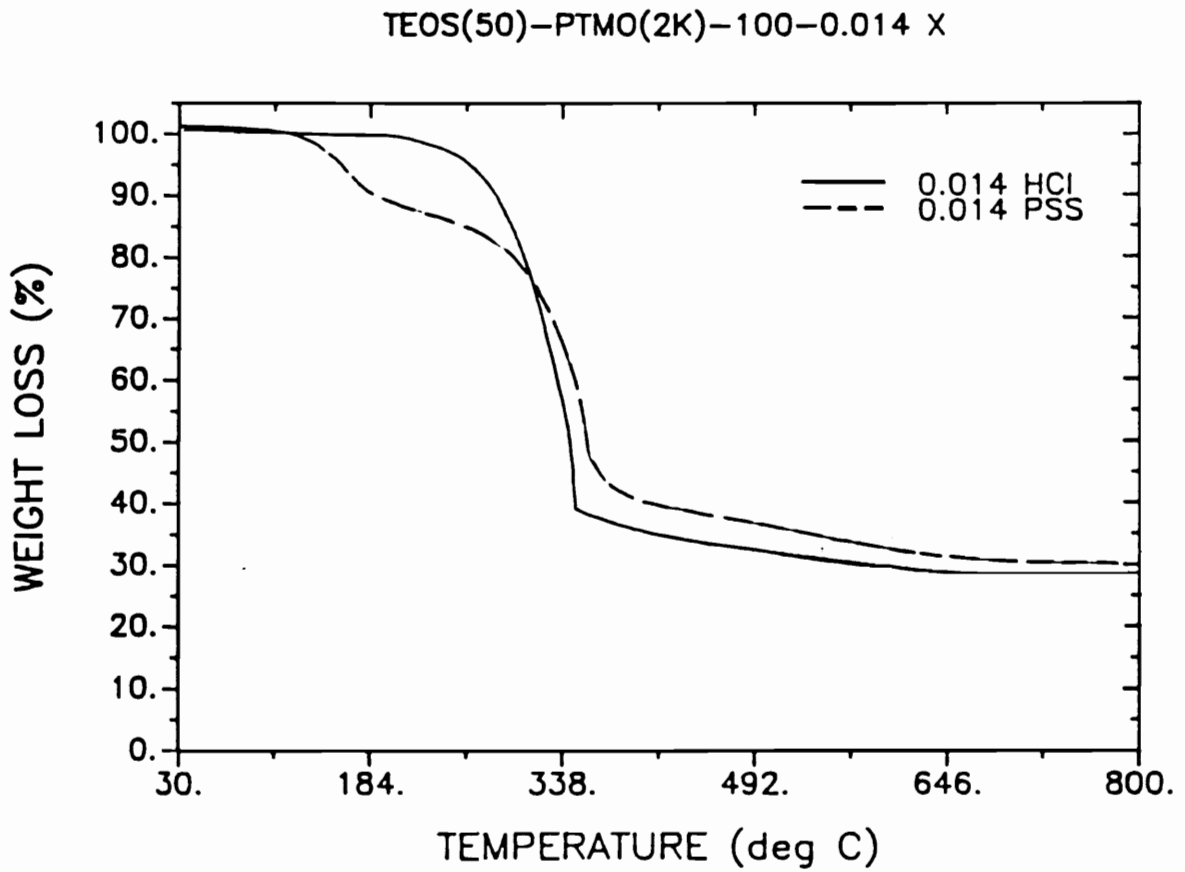
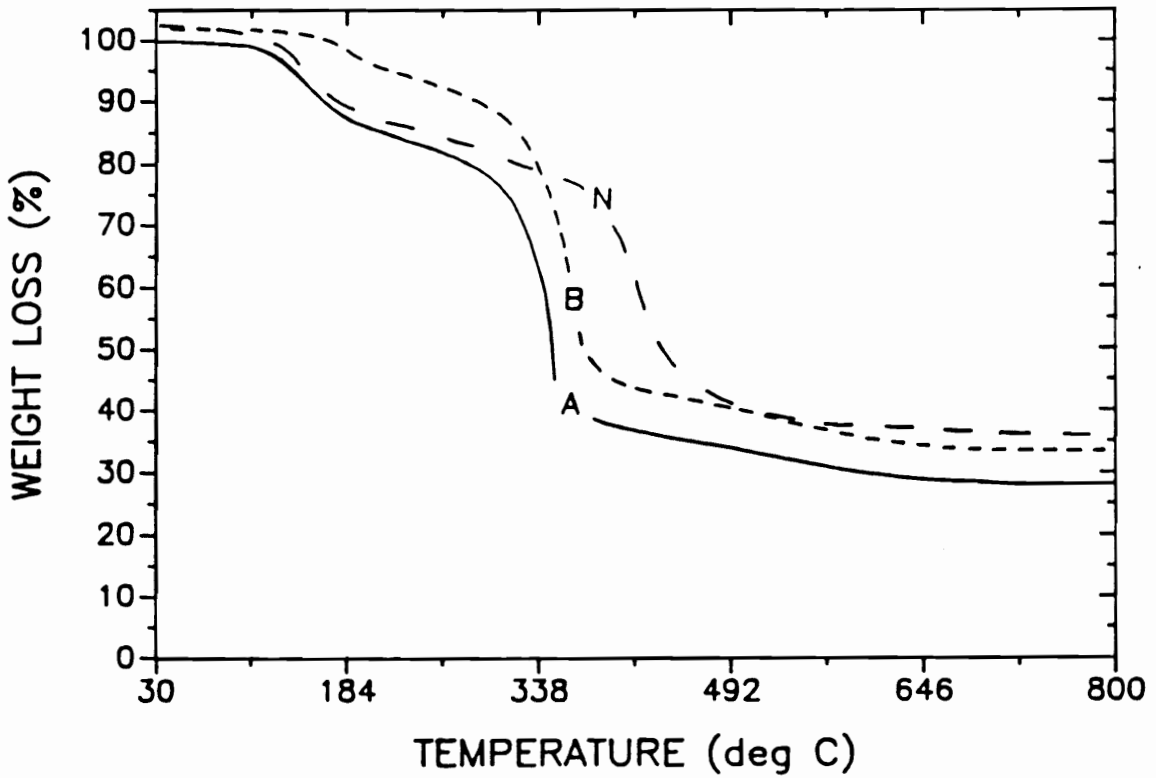


Figure 4-26 Thermogravimetric behavior of CERAMERS as a function of catalyst type: TEOS(50)-PTMO(2K)-100-0.014 X

TEOS(50)-PTMO(2K)-100-0.014 PSS



A - Air
B - Air, sample pretreated at 60°C, 3hrs
N - Nitrogen

Figure 4-27 Thermogravimetric behavior of PSS catalyzed CERAMER as a function of purge gas.

4.2.5.2 Effect of Purge Gas

It was considered likely that the instability of the PSS catalyzed CERAMERs in the SEM may be related to the weight loss detected at temperatures below ca. 160°C (Fig. 4-26). A difference in the degradation mechanism was considered highly probable based upon the instability of the PSS catalyzed CERAMERs under the electron beam. The only difference between the PSS catalyzed and the HCl catalyzed CERAMERs was the catalyst itself. Thus, the weight loss of the hybrid composition TEOS(50)-PTMO(2K)-100-0.014 PSS was measured as a function of two different purge gases, air and pre-purified nitrogen. Curves A and N, representing air and nitrogen as purge gases, respectively in Figure 4-27 indicate that the reaction rates and/or mechanism for the thermal degradation process up to ca. 200°C are not dependent upon the atmosphere [92]. There was a shift in the onset of the second stage of degradation at ca. 300°C to a higher temperature, ca. 380°C under a N₂ gas purge. The second possibility, residual solvent, was considered unlikely since the boiling points of THF and IPA are 60°C and 74°C, respectively. Thus, any loss due to the solvents should have occurred at temperatures lower than 100°C assuming of course that the diffusion rates were rapid compared to the heating rate. Residual solvents also would be expected in the HCl catalyzed materials at the same concentration since both were aged the same amount (approximately 14 days). A

third sample from the same PSS CERAMER was treated isothermally at 60°C for 120 minutes prior to the TGA analysis (Curve B, Fig. 4-27) to eliminate any possible entrapped or adsorbed solvents from the network. The temperature selected represents the upper end of the broad loss dispersion behavior (Fig. 4-1). Thus, the network chains should have increased mobility to enhance diffusion of solvent molecules through the pore structure. The weight loss of only 7% for the temperature range of 110°C to 160°C after the isothermal treatment indicated some of the observed loss was due to entrapped solvents. However the evidence was not conclusive and did not explain all of the weight loss observed for the PSS CERAMER between 110° and 160°C.

4.2.5.3 Effect of TEOS to Acid Ratio

The effect of the level of PSS acid catalyst in the CERAMER gels was evaluated by TGA with the expectation that the low temperature weight losses measured would decrease if they were directly attributable to the PSS acid. The results in Figure 4-28 appear to confirm the weight loss below 200°C in the PSS CERAMER gels promoted by to the PSS catalyst. The lowest acid to alkoxy ratio of 0.002 had no detectable weight loss below 200°C such that the overall profile closely resembled that of the HCl catalyzed CERAMER.

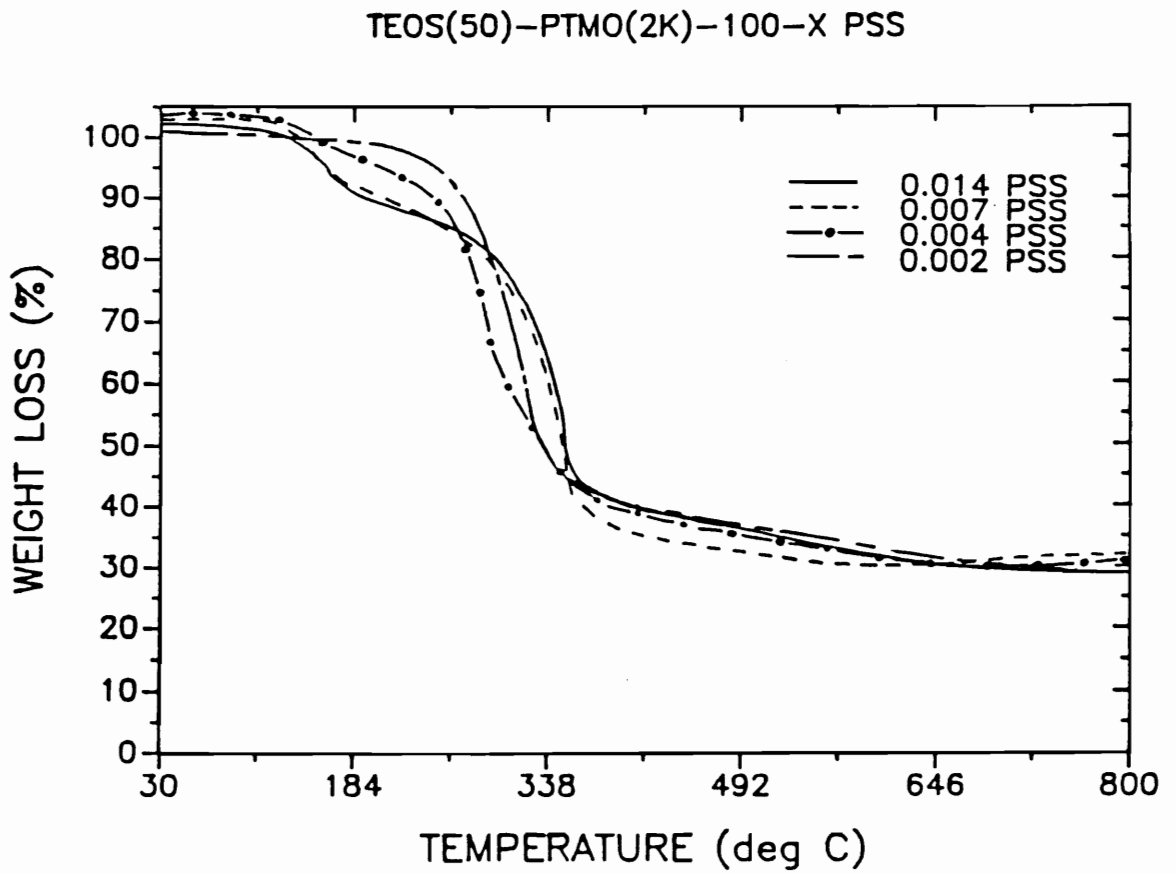


Figure 4-28 Thermogravimetric behavior of CERAMER as a function of PSS to TEOS ratio: TEOS(50)-PTMO(2K)-100-X PSS.

The final weight loss of all samples in Fig. 4-26, Fig. 4-27 and Fig. 4-28 occurred between 200°C and 500°C which was tentatively associated with oxidative degradation of the alkyl substituents of PTMO. The fact that the onset of this weight loss between 200°C and 500°C is delayed by the non-oxidative nitrogen purge gas and the relative weight fractions of the components support this claim.

4.2.6 TGA/FTIR Analysis

The results thus far have indicated that the PSS catalyzed CERAMER formulations consistently reached a higher extent of conversion of the alkoxides to oxide bonds, i.e. silicates. The DMA behavior, mechanical behavior, SAXS intensities and the swelling studies offer strong support for the existence of a lower quantity of unreacted alkoxide and/or alcohols in the PSS catalyzed gels. A method that was employed to study this in more depth was TGA/FTIR (Thermogravimetric analysis interfaced with an FT infrared spectrometer). The method offers one to analyze the gas phase effluent from a TGA by gas phase FTIR. The method is in no means truly quantitative, but qualitatively one can determine at least the presence of species for which vibrational modes are allowed in the infrared region. The idea associated with this pursuit was that if the gel compositions were relatively equivalent, i.e. PSS versus HCl catalyzed, with the only differences associated with the extent of conversion, analysis of the gaseous products of the decomposition of a

gel should contain either water or ethanol if there were residual silanol and/or ethoxy groups bonded to the silicate structure. This of course assumes that the release of these products would not differ significantly between the two gels. The rate of release may differ slightly if the differences in cross-link density were significant enough to reduce the diffusion of the species, however, this was not considered likely. The two samples analyzed were of the composition TEOS(50)-PTMO(2K)-100-0.014 which was catalyzed by either HCl or PSS. The sample sizes were equivalent in mass and surface area within ca. 10% to reduce any differences attributable to either diffusion of the species of interest out of the network or the purge gas.

The illustrations in Figures 4-29 and 4-30 represent the profiles for total evolved gas and the weight remaining as a function of the experiment temperature for the PSS catalyzed and the HCl catalyzed samples, respectively. The method of analysis involves regular sampling of the effluent from the TGA by the FTIR in a vapor phase cell and storage of the spectra. The data analysis is accomplished by comparison of the FTIR spectra at specified times against a library of known materials. A spectral matching routine determines the "best fit" for the unknown and plots its spectra along with those of the next three closest fits. This method allows one to compare the products of degradation and compare them for the two different CERAMERs for the same temperatures. The first thing that one notices in the illustrations of Fig. 4-29 and Fig. 4-30 is the dramatic difference in the profile of the

total evolved gas for the PSS catalyzed CERAMER and the HCl catalyzed CERAMER. There is a rather significant effluent derived from the PSS catalyzed gel at a temperature of ca. 200°C compared to a very insignificant amount for the HCl sample until ca. 330°C. The FTIR spectral match indicated that the early evolved gas from the decomposition of the PSS catalyzed gel was mostly THF which is believed to be the by-product of the decomposition of PTMO [93]. Indeed, throughout the entire decomposition of the CERAMER TEOS(50)-PTMO(2K)-100-0.014 where the acid used was either PSS or HCl, the major constituent of the effluent appears to have been THF. However, very low levels of both CO₂ and methanol were also detected for both CERAMERs.

The second major difference between the PSS catalyzed sample and the HCl sample was the detection of ethanol and water. The effluent from the PSS decomposition reaction did not contain sufficient quantities of ethanol for detection early in the reaction ca. upto 450°C, whereas ethanol was present in sufficient quantities for detection in the effluent of from thermal degradation of the HCl sample. The evolved gas profile versus temperature of both samples, i.e. PSS and HCl catalyzed gels, in Fig. 4-29 and 4-30 illustrates that at a temperature of ca. 280°C both samples outgas. The actual temperature that generates the effluent is most likely somewhat lower since the heating rate of the experiments was 20°C per minute. In any event, the spectra of the evolved gas which was obtained at a time of approximately 11 minutes for samples, PSS catalyzed and HCl catalyzed, are

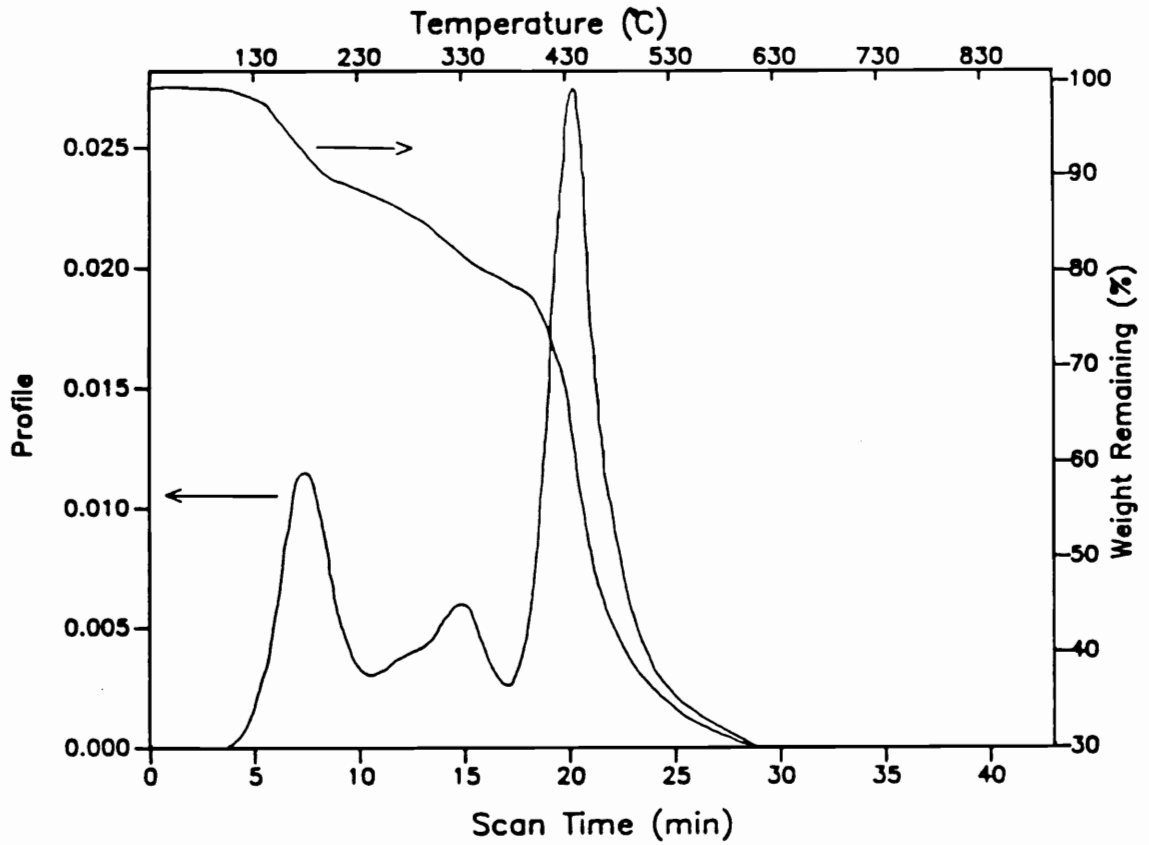


Figure 4-29 Evolved gas and retained weight as a function of temperature. TEOS(50)-PTMO(2K)-100-0.014 PSS.

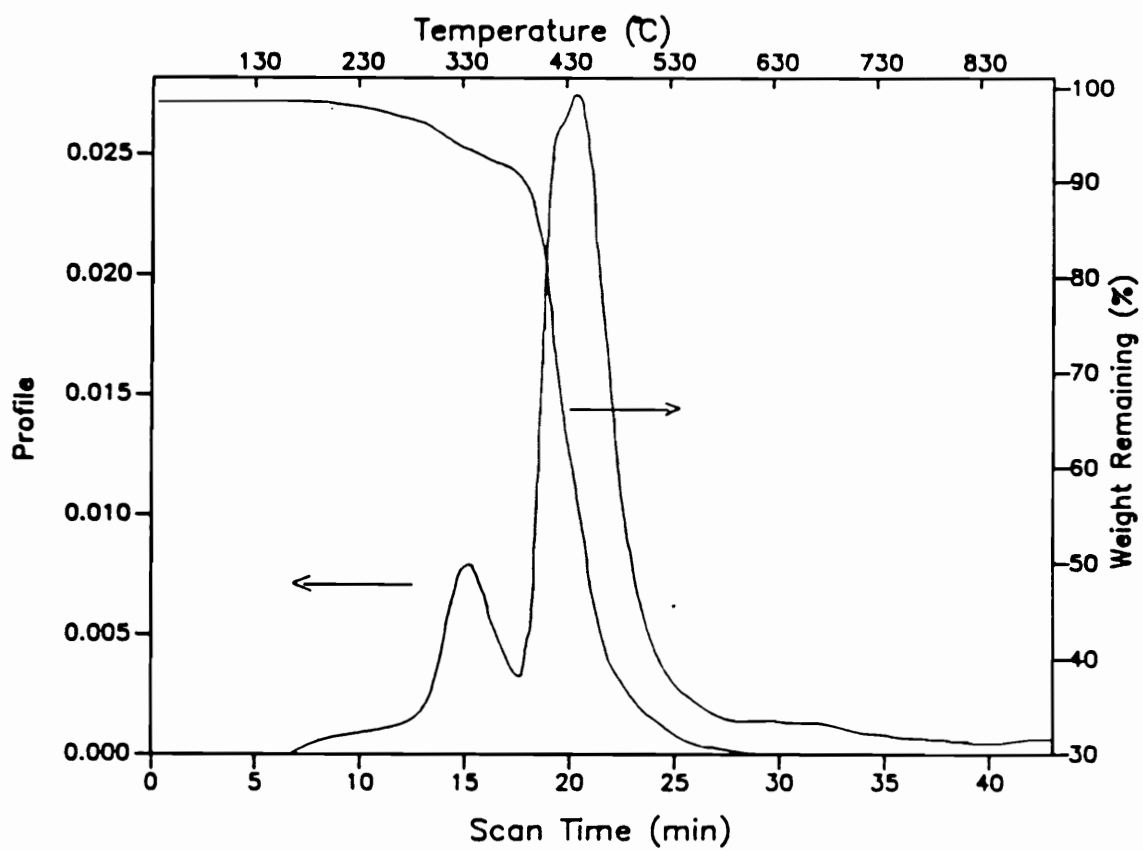


Figure 4-30 Evolved gas and retained weight as a function of temperature. TEOS(50)-PTMO(2K)-100-0.014 HCl.

reproduced for each in Figures 4-31 and Fig. 4-32, respectively. The key differences are the relatively large concentration of CO_2 (ca. 2200cm^{-1}) in the spectra from the evolved gas from the decomposition of the PSS sample (Fig. 4-31) and the large quantity of water (3500 to 4000 cm^{-1} and ca. 1300 to 1600 cm^{-1}) and ethanol (ca. 1300 to 1400 cm^{-1}) present in the spectra in Fig. 4-32. Both spectra reveal a large concentration of THF (ca. 900 cm^{-1} and 1100 cm^{-1}) as stated earlier. The differences observed in these early spectra were typical up to temperatures of ca. 450°C at which time the evolved gases of both samples was mostly CO_2 and THF. Thus, the presence of ethanol and water in the gases generated by the thermal decomposition of the HCl CERAMER of composition TEOS(50)-PTMO(2K)-100-0.014 under a nitrogen atmosphere compared to the undetectable quantities of both in the gas evolved during the decomposition of the PSS CERAMER, strongly supports the other data that the PSS CERAMER of the same composition has a lower percentage of unreacted species.

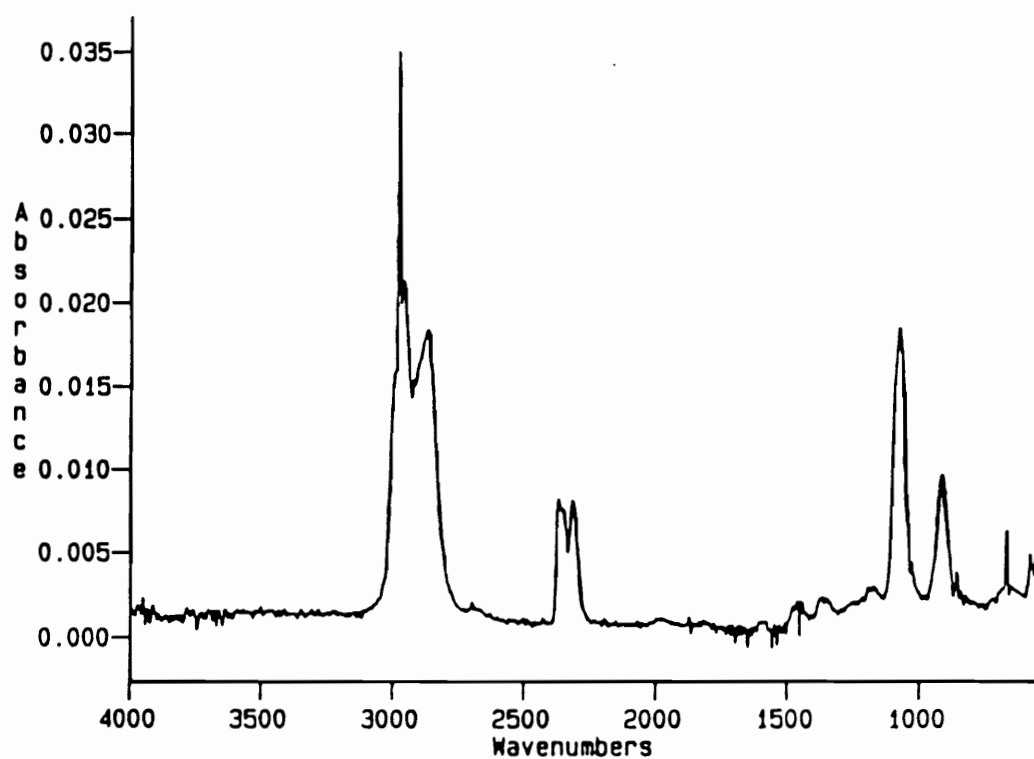


Figure 4-31 FTIR of the evolved gas from the thermal decomposition of TEOS(50)-PTMO(2K)-100-0.014 HCl at the elapsed time of 11.7 min.

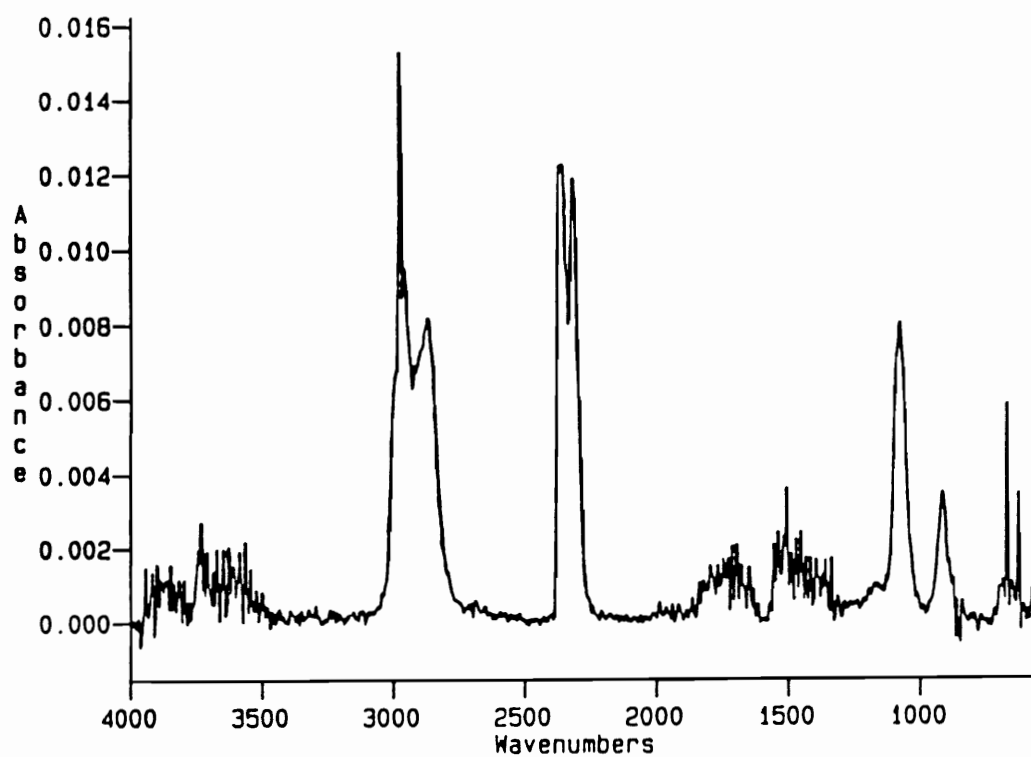


Figure 4-32 FTIR of the evolved gas from the thermal decomposition of TEOS(50)-PTMO(2K)-100-0.014 HCl at the elapsed time of 11.7 min.

4.3 CONCLUSIONS

Poly(styrene sulfonic acid) was shown to be an effective catalyst for the preparation of the novel CERAMERs. The use of the polymeric acid catalyst PSS promotes a higher level of condensation in gels prepared from PTMO/TEOS via a sol gel process. The loss dispersion behavior of these materials, which is quite broad, is attributed to molecular relaxations of PTMO segments constrained by the silicate structure derived from the hydrolysis and condensation reactions of the silicon alkoxides. There are two general classifications for these restrictions on the PTMO segments referred to as TYPE 1 and TYPE 2 which describe endgroup restrictions and segmental restrictions, respectively.

The magnitude of the loss dispersion behavior of a PSS CERAMER was lower than that of gel prepared with HCl as the catalyst. The elastic modulus at ambient conditions increased from 25 to 220 MPa as a function of an increasing level of TEOS from 40 to 70 wt%. The stress at break, also at ambient, (12 MPa) and modulus (56 MPa) were higher for the PSS catalyzed CERAMER compared to the HCl catalyzed material. Overall, slight changes were detected in the ultimate mechanical properties for a comparable degree of reaction using the PSS catalyst. The SAXS behavior was similar for both systems indicating similar morphological features. The d_{SAXS} spacings for CERAMERs of the general composition TEOS(0)-

PTMO(X)-100-0.014 PSS, where X was either 650 g/mol, 1000 g/mol, 2000 g/mol or 2900 g/mol, scaled with the square root of the oligomer molecular weight. The PSS catalyzed hybrid materials were quite unstable under an electron beam compared with equivalent compositions catalyzed with HCl. There was an initial weight loss measured by TGA between ca. 100°C and 200°C for the PSS CERAMER which is not observed for HCl CERAMER of the same composition. However, the overall residue on ignition (to 800°C) is higher for the PSS CERAMER which supports a higher extent of reaction in the PSS CERAMER compared with an HCl CERAMER. The TGA/FTIR data revealed a significant level of water and ethanol in the evolved gases from the decomposition of the HCl catalyzed CERAMER while none was detectable for the equivalent PSS catalyzed CERAMER composition. Thus, one can conclude that the PSS catalyzed gels were further condensed than the HCl catalyzed CERAMERs in view of the supporting data of all the methods described in Chapter 4. Yet, the THF loss is disturbing and unexplained at this time.

In summary, the poly(styrene sulfonic acid) is an effective catalyst for these novel hybrid materials which suggests they may apply equally as well for classical sol gel reactions. Observed changes in the sol viscosity upon addition of these catalysts, indicate a possible method for modification of rheological behavior of the sols.

CHAPTER 5

ALUMINA/ETHYL ACETOACETATE AND TITANIA/ETHYL ACETOACETATE CERAMERS

5.1 INTRODUCTION

The incorporation of metal alkoxides other than those based upon silicon, i.e. tetraethylorthosilicate and tetramethylorthosilicate, in the inorganic/organic hybrid network material, identified as a CERAMER, has been of interest both from an academic perspective and an industrial approach. The structure/property relationships of the CERAMERs are dependent upon the metal alkoxide and the functionalized oligomer and of course the sol-gel process itself [27,28,29,30]. The TEOS type CERAMERs have been studied with PDMS oligomers [16,17,18], PTMO oligomers [19], multi-functional PTMO type oligomers [28] and PEK oligomers [29]. Glaser was the first to report the modification of the TEOS type CERAMERs with the inclusion of titanium tetraisopropoxide and later with other metal alkoxides [27].

The other metal alkoxides Glaser investigated, aluminum tri-sec-butoxide, zirconium (IV) acetylacetonate and zinc acetylacetonate hydrate [29], were combined with TEOS and the functionalized PTMO. The incorporation of aluminum, titanium, and zirconium alkoxides offers the potential for the development of coatings with improved abarasion resistance, moisture absorption, and permeability [1,55,71].

The purpose of this chapter is to describe the general structure-property relationships of a new class of CERAMERs prepared by the total substitution of TEOS in the TEOS/PTMO hybrids with either aluminum ethylacetoacetate (Al/EACAC) or titanium ethylacetoacetate (Ti/EACAC). The methods for producing the EACAC modified CERAMERs were developed by Dr. Bing Wang.

5.2 RESULTS AND DISCUSSION

5.2.1 Dynamic Mechanical Behavior

The dynamic mechanical response of the CERAMER [X]Al/EACAC(67)-PTMO(2K)-33-0, where X was either 1.0, 1.33, or 2.0, is plotted as a function of temperature (Figure 5-1). The storage modulus of the Al/EACAC CERAMER below ca -80°C was approximately 1 GPa which is typical for a polymer below its T_g . However, unlike the response of the PSS catalyzed TEOS/PTMO hybrids (Chapter 4), as well as the other TEOS/PTMO hybrids [30], the storage modulus undergoes a broad gradual decline during the glass transition, which extends from ca. -70°C to nearly 100°C. The storage modulus of the composition [2.0]Al/EACAC(67)-PTMO(2K)-33-0, drops two orders of magnitude from -80°C to 100°C at which point it undergoes a relatively sharp incline. The response of the storage modulus of all three compositions to temperature (Fig. 5-1) was similar overall except for the magnitude of the changes. The storage modulus of the two CERAMERs containing the lower ratios of Al(sec-OBu) i.e. 1.0 and 1.33, exhibited two rather distinct reductions occurring at ca. -80°C and ca. 50°C. The storage modulus of the Al/EACAC/PTMO CERAMERs increased as the ratio of Al(secOBu) to EACAC increased from 0.5:1.0 to 1:1. The increase in storage modulus was attributed to an increase in the average functionality of the system which determines the ability of the

reactants to form a network. The lowest ratio of Al(secOBu) to EACAC, i.e. 0.5:1, will result in a metal complex which has, on the average, only one hydrolyzable group based upon the reaction conditions described in Chapter 3. The broadness of the T_g of the three CERAMER compositions represented in Fig. 5-1 was ascribed to a mixing of the PTMO chains with the inorganic phases much in the same manner as that observed in the TEOS/PTMO inorganic/organic hybrid materials.

The loss dispersions of the Al/EACAC/PTMO gels (Fig. 5-1) provide additional information regarding the nature of their molecular relaxations. This can reveal some indication of their morphology based upon the structure-property relationships developed for the TEOS/PTMO CERAMERs. The first aspect that one encounters with the composition [1.0]Al/EACAC(67)-PTMO(2K)-33 is the rapidly increasing magnitude of the loss dispersions from ca. -80°C to ca. 80°C which was unlike any of the other compositions evaluated. The reader is reminded again that the $\tan \delta$ response increases as a function of increasing loss due to molecular relaxations within the structure. Thus, the extremely large loss dispersions along with the rapidly decreasing storage modulus of the gel with the lowest ratio of Al(OBu) to EACAC were ascribed to a structure with little cross-linking. The broadness of the loss dispersions and their onset at ca. -70°C strongly indicates as stated above that the inorganic and PTMO regimes are well mixed. The loss dispersions of the two other compositions, ratios of Al(OBu):EACAC of 1.33:1.0 and 2.0:1.0, represented in Fig. 5-1 reflect some mixing of the different phases, however, on a significantly

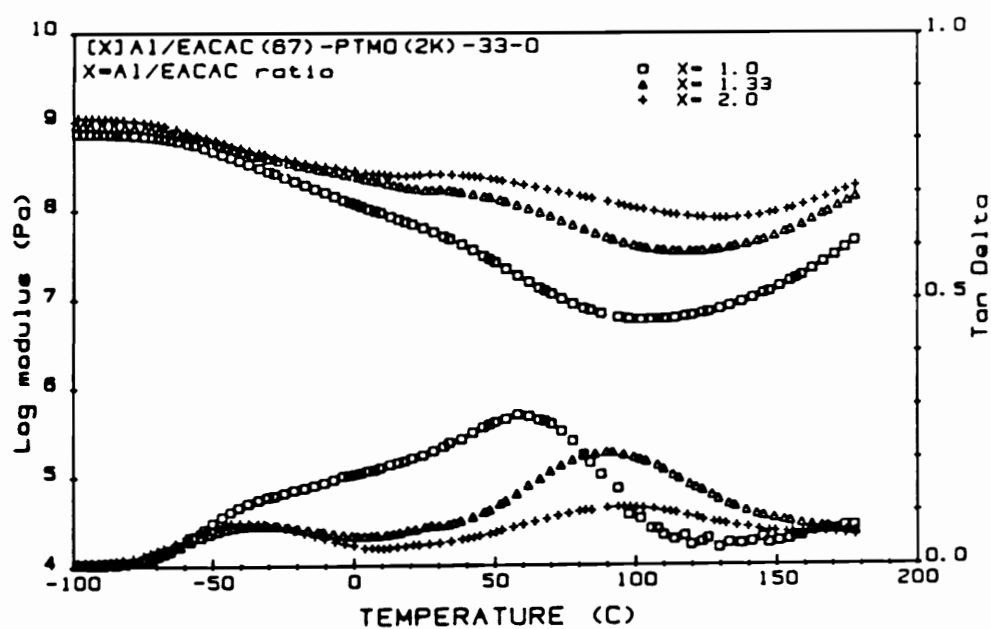


Figure 5-1 Dynamic Mechanical Behavior as a function of $\text{Al}(\text{OBu})_3$ to EACAC ratio: [X]Al/EACAC(67)-PTMO(2K)-33-0.0. (Freq = 11 hz.)

smaller scale than the composition which has a ratio of Al(OBu):EACAC of one to one. The second $\tan \delta$ peak which begins at ca. 50°C and extends to ca. 150°C was associated with a curing mechanism which also involved the release of a Al/EACAC complex [83]. The storage modulus and $\tan \delta$ behavior of the CERAMER [1.33]Al/EACAC(67)-PTMO(2K)-33-0 before and after extraction are illustrated in Figure 5-2. The storage modulus was much higher above ca. 0°C following extraction in MeCl₂ at 40°C, compared to the as gelled sample. The large $\tan \delta$ peak beginning at ca. 50°C was practically eliminated by the extraction also. Approximately 16% of the total weight of sample [1.33]Al/EACAC(67)-PTMO(2K)-33-0 was extracted [83]. The other samples had either a high extractable portion or lower extractable portion corresponding to either a lower ratio of Al(OBu):EACAC or higher ratio of Al(OBu):EACAC, respectively. The results indicated a curing mechanism involving the condensation of alkoxides (or hydroxides) and/or the elimination of a volatile component which acted as a plasticizer in the system. Wang et. al. reported that the extractable portion of the gels was a derivative of the Al/EACAC complex [83].

The Ti/EACAC CERAMERs exhibited a higher storage modulus and lower loss dispersion for a comparable ratio of Ti(OPr) to EACAC than the Al/EACAC hybrids, but a lower overall inorganic content (see Table 3-5). Figure 5-3 depicts the dynamic mechanical behavior which was characteristic of Ti/EACAC hybrids of the general composition [X]Ti/EACAC(54)-PTMO(2K)-25-0, where X was either 0.8 or

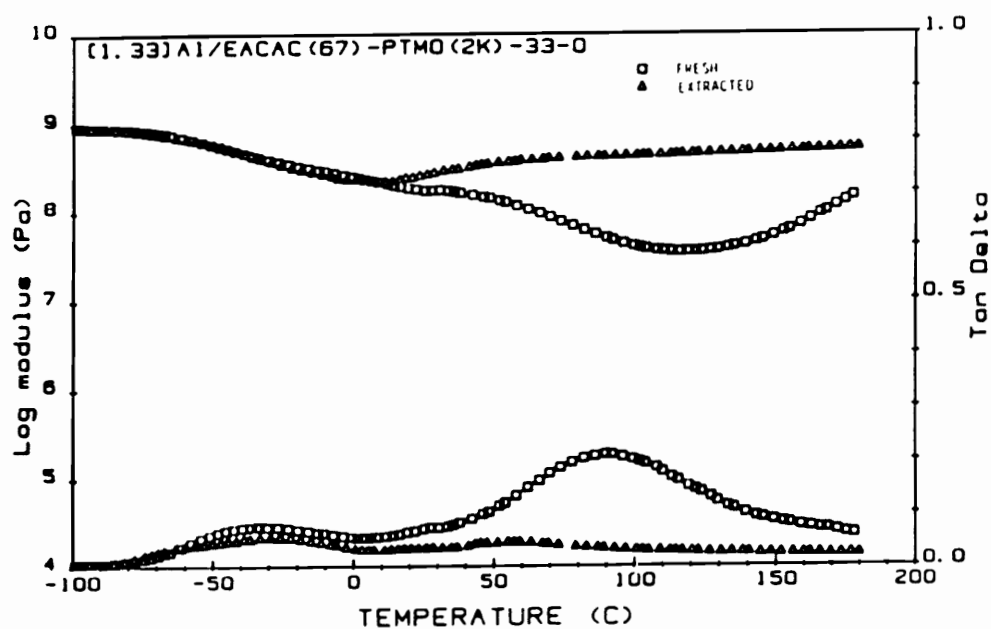


Figure 5-2 Effect of extractable sol fraction on dynamic mechanical behavior of Al/EACAC CERAMERS: [1.33]Al/EACAC (67)-PTMO(2K)-33-0.0. Frequency = 11 hz.

0.5 for the ratio of Ti(OPr) to EACAC. The storage modulus which was on the order of 1 GPa below ca. -80°C , reflects the onset of the glass transition near ca. -70°C which typifies the CERAMERs prepared with the PTMO oligomers [28,30]. Unlike the CERAMERs based on the Al/EACAC metal complex and PTMO, the Ti/EACAC/PTMO hybrids had a storage modulus typical of a filled elastomer, ca. 108 Pa, over the temperature range of ca. 30°C to 175°C . There was a slight rise in the storage modulus from ca. 130°C upto 175°C which was indicative of further curing. The $\tan \delta$ behavior of the Ti/EACAC CERAMERs is characterized by three rather distinct regimes. The first beginning at ca. -150°C and ending at -100°C , as described previously, is due to the crankshaft type motion of the tetramethylene chain segments of the PTMO oligomers. The second loss dispersion which begins at ca. -80°C was attributed to the PTMO rich regimes of the network. The third loss dispersion starting at ca. 30°C has not been clearly defined at this time. However, the separation of the second and third peaks of the $\tan \delta$ response of these CERAMERs suggests the Ti/EACAC/PTMO materials have a higher degree of phase separation than the corresponding Al/EACAC/PTMO CERAMERs or the TEOS/PTMO hybrid networks. (The morphology of these hybrid materials based upon M/EACAC where M represents Al or Ti, will be discussed in more detail in Section 5.3.) The lack of the higher temperature decrease in the storage modulus and corresponding large loss dispersions (at ca. 50°C and above) in the dynamic mechanical behavior of the Ti/EACAC/PTMO materials (Fig. 5-3) indicates that the

structure of the gel was more highly cross-linked than that of the Al/EACAC/PTMO gels represented in Fig. 5-1. This was substantiated by the much lower weight percent of ca. 1 to 3% which was extracted from the Ti/EACAC compositions whose dynamic mechanical behavior was illustrated in Fig. 5-3. These trends reflect the ability of titanium isopropoxide to form a complex with the EACAC by expansion of its coordination number and thus retain a higher functionality in terms of a sol-gel process [55,57]. In other words, the titanium alkoxides reacted with the EACAC in the mole ratios described here are still capable of reacting with the PTMO oligomers to form three dimensional networks.

5.2.2 Mechanical Behavior

The stress-elongation response of the series of Al/EACAC CERAMERS, [X]Al/EACAC(67)-PTMO(2K)-33-0.0 where X was varied from 1.0 to 2.0, exhibited the effect of the poor network formation in the hybrid with the highest amount of EACAC (Figure 5-4). The CERAMER with an Al/EACAC ratio of 2.0 elongated less than 10% prior to failure compared to the CERAMERS with Al/EACAC ratios of 1.0 or 1.33 which elongated nearly 65% and 90%, respectively, of their initial length. The stress-elongation response of the Al/EACAC CERAMERS (Fig. 5-4) illustrate a yield point for these materials which normally indicates the material was tested below the T_g as was observed by Glaser with the TEOS/Ti(OPr)₄/PTMO

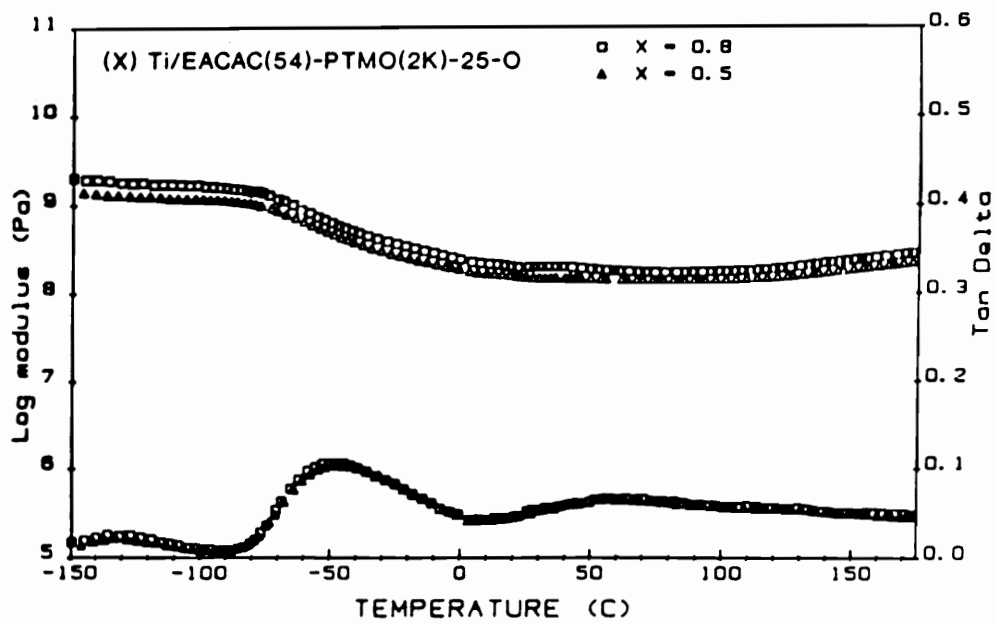


Figure 5-3 Dynamic mechanical behavior of Ti/EACAC CERAMERS: [X]Ti/EACAC(54)-PTMO(2K)-25-0.0. (Freq = 11 hz.)

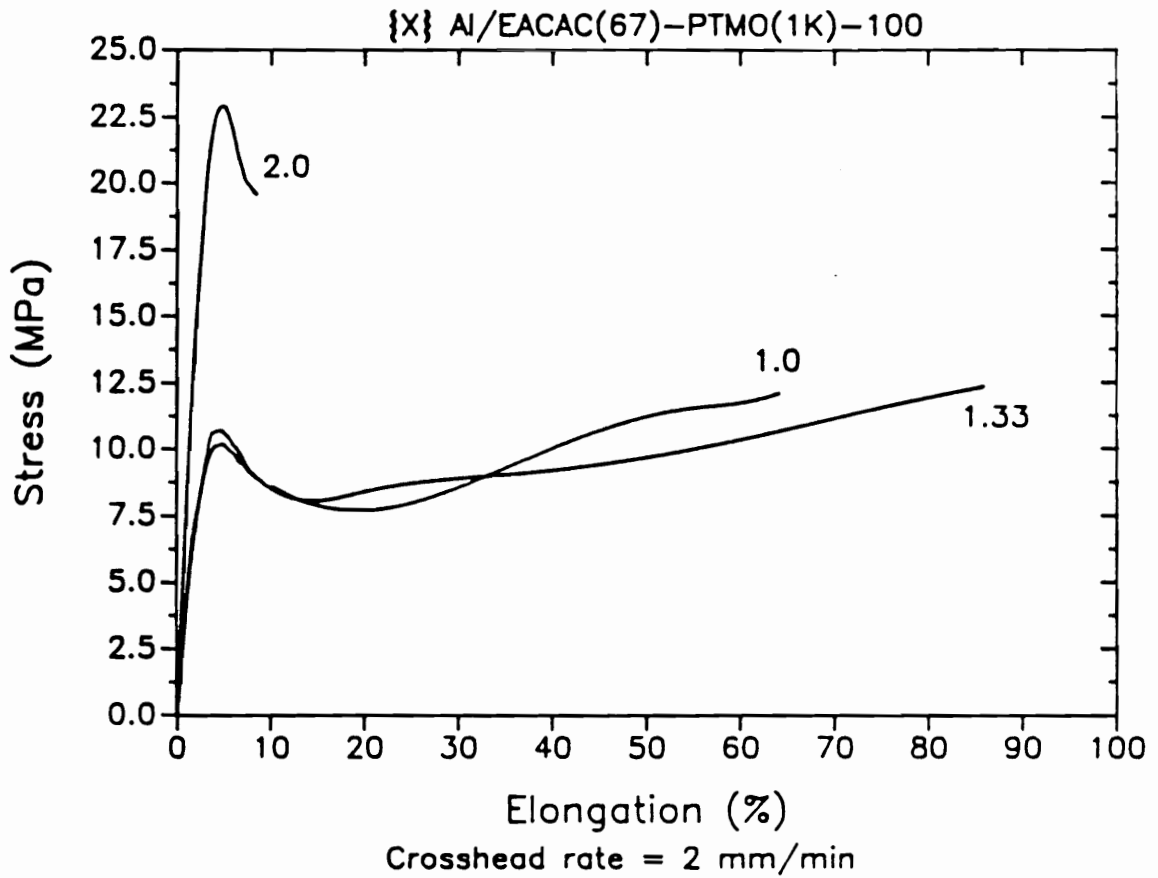


Figure 5-4 Mechanical behavior of Al/EACAC CERAMERs as a function of Al/EACAC ratio: [X]Al/EACAC(67)-PTMO(2K)-33-0. (Freq = 11 hz.).

hybrid materials [27]. The dynamic mechanical behavior of these materials (Fig. 5-1) both in terms of the decline in the storage modulus and the $\tan \delta$ behavior would indicate that the T_g of the Al/EACAC hybrid systems was slightly greater than ambient. This would also be predicted from the method of preparation of these materials. The Al/EACAC CERAMERs were prepared by adding the PTMO oligomer which was heated to 60°C (Chapter 3.0, Section 3.3.2), and thus the reaction temperature would be higher than ambient, ca. 22°C. The system would be capable of developing a network with a T_g at least equal to the reaction temperature as predicted by the TTT phase diagram. The higher elongation of the hybrids with lower levels of EACAC was attributed to improved incorporation of the metal complex into the network. However, as reflected in the stress-elongation behavior illustrated in Figure 5-5, extraction of the CERAMER [1.33]Al/EACAC(67)-PTMO(2K)-33-0.0 with MeCl_2 , decreased the elongation at break from nearly 90% to less than 10%. This supports the concept of poorer network formation due to the presence of an Al/EACAC complex. The presence of the high sol fraction also plasticized the system to increase the elongation.

The Ti/EACAC gels, in contrast to the Al/EACAC materials, had a much different stress-elongation response profile as depicted in Figure 5-6 for the two Ti/EACAC ratios of 0.8 and 0.5 using the 2000 g/mol PTMO oligomer. The higher ratio of Ti/EACAC somewhat increased the stress at break. The overall elongation of the two materials was nearly identical at 38% and 40% for the Ti/EACAC ratios

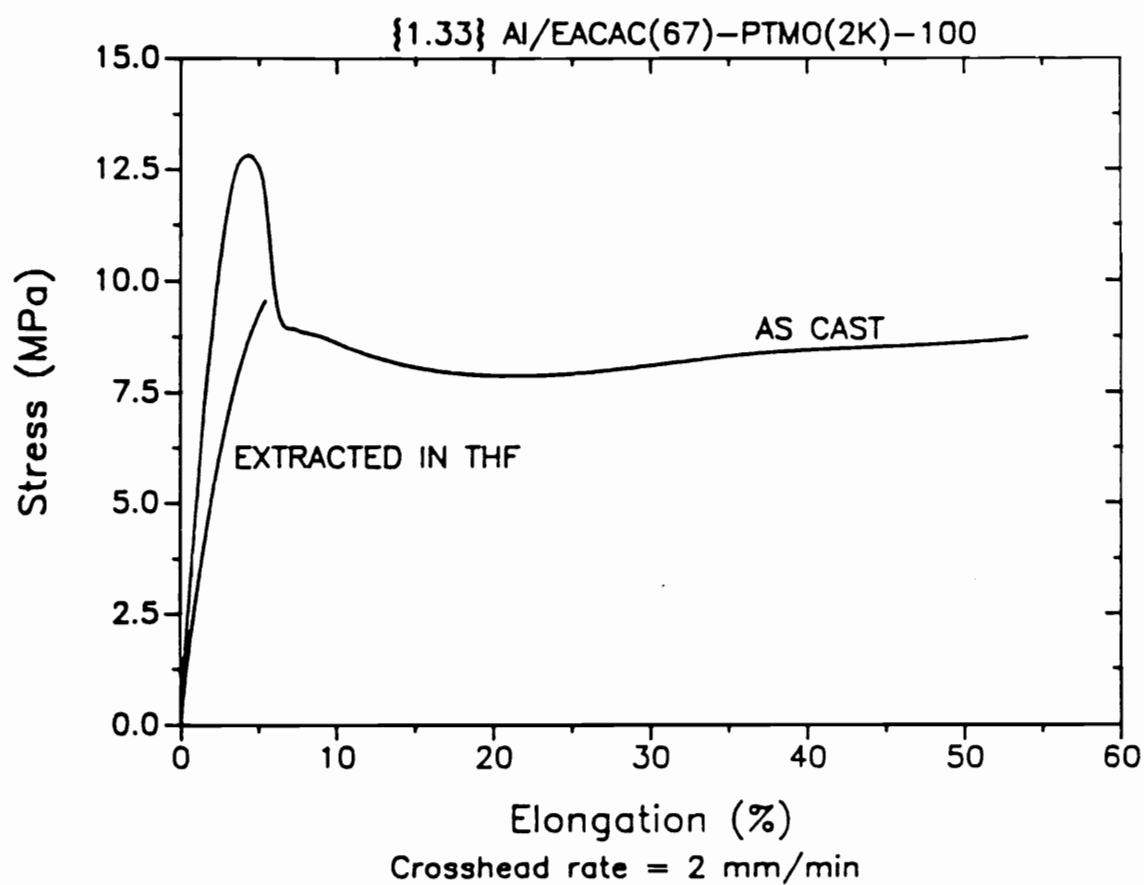


Figure 5-5 Effect of extractable sol fraction on mechanical response of Al/EACAC CERAMER:[1.33]Al/EACAC(67)-PTMO(2K)-33-0

of 0.8 and 0.5, respectively. The Young's modulus was also enhanced slightly by the higher ratio of Ti(OPr) to EACAC. Thus, the mechanical behavior of the Ti/EACAC supports the dynamic mechanical behavior which was representative of a filled elastomeric network compared to a poorly defined network obtained with the Al/EACAC/PTMO CERAMERs. The other important difference between the Al/EACAC/PTMO hybrid materials and the Ti/EACAC/PTMO hybrids was the initial reaction temperature. The Ti/EACAC/PTMO CERAMERs were prepared at ambient conditions compared to the higher reaction temperature of 60°C for the Al/EACAC/PTMO gels. The mechanical behavior reflects this difference in that the Ti/EACAC/PTMO CERAMERs did not have as sharp a yield point as that exhibited by the Al/EACAC/PTMO gels.

5.2.3 Small Angle X-ray Scattering Behavior

The dynamic mechanical behavior of the Al/EACAC/PTMO CERAMERs was representative of a network with a high level of mixing between phases in contrast to the dynamic mechanical response of the TEOS/PTMO CERAMERs described in Chapter 4 of this thesis as well as the numerous other examples in the literature [23,28,30]. The SAXS profiles of the Al/EACAC/PTMO gels reflect the effect of mixing within these materials. Figure 5-7 illustrates the effect of mixing between the two phases, i.e. Al/EACAC and PTMO, on the SAXS behavior of these

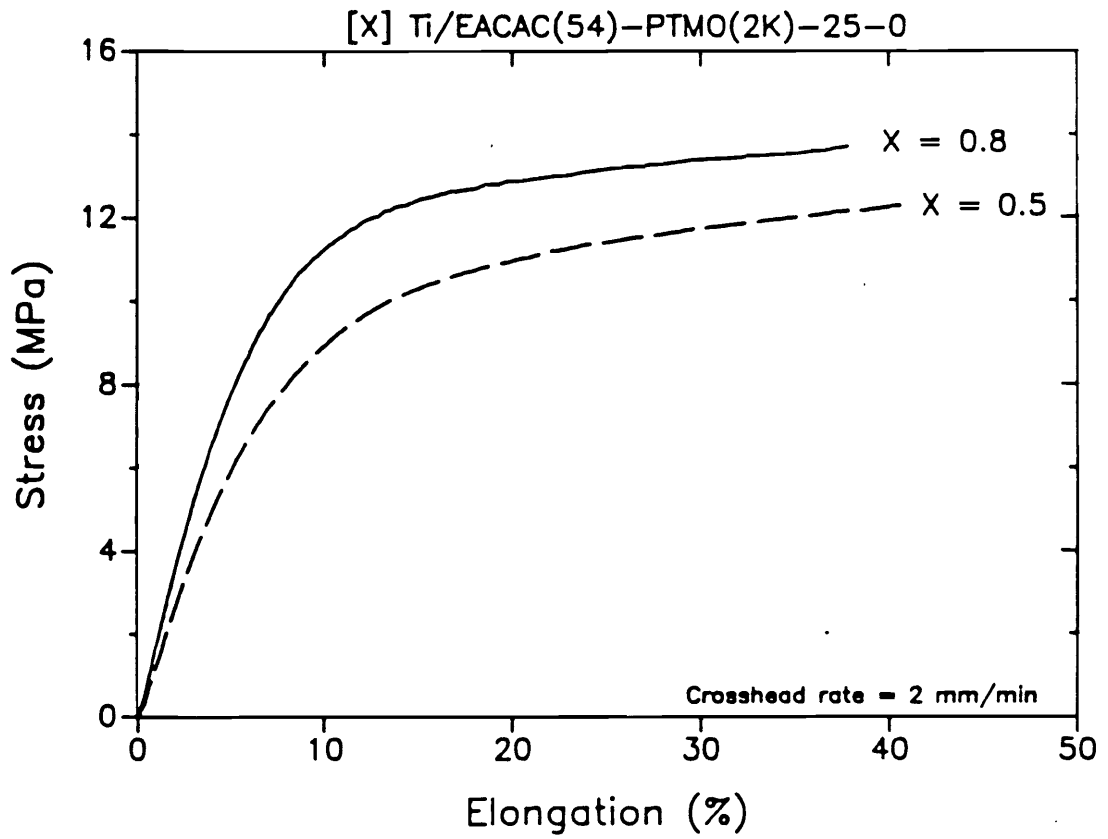


Figure 5-6 Mechanical response of Ti/EACAC/PTMO CERAMERS:
[X]Ti/EACAC(54)-PTMO(2K)-33-0.0

novel hybrid materials. The overall form of the SAXS profiles with a maxima occurring at ca. an s value of ca. 0.10 nm^{-1} are similar to those described for TEOS/PTMO CERAMERS (Chapter 4). The characteristic spacing of 10.0 nm in the Al/EACAC/PTMO CERAMERS indicates the general morphological features on this scale are similar to those of the TEOS/PTMO CERAMERS (Chapter 4). The presence of the maxima in the SAXS profiles indicates that there was some microphase separation in these Al/EACAC/PTMO CERAMERS. The optical clarity of the Al/EACAC/PTMO hybrid networks reinforces this concept.

The high extractable sol fraction in the Al/EACAC/PTMO contributed to a reduction in the overall mean electron density fluctuation in the gels microstructure as indicated in the change of the SAXS behavior following extraction. Figure 5-8 represents the increase in the magnitude of the SAXS scattered intensity at an s value of ca. 0.10 nm^{-1} for the composition [1.33]Al/EACAC(67)-PTMO(2K)-33-0.0 before and after extraction with methylene chloride. The large increase in the scattered intensity was attributed to the elimination of the sol fraction. The presence of a material such as the sol fraction or a solvent within the inorganic structure and the PTMO phase would reduce the mean square electron density fluctuation of the system and thus lower the scattered intensity. The other factor to consider, however, was the effect of extraction at 40°C to remove the soluble portion. This would be expected to increase the extent of condensation in the inorganic structure, even though the mechanical properties did not support this point.

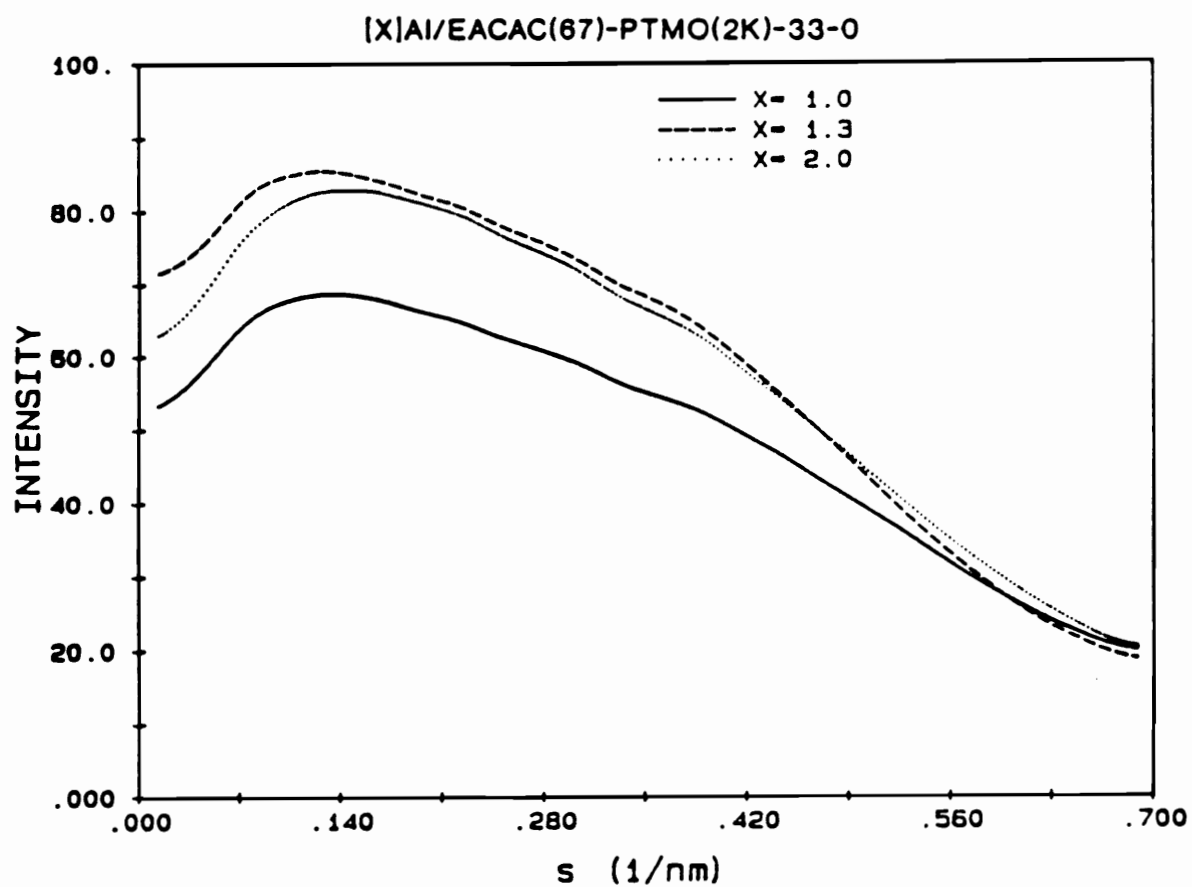


Figure 5-7 SAXS behavior of the Al/EACAC/PTMO CERAMERS:[X]Al/EACAC(67)-PTMO(2K)-33-0.0

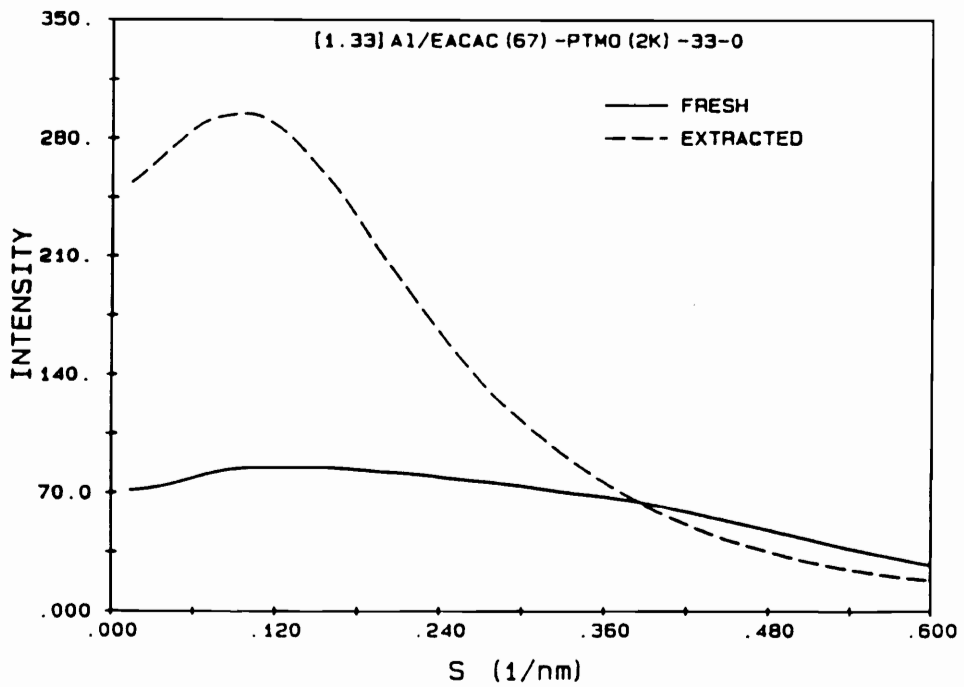


Figure 5-8 SAXS profile of Al/EACAC/PTMO CERAMER before and after extraction: [1.33]Al/EACAC(67)-PTMO(2K)-33-0.0

The SAXS profiles of the Ti/EACAC/PTMO gels of composition [X]Ti/EACAC(54)-PTMO(2K)-25-0, where X was either 0.8 or 0.5, are depicted in Figure 5-9 as plots of the scattered intensity versus s . The SAXS profiles are again quite similar to those of the TEOS/PTMO CERAMERs. However, the maximum intensity which occurred at an s value of ca. 0.11 nm^{-1} , was nearly three times greater for the Ti/EACAC/PTMO materials than that measured for either the TEOS/PTMO CERAMERs or the unextracted Al/EACAC/PTMO gels. The explanation for this behavior was given previously in rather general terms (Chapter 4, Section 4.2.3). The higher electron density of the titanium would increase the mean square electron density fluctuation in this microphase separated system, as the maxima in the profile indicates, and thus increase the maximum scattering intensity. The other feature of the SAXS profiles in Fig. 5-9 is that the width of the overall profile was narrower than those in Fig. 5-7.

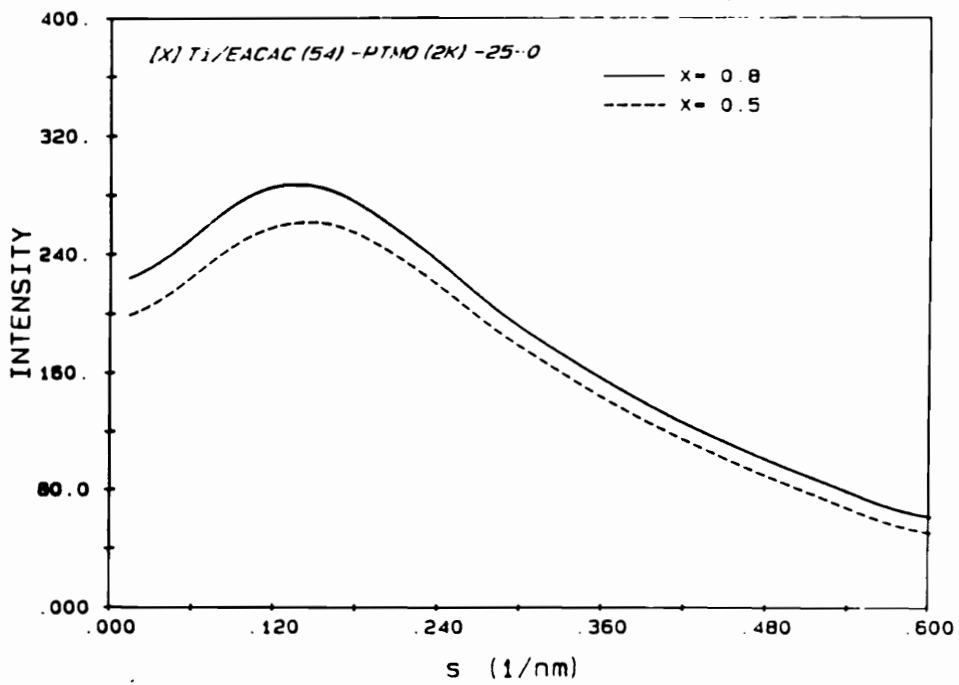


Figure 5-9 SAXS profiles of Ti/EACAC/PTMO CERAMERS:
[X]Ti/EACAC(54)-PTMO(2K)-25-0.0

5.3 CONCLUSIONS

A new class of CERAMERs was developed which was based upon the formation of metal complexes by reaction of metal alkoxides with ethyl acetoacetate which were coreacted with functionalized PTMO oligomers. These CERAMERs prepared with the two metal alkoxides, aluminum tri-sec-butoxide and titanium tetra-iso-propoxide, represent the first example of the total replacement of the silicon based metal alkoxides in CERAMERs [83]. The gels formed were optically clear and monolithic in form. The dynamic mechanical behavior of the Al/EACAC/PTMO gels indicated that as the level of EACAC was increased the storage modulus decreased and the loss dispersions increased. The mechanical response of the Al/EACAC/PTMO hybrids, which exhibited a distinct yield point, decreased in overall elongation with increasing levels of EACAC along with an increase in stress at break. The Al/EACAC/PTMO gels contained rather large sol fractions ranging from ca. 10% to nearly 20%.

The Ti/EACAC/PTMO CERAMERs were prepared at lower Ti/EACAC ratios 0.8 and 0.5 compared to the Al/EACAC/PTMO hybrids which were prepared with ratios of Al/EACAC that ranged from 1.0 to 2.0. The mechanical properties of the Ti/EACAC were similar to the Al/EACAC materials in the stress at break and the modulus, however, the yielding behavior was not as sharp for the Ti/EACAC/PTMO CERAMERs. The SAXS behavior of the extracted gels of

Al/EACAC/PTMO and the Ti/EACAC/PTMO materials was similar in that both exhibited a maxima in the scattered intensity at an s value of approximately 0.1 nm^{-1} , which gives a characteristic spacing of ca. 10.0 nm. Both systems overall profiles resembled those of the TEOS/PTMO CERAMERs and thus the general morphological features are believed to be similar.

CHAPTER 6

TITANIUM/PTMO HYBRIDS AND ZIRCONIUM/PTMO HYBRIDS

6.1 INTRODUCTION

The substitution of TEOS with other metal alkoxides, such as titanium isopropoxide, in CERAMERs based upon the silane endcapped PTMO exhibit a higher Young's modulus and higher stress at break compared with ceramers made with TEOS as the metal alkoxide [24,30]. In Chapter 5, the structure-property relationships of an Al/EACAC/PTMO hybrid material and a Ti/EACAC/PTMO hybrid material were described. The Al/EACAC/PTMO CERAMERs contained a large sol-fraction of nearly 20% in some formulations which was attributed to a complex formed by the chelating agent ethylacetoacetate. The Ti/EACAC/PTMO had a much lower extractable sol, which still represented approximately 4% of the overall mass of the gel. The chelating agents were used to lower the reactivity of the metal alkoxides which tend to self condense prior to reaction with the functionalized oligomers and thus form a precipitate . However, the presence of the relatively large

sol fraction reduces the performance of the network. It will also contribute to aging as the sol diffuses out of the network due to incompatibility between the two phases.

Glaser [27] had developed procedures similar to those reported by Parkhurst et. al. [23] that required a preliminary partial hydrolysis of the highly reactive metal alkoxides such as titanium tetra-iso-propoxide. An "anhydrous" sol was prepared by pre-blending the metal alkoxides, e.g. TEOS and $\text{Ti}(\text{OPr})_4$, with the PTMO oligomer to form a stable system without the need for chelating agents to reduce the metal alkoxides reactivity. The water and catalyst were added 24 hours later to convert the sol into a gel. The total water added was less than the stoichiometric quantity required to hydrolyze all of the alkoxide functional groups. The mechanical properties of the TEOS/TiOPr/PTMO CERAMERs were indicative of more highly cross-linked networks compared with TEOS/PTMO CERAMERs prepared by the same methods [27]. Thus, it was demonstrated by Glaser that more reactive metal alkoxides could be incorporated into the PTMO hybrid systems without the need for chelating agents.

A novel procedure was developed by Dr. Bing Wang [83] to form stable sol-gel derived hybrid networks by the co-condensation of $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ or $\text{Zr}(\text{OC}_3\text{H}_7)_4$ with silane functionalized PTMO oligomers. The process developed by Dr. Wang reduced the overall processing time significantly and eliminated the need for chelating agents to reduce the reactivity of the metal alkoxides. The dynamic mechanical behavior, the mechanical properties, and the small angle scattering

behavior (SAXS) of the ceramers formulated with titanium tetraisopropoxide (or zirconium tetra n-propoxide) and functionalized PTMO will be described in this chapter.

6.2 RESULTS AND DISCUSSION

6.2.1 Dynamic Mechanical Behavior

6.2.1.1 Effect of Metal Alkoxide to PTMO Ratio

The storage modulus of the CERAMER compositions reported, has consistently been shown to increase with the level of metal alkoxide added initially. The TiOPr/PTMO CERAMERs exhibit similar trends in terms of the dynamic modulus. A plot of the storage moduli, E' , versus temperature for a series of CERAMERs of the general composition TiOPr(X)-PTMO(2K)-25-0.06, where the level of titanium isopropoxide (X) was increased from 49% to 66% is depicted by Fig. 6-1. All four compositions have comparable storage moduli in the glassy state, ca. 1 GPa, below -100°C , which is what one would expect for a polymeric network below its T_g . The onset of the T_g begins at approximately -70°C for the CERAMER composition TiOPr(49)-PTMO(2K)-25-0.06 as indicated by the decrease in the storage modulus. This is contrasted by an apparent delay in the onset of the T_g of approximately 10°C with the higher level (66%) of titanium isopropoxide. The rubbery plateau above T_g increased with the incorporation of higher weight fractions of titanium isopropoxide, i.e. 49% to 66%, in the hybrid network by nearly one order of magnitude. The higher rubbery modulus, as a function of the increasing ratio of

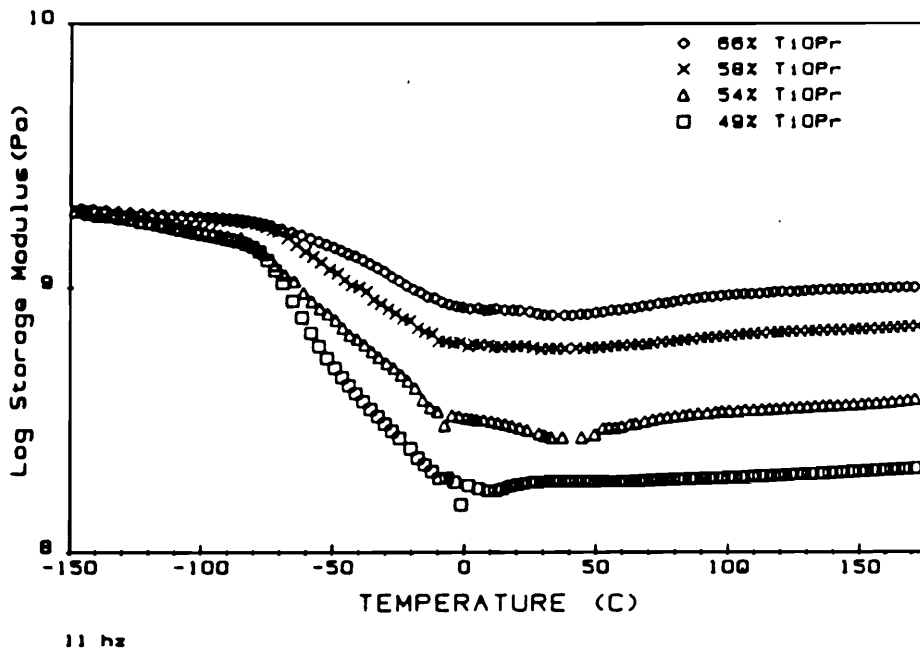


Figure 6-1 Storage modulus of CERAMERS as a function of TiOPr to PTMO ratio: TiOPr(X)-PTMO(2K)-25-0.06 HCl. (Freq = 11 hz.)

titanium isopropoxide to PTMO, is believed to be related to the reinforcement effect of the inorganic structure on the matrix. This behavior correlates well with the TEOS/PTMO CERAMERs previously described [27,30]. Mark et. al. [20,21] reported similar trends, i.e. increasing modulus with level of metal alkoxide added, in networks formed by the in situ hydrolysis of titanium isopropoxide and (dimethyl siloxane) and poly (methyl phenyl siloxane).

The $\tan \delta$ behavior (Figure 6-2) provides more information as to the molecular relaxations in these hybrid materials. A rather strong dependence of the β relaxation on the level of titanium isopropoxide was noted for these CERAMERs. The β transition which begins at ca. -140°C and ends near ca. -120°C increases as the weight fraction of the TiOPr is decreased. This transition is due to the crankshaft type molecular motion of the tetramethylene unit of the PTMO oligomer [94]. The magnitude of change associated with this molecular motion, as a function of the weight percent titanium isopropoxide in the TiOPr/PTMO CERAMERs, was not observed in the other CERAMER compositions where silica was the major portion of the inorganic phase. The dependence of these short range molecular relaxations associated with the tetramethylene units and the titanium isopropoxide may suggest a different type of interaction between the two phases compared to a TEOS/PTMO system. This point will be addressed later in conjunction with an explanation for the higher temperature loss dispersion peak beginning at ca. 15°C .

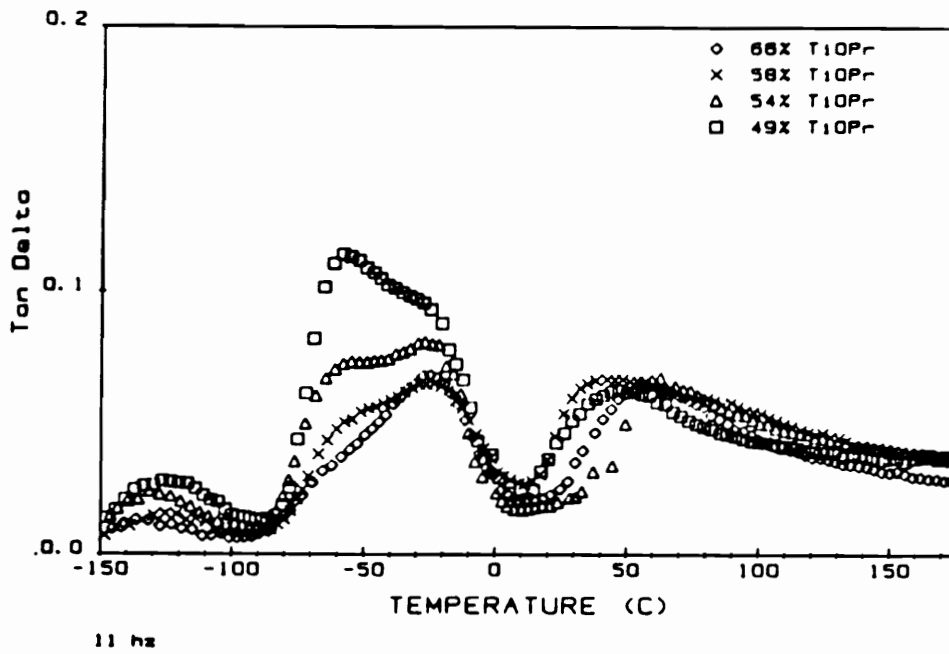


Figure 6-2 Tan δ behavior of CERAMERs as a function of TiOPr to PTMO ratio: TiOPr(X)-PTMO(2K)-25-0.06 HCl. (Freq = 11 Hz)

The next loss dispersion peak in Fig. 6-2 begins at ca. -70°C and ends at ca. -20°C which is similar in nature to that of the previously reported CERAMERs composed of TEOS and PTMO, albeit a bit narrower for the titanium and zirconium based CERAMERs. The broadness of this glass transition loss behavior again reflects the diversity of the molecular environments formed in these hybrid networks [18,24,30]. The model which was proposed and described in detail earlier (Chapters 2 and 4) for these hybrid systems characterizes the $\tan \delta$ behavior in terms of the two general types of restrictions referred to as TYPE 1 and TYPE 2 [18]. The maximum of the loss dispersion that occurs near ca. -50°C for TiOPr(49)-PTMO(2K)-25-0.06 is nearly 40°C lower than the maximum for an equivalent composition of the TEOS/PTMO CERAMER [24]. The position of the maxima of this loss dispersion peak at ca. -50°C for the TiOPr(49)-PTMO(2K)-25-0.06 HCl hybrid is close to that of the sample TEOS(0)-PTMO(2K)-100-0.014 catalyzed with HCl which was presented in Figure 4-3 of this thesis. Recall that the shift of the PTMO loss dispersions to higher temperatures in the CERAMERs was attributed to the mixing with the inorganic phase. Thus, less mixing between phases would cause the loss dispersion of the TiOPr/PTMO (Fig. 6-2) to occur at a temperature close to that of the cross linked functionalized PTMO which had no metal alkoxide added. This supports the earlier statement that the magnitude of the β transition was due to a more sharply phase separated system in the TiOPr/PTMO CERAMER compared with a comparable TEOS/PTMO CERAMER. Indeed, this is even more evident in

that the loss dispersion peak beginning at ca. -70°C appears to be two loss dispersion peaks which are not well resolved. The lower temperature portion of the bimodal peak beginning at ca. -70°C , for the TiOPr/PTMO hybrid materials was attributed to molecular relaxations in a PTMO rich region (TYPE 1). The molecular relaxations defined by the higher temperature portion of the peak are believed to be due to TYPE 2 restrictions. Another critical difference between the $\tan \delta$ behavior of the TiOPr(49)-PTMO(2K)-25-0.06 hybrid gel and a TEOS/PTMO CERAMER of equivalent composition, was the relative magnitude of the broad $\tan \delta$ peak at ca. -50°C compared to the loss dispersions in Figure 4-3. In addition, to the relative magnitude differences, the $\tan \delta$ peak maxima at ca. -50°C in Fig. 6-2 did not shift along the temperature axis as the level of TiOPr was varied in the hybrid materials. However, the magnitude of the loss dispersion beginning at ca. -70°C does decrease with increasing weight fraction of TiOPr which one would predict if the lower temperature portion of the dispersion was due to molecular relaxations in regimes of PTMO segments with little mixing with the TiOPr structure.

The molecular relaxations characterized by the $\tan \delta$ peak beginning at ca. 15°C and continuing beyond ca. 100°C for the TiOPr(49)-PTMO(2K)-25-0.06 (Fig. 6-2) are somewhat different than observed in other hybrid materials based upon TEOS/PTMO (Figure 4-1). The loss dispersion peak (Fig. 6-2) was separated more from the lower temperature peaks for the TiOPr/PTMO CERAMERs compared with the hybrids of TEOS/PTMO [18,19,24,30]. The distinct separation of the higher

and lower temperature loss dispersion peaks, ca. -70°C to 0°C and ca. 15°C to 175°C , was attributed to a higher degree of phase separation in these newer hybrid systems. This has been demonstrated in TEOS/PTMO systems in which dimethyl formamide and isopropanol was used as the solvent system rather than the normal for the CERAMERs prepared with the functionalized PTMO oligomers which was tetrahydrofuran and isopropanol [26]. The peak at ca. 15°C to 175°C (Fig. 6-2) did not change dramatically with the different levels of TiOPr in the TiOPr/PTMO hybrid networks. The overall form remained reasonably constant throughout. The peak at ca. 15°C to 175°C (Fig. 6-2) did coincide with a slight increase in the storage modulus (Fig. 6-1) which indicated a possible curing mechanism or the elimination of residual solvent. This will be addressed in more detail in Section 6.2.3.

The storage moduli of the ZrOPr/PTMO CERAMERs are quite similar to the trends observed in the response of the TiOPr/PTMO materials and the TEOS/PTMO materials to changes in the level of the metal (Figure 6-3). The storage moduli are significantly less, however, for the ZrOPr/PTMO CERAMERs (Fig. 6-3) when compared with TiOPr/PTMO CERAMERs of equivalent weight fractions of metal alkoxide (Fig. 6-1). As an example, the value of E' (at ambient) of the CERAMER ZrOPr(57)-PTMO(2K)-0-0.06 was nearly one half an order of magnitude higher than E' for the equivalent composition of TiOPr(58)-PTMO(2K)-

25-0.06 (in terms of the metal alkoxide). The lower storage modulus would for the ZrOPr/PTMO CERAMERs strongly indicates a less highly cross-linked network as shown in Chapter 4 of this thesis for TEOS/PTMO CERAMERs.

The $\tan \delta$ behavior of the ZrOPr/PTMO CERAMERs tend to support the idea of a "looser" network (Figure 6-4). The maxima of the loss dispersions at ca. -70°C are much higher in magnitude, ca. 0.1, for the composition ZrOPr(57)-PTMO(2K)-0-0.06 compared with the CERAMER TiOPr(58)-PTMO(2K)-25-0.06 which displayed a value of 0.04 for the $\tan \delta$ maxima at ca. -70°C . The loss dispersion from -70°C to 0°C exhibits the same overall general decrease as the weight fraction of metal alkoxide added was increased. However, the $\tan \delta$ peak beginning at ca. -70°C and extending to ca. -40°C decreased consistently as the weight fraction of PTMO was reduced in the TiOPr/PTMO CERAMERs, while the peak extending from -40°C to ca. 10°C decreased very little. This was attributed to TYPE 2 restrictions in the TiOPr/PTMO CERAMERs which were the result of mixing between the two phases. The lower temperature portion ca. -70°C to ca. -40°C was ascribed to molecular relaxations of PTMO chains within regimes with very low inorganic content. The ZrOPr/PTMO loss dispersions over the same temperature range, however, differ in a fundamental manner. The portion of the $\tan \delta$ peak which extends from ca. -40°C to 10°C remains relatively low in all the formulations tested and shows a slight increase at the change from 50% ZrOPr to 57% ZrOPr. It was postulated that the ZrOPr/PTMO CERAMERs were more

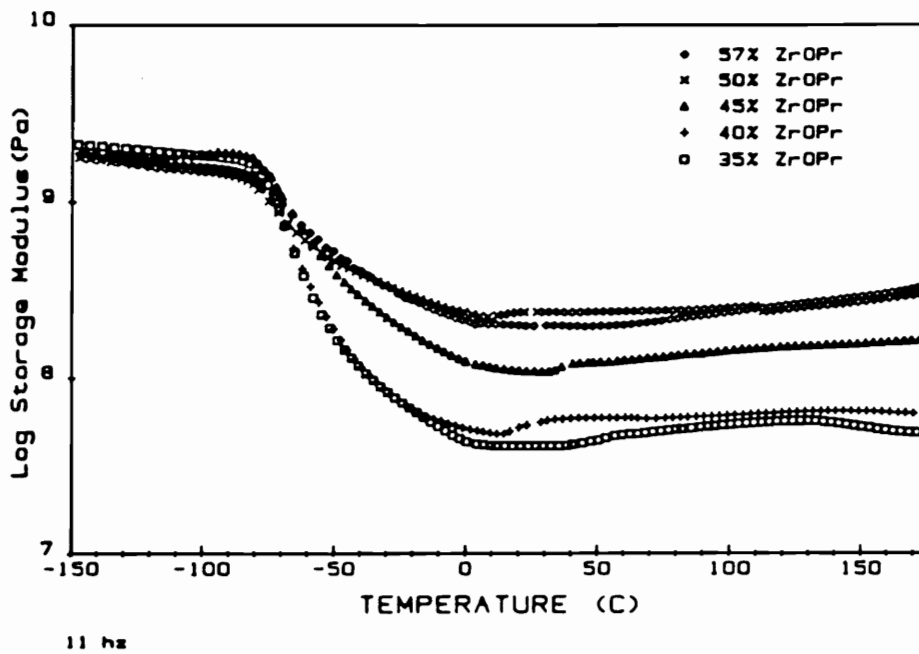


Figure 6-3 Storage modulus of CERAMERS as a function of ZrOPr to PTMO ratio: ZrOPr(X)-PTMO(2K)-0.0-0.06. (Freq = 11 Hz)

mixed than the comparable TiOPr/PTMO CERAMERs or that the inorganic phase was less highly structured due to lower extents of reaction. The basis of this argument was that the ZrOPr/PTMO CERAMERs contained less water for hydrolysis early in the reaction compared to the TiOPr/PTMO gels. This was necessary to prevent premature precipitation of the ZrOPr from the sols. The other interesting difference observed in the $\tan \delta$ behavior of the ZrOPr system was the absence of any noticeable differences in the magnitude of the β transition (ca. -150°C to -110°C). The β transition response of the ZrOPr/PTMO CERAMERs to the level of metal alkoxide was quite similar to that of the TEOS/PTMO CERAMERs (Fig. 4-2).

6.2.1.2 Effect of Aging

The storage moduli in the rubbery regime of the dynamic mechanical spectra illustrated in Fig. 6-1 exhibit a gradual increase with rising temperatures from ca. 40°C to 175°C. The response of the storage modulus above room temperature in the CERAMERs gelled at ambient conditions has typically been dependent upon the extent of conversion of the alkoxides or presence of residual solvents [24,27,29]. Figure 6-5 illustrates the change in the storage modulus of a sample, TiOPr(50)-PTMO(2K)-25-0.06 HCl, following an analyses in the Rheovibron which involves cooling to -150°C and then heating it to 175°C at 1°C/min to 2°C/min. The glassy

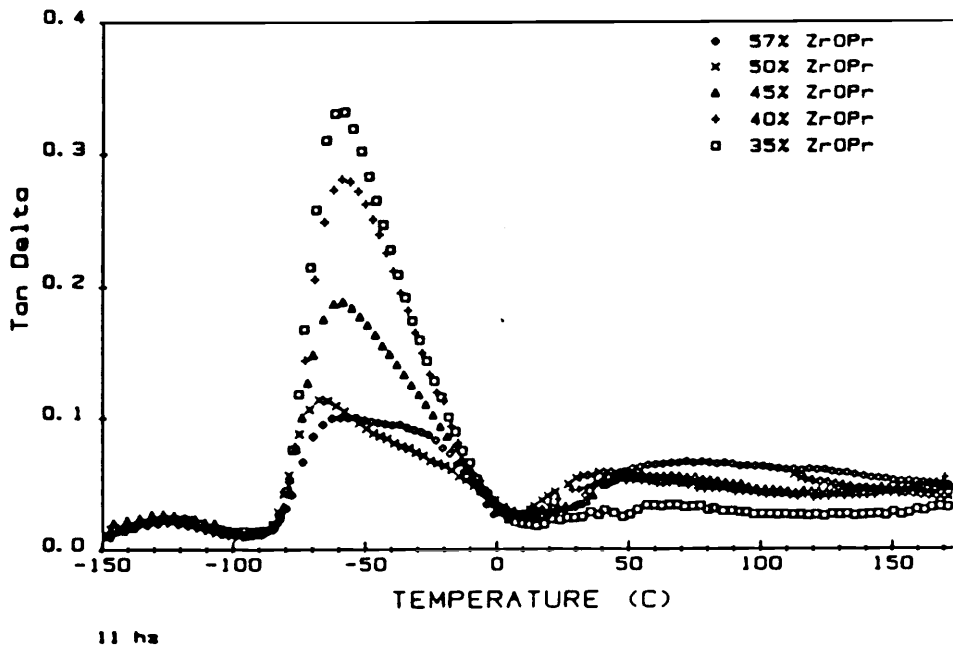


Figure 6-4 Tan δ behavior of CERAMERs as a function of ZrOPr to PTMO ratio: ZrOPr(X)-PTMO(2K)-0.0-0.06. (Freq = 11 Hz.)

modulus did not change as indicated by E' below ca. -70°C , but above onset of the glass transition temperature of ca. -70°C , the value of E' increased to ca. $10^{8.5}$ Pa at ca. 20°C compared to ca. $10^{7.5}$ Pa. during the first analysis (Fig. 6-5). The final value of E' was approximately equivalent at the end of both runs which indicated that the first analysis either completed the sol-gel reactions of hydrolysis and condensation or residual solvents acting as plasticizers were eliminated.

The $\tan \delta$ behavior illustrates two interesting changes as a result of heating the CERAMER TiOPr(50)-PTMO(2K)-25-0.06 to 175°C in the Rheovibron. First as determined for the TEOS(50)-PTMO(2K)-100-0.014 HCl catalyzed CERAMERS [30], the loss dispersion associated with the glass transition of the gel beginning at ca. -70°C decreases in magnitude and the maxima at ca. -55°C appears to shift slightly to a lower temperature, ca. -65°C (Figure 6-6). The upper temperature loss dispersion beginning at ca. 20°C also decreases slightly overall in the magnitude, but the temperature at which the loss dispersion reached its maximum value was shifted slightly to a higher temperature. The value of E' (Fig. 6-6) for the two different runs increased above 20°C rather sharply, followed by a gradual increase from ca. 40°C to 50°C upto the final temperature of 175°C . There was a weight loss, albeit rather small, detected by TG/DTA which occurs in the temperature range of from ca. 20°C to 100°C that corresponds to the loss behavior in the same temperature range. This will be described in more detail in Section 6.2.4.

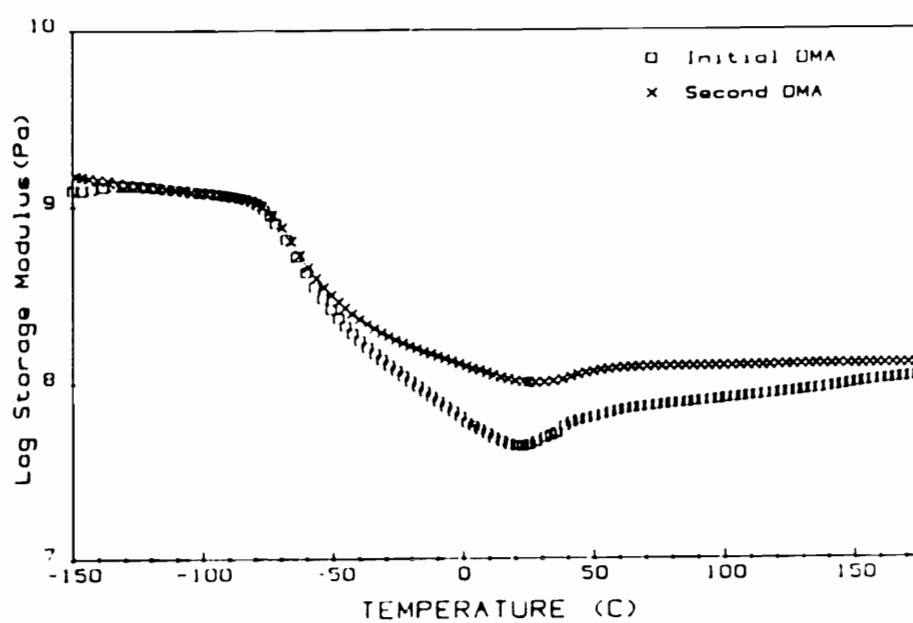


Figure 6-5 Storage modulus as a function of heating sample to 175°C:
TiOPr(50)-PTMO(2K)-25-0.06. (Freq = 11 hz.)

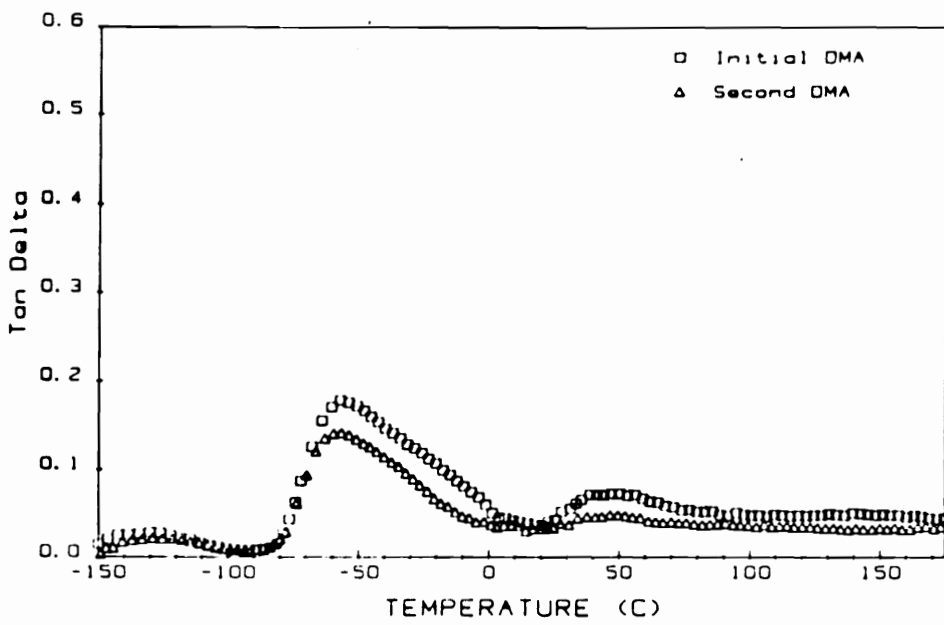


Figure 6-6 Tan δ behavior as a function of heating sample to 175°C: TiOPr(50)-PTMO(2K)-25-0.06. (Freq = 11 hz.)

The loss dispersion above ca. 20°C considered was the elimination of solvents which are generated by further condensation within the inorganic phase upon heating. It has been reported that the acidic catalyzed sol-gel structure with sufficient water for hydrolysis and condensation will be a lightly branched rather continuous structure [1]. The TYPE 1 and TYPE 2 restrictions described for the TEOS/PTMO CERAMERs are based upon a silicate structure which can mix with the PTMO oligomers. The contribution of the inorganic phase to the $\tan \delta$ behavior of the CERAMERs was evaluated by preparation and analysis of monolithic films of TEOS, methyltriethoxysilane (MTEOS) and dimethyldiethoxysilane (DMDEOS). These materials were prepared according to procedures described by Glaser and studied by solid-state ^{29}Si NMR to determine the overall extent of conversion [27]. Figure 6-7 illustrates the effect of introducing defects in the silicate structure with little change in the average functionality of the system. The formula 37D/33M/30T was prepared by mixing DMDEOS, MTEOS, and TEOS in the ratio of 0.37:0.33:0.30, respectively. The formula 0D/100M/0T contained only MTEOS. The average functionality based upon the contribution of each component on the basis of weight, was 2.93 for the formula 37D/33M/30T and 3.0 for the formula 0D/100M/0T. The storage moduli did not exhibit a clear glass transition, but had a gradual increase of less than one order of magnitude over the temperature range of -150°C to 200°C. The much higher value of E' above ambient was indicative of the brittle nature of these samples which often fractured at the end of the analysis. The most significant

aspect of the dynamic mechanical behavior of the two materials in Fig. 6-7 was the loss dispersions occurring at ca. -20°C and ca. 40°C . These two peaks are significantly enhanced by the higher content of methyl groups bonded to the silicon atom. There is a strong correlation between the $\tan \delta$ peaks in Fig. 6-7 and those in Figs. 6-2 and 6-6 as well as those previously reported by Huang et. al. [24] and Glaser [27].

6.2.2 Mechanical Behavior

6.2.2.1 Effect of Metal Alkoxide to PTMO Ratio

A plot of the engineering stress versus elongation at a crosshead speed of 2 mm/min is provided in Fig. 6-8 for the TiOPr/PTMO CERAMERs. The modulus of these materials increases with the level of TiOPr added initially, i.e. the modulus increases with increasing levels of titanium which was observed in terms of E' in the previous section. Yielding was also detected in the TiOPr/EACAC/PTMO hybrid materials described in Chapter 5 of this thesis. The maximum stress measured (Table 6-1) increases from 19 MPa to 40 MPa for the TiOPr(X)-PTMO(2K)-25-0.06 CERAMERs when X varied from 49% to 66%, respectively. The percent elongation at break decreased from ca. 60% to ca. 10% for the same range of composition of TiOPr(X)-PTMO(2K)-25-0.06 (Table 6-1). These materials are significantly stronger

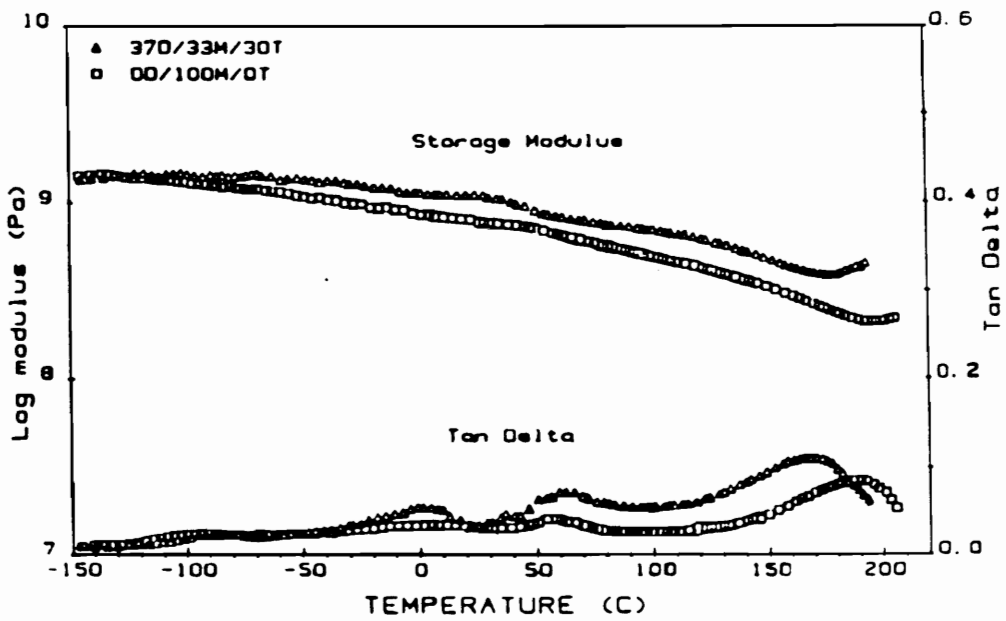


Figure 6-7 Dynamic mechanical behavior as a function of metal alkoxide functionality

than comparable compositions in which TEOS was the metal alkoxide [18,24,30]. The yield point which has not been observed in CERAMERs prepared with the silane end capped PTMO and TEOS, was displayed by other CERAMERs prepared with mixtures of TiOPr and TEOS [24,27] and a novel class of CERAMERs prepared with a multi-functional PTMO type oligomer [28]. The T_g , as determined by dynamic mechanical measurements at a frequency of 11 hz., was higher than 25°C for the mixed metal alkoxide system containing TEOS and TiOPr as well as the CERAMER based on the multifunctional PTMO. All stress/elongation measurements were at ambient conditions which typically equate to a laboratory temperature of ca. 22°C. Consequently the mixed metal alkoxide CERAMER and the multi functional PTMO CERAMERs would be glassy materials at test conditions and thus would display yield behavior in the stress-elongation response. The same conditions, however, do not exist for the TiOPr/PTMO CERAMERs as indicated by the $\tan \delta$ behavior (Fig. 6-2). There is a some loss dispersion behavior above ambient temperature, ca. 22°C, however, it was not attributed to the T_g which, as stated earlier, occurs over a temperature the range from ca. -50°C to ca.-10°C.

The mechanical response of the zirconium/PTMO CERAMERs as a function of increasing the ratio of ZrOPr to PTMO was similar to that of the TiOPr/PTMO gels (Figure 6-9). However, at the lower levels of ZrOPr at 35 wt% and 40 wt%, there was little indication of yielding behavior. The CERAMER compositions ZrOPr(50)-PTMO(2K)-0.0-0.06 and ZrOPr(57)-PTMO(2K)-0.0-0.06 both had rather

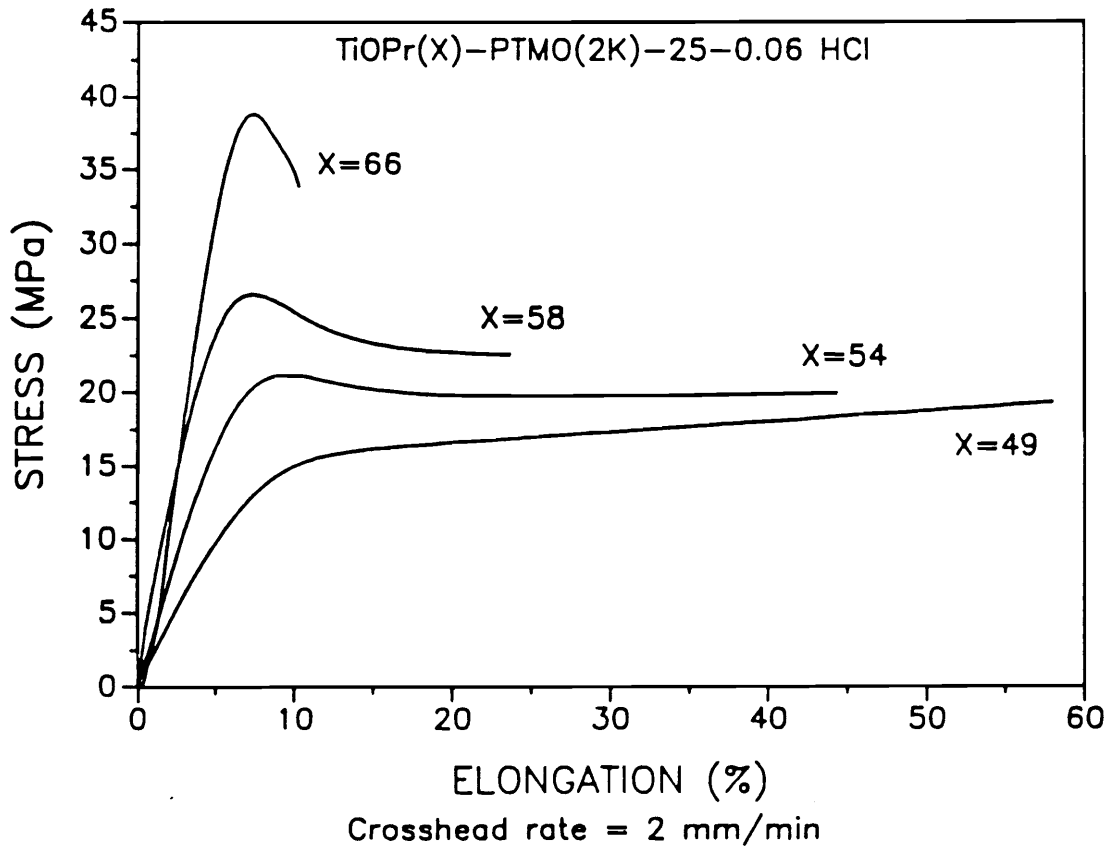


Figure 6-8 Mechanical response of CERAMERS as a function of TiOPr to PTMO ratio: TiOPr(X)-PTMO(2K)-25-0.06

Table 6-1 Mechanical properties of CERAMERs as a function of TiOPr to PTMO ratio: TiOPr(X)-PTMO(2K)-25-0.06

TiOPr(X)-PTMO(2K)-25-0.06 HCl			
TiOPr (wt%)	Young's Modulus (MPa)	Stress at Break (MPa)	Elongation at Break (MPa)
49%	101	19	58
54%	185	20	51
58%	244	23	25
66%	411	34	10

distinct yield points. The equivalent compositions of the TiOPr/PTMO CERAMERs (Fig. 6-8) had a distinct decrease in stress with increasing elongation beyond the yield point followed by a plateau of increasing elongation at a steady stress. The ZrOPr/PTMO CERAMERs containing 50 wt% and 57 wt% did not behave in the same manner. The stress at break of sample ZrOPr(50)-PTMO(2K)-0.0-0.06 was approximately 0.7 of the stress at break of sample TiOPr(58)-PTMO(2K)-25-0.06. The elongation at break, in percent, was 55% for the composition ZrOPr(50)-PTMO(2K)-0.0-0.06 compared to 25% for the equivalent composition of the TiOPr/PTMO CERAMER. Thus the trends in the stress-elongation response as a function of metal alkoxide to PTMO are similar for the two different classes of CERAMERs, i.e. TiOPr/PTMO and ZrOPr/PTMO, yet the mechanical properties at failure were significantly lower for the ZrOPr/PTMO hybrid gels. One factor that may contribute to the observed differences was that the final mole fraction of zirconium was somewhat lower due to the higher atomic weight of zirconium compared with titanium. A compilation of the different relationships between the weight fraction and mole fraction is provided in Table 6-3. The weight fraction of the metal oxide was determined using the initial moles of metal alkoxide and assuming complete conversion to the oxide form. The mole fraction of the ZrOPr was typically 10% lower than that of the TiOPr using the assumption as stated previously. A 10% decrease in the metal alkoxide TiOPr as given by the difference between the compositions TiOPr(50)-PTMO(2K)-25-0.06 and ZrOPr(57)-PTMO(2K)-

25-0.06 could account for the differences in mechanical properties between the ZrOPr/PTMO and TiOPr/PTMO CERAMERs. Another possible reason for the lower ultimate stress in Zr/PTMO CERAMERs versus the Ti/PTMO CERAMERs, is that the water supplied for the hydrolysis and condensation reactions was 25 times higher in the TiOPr/PTMO compositions than the ZrOPr/PTMO CERAMERs. It has been demonstrated in the TEOS/PTMO CERAMERs that as the samples are aged the ultimate stress increases and ultimate elongation decreases which was attributed to a higher extent of reaction and/or elimination of residual solvents [18,24]. Thus, the lower mechanical strength of the Zr/PTMO CERAMER compared with the Ti/PTMO CERAMERs may also be related to a lower extent of reaction. This would be supported in part by the $\tan \delta$ behavior which was much higher for the ZrOPr/PTMO CERAMERs compared to the TiOPr/PTMO CERAMERs.

The similarity of the mechanical response of the two CERAMERs based upon TiOPr or ZrOPr prompted the evaluation of their modulus as a function of the mole fraction of the metal alkoxide. Table 6-3 contains the weight fraction of each of the three metal alkoxides, TiOPr, ZrOPr, and TEOS, calculated as a total percent of the final gel, assuming complete conversion of the alkoxides to the oxide form. In addition to weight fractions with respect to the hydrolyzed PTMO, the mol fraction (%) is included as well as the moles of metal oxide with respect to the weight of PTMO. A plot of the Young's modulus versus the ratio of moles of the metal oxide

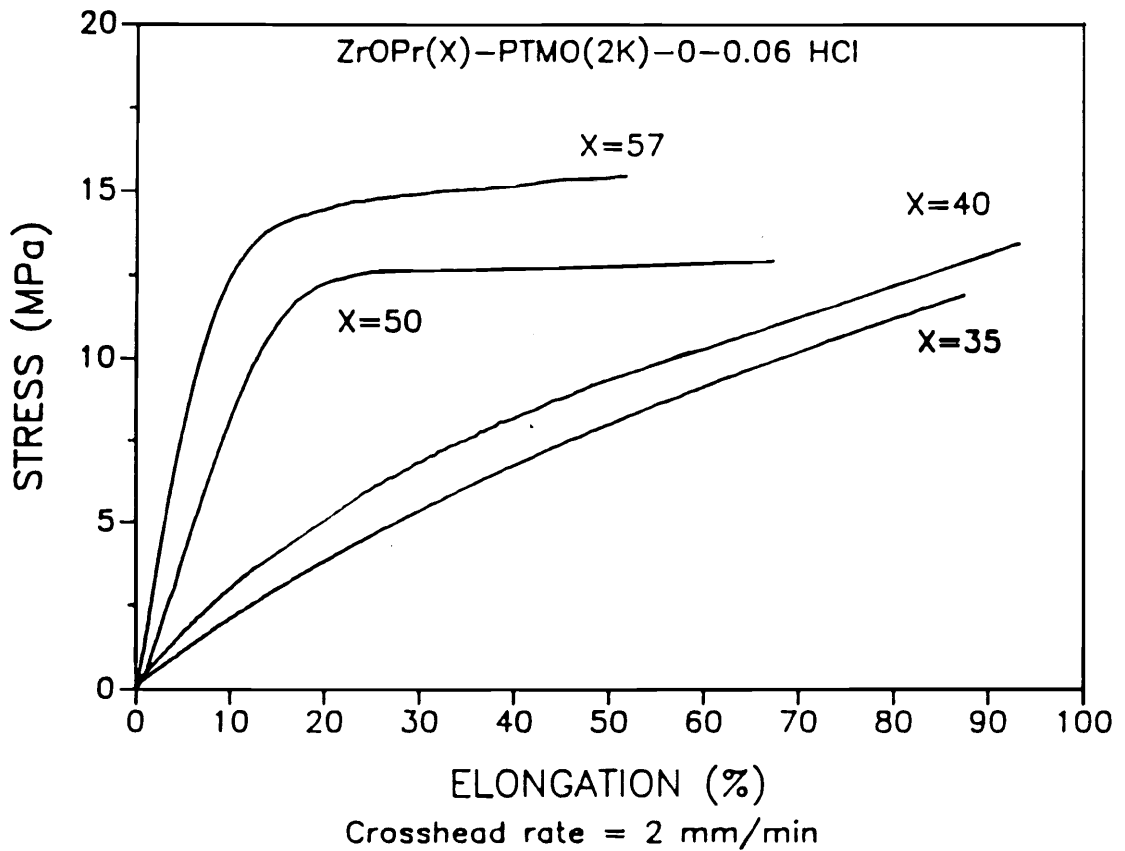


Figure 6-9 Mechanical response of CERAMERS as a function of ZrOPr to PTMO ratio: ZrOPr(X)-PTMO(2K)-0.0-0.06

Table 6-2 Mechanical properties of CERAMERs as a function of ZrOPr to PTMO ratio: ZrOPr(X)-PTMO(2K)-0.0-0.06

ZrOPr(X)-PTMO(2K)-0.0-0.06 HCl			
ZrOPr (wt%)	Young's Modulus (MPa)	Stress at Break (MPa)	Elongation at Break (MPa)
35%	20	12	85
40%	27	13	95
50%	198	15	35
57%	187	17	49

Table 6-3 Contribution of metal alkoxides and metal oxides to mass of CERAMERs

M(X)-PTMO(2K)-25-0.06 HCl			
TiOPr (wt%)	TiO ₂ (wt%)	TiO ₂ (mol%)	TiO ₂ /PTMO (mol/wt)
49%	22.5	89.3	3.7e-3
54%	26.2	91	4.5e-3
58%	29.5	92.3	5.2e-3
66%	37	94.3	7.3e-3

M(X)-PTMO(2K)-0.0-0.06 HCl			
ZrOPr (wt%)	ZrO ₂ (wt%)	ZrO ₂ (mol%)	ZrO ₂ /PTMO (mol/wt)
35%	17.9	80.2	1.77e-3
40%	21.3	83.3	2.19e-3
50%	28.8	88.2	3.3e-3
57%	34.9	90.9	4.4e-3

M(X)-PTMO(2K)-100-0.014 PSS			
TEOS (wt%)	TEOS (wt%)	TEOS (mol%)	TEOS/PTMO (mol/wt)
40%	17.1	88.6	3.4e-3
50%	23.7	92.2	5.2e-3
60%	31.7	94.7	7.8e-3
70%	41.9	96.5	12.2e-3

to grams of PTMO for the three types of CERAMER, TiOPr/PTMO, ZrOPr/PTMO, and TEOS/PTMO illustrates a linear relationship (Figure 6-9). The Young's modulus data for the TEOS system was obtained from the TEOS/PTMO system catalyzed with poly(styrene sulfonic acid) which was described in Chapter 4. The poly(styrene sulfonic acid) catalyzed TEOS/PTMO CERAMER was selected for this comparison since it has been shown these materials have a higher extent of conversion than comparable systems catalyzed with HCl (Chapter 4). The mechanical response and $\tan \delta$ behavior of the TiOPr/PTMO CERAMERs indicate the networks are also cross-linked more extensively than the equivalent composition of TEOS/PTMO catalyzed with HCl [27] and thus the PSS catalyzed TEOS/PTMO gels were selected for this comparison. The linear relationship as indicated in Fig 6-9 between the three different systems suggests a dependence of the elastic modulus on the volume fraction of the inorganic phase. The fact that the plots of the TiOPr/PTMO CERAMERs and the ZrOPr/PTMO CERAMERs had similar slopes to each other, but significantly different than the TEOS/PTMO CERAMERs, suggested an interaction beyond a simple volume fraction relationship.

Recently, Vollenberg and coworkers determined the Young's modulus of a number of different "filled" polymeric composites as a function of filler particle size and surface treatment [95,96]. The polymers used as the matrix phase were polystyrene, polycarbonate and polypropylene. The fillers were either alumina beads or glass beads which ranged in size from 0.035 μm to 100 μm . Vollenberg et. al.

reported that the modulus was dependent upon the filler particle size when the particles were not pretreated with silane coupling agents. However, when the surface of the particle was conditioned with a silane coupling agent, the Young's modulus was dependent upon the volume fraction of filler particles and not the particle size. The inorganic phases in the CERAMERs represent an optimally modified surface for bonding to with respect to the oligomers used. The silane functionalization of the oligomers, e.g. PTMO, enhances the chemical bonding of the polymer chain ends to the growing filler particle, i.e. the inorganic phase. Thus, the linear relationship demonstrated in Fig. 6-9 was re-examined in terms of the volume fraction of the inorganic phase.

The term moles TiO_2 /mass PTMO can be converted to the ratio of the volume fractions of the TiO_2 to the volume fraction of PTMO by first converting the moles TiO_2 to grams TiO_2 and then dividing by the specific volume, i.e. the reciprocal of its density. Dividing the mass of PTMO by its specific density yields the term TiO_2 /PTMO with units of volume/volume. Since the plot for each of the three CERAMER types was linear (Fig. 6-9), then one can readily show that:

$$E = m\left(\frac{\text{TiO}_2(cc)}{\text{PTMO}(cc)}\right) + b \quad [6-1]$$

where E is the Young's modulus, m is the slope and b is the y-intercept. The volume ratio of TiO_2 to PTMO can readily be rearranged such that it is a representation of the volume fraction of TiO_2 to the volume fraction of PTMO. The plots of the three metal oxide modified CERAMERs Young's moduli versus the volume fraction of the inorganic phase to the matrix, i.e. PTMO are illustrated in Figure 6-10 (The values of the specific volume were obtained from reference 1.). The Young's modulus of the TiOPr/PTMO CERAMERs increases at a rate of 4.5 GPa compared to the elastic modulus of the ZrOPr/PTMO CERAMERs which changed at rate of 3.4 GPa as a function of the ratio of volume fractions of TiO_2 to PTMO (Fig. 6-10). The values are reasonably close in consideration of the large variation in the measured values of the elastic modulus of the ZrOPr/PTMO CERAMERs (Table 6-3). The Young's modulus of the TEOS/PTMO CERAMER which was much less sensitive to the level of metal alkoxide added, increased at a rate of only 0.7 GPa as plotted in Figure 6-10. The exact relationship of the slope was not determined, but, one might predict it scales with the sum of two other moduli, the modulus of the inorganic phase and the modulus of the interphase which would be defined by the nature of mixing between the inorganic structure and the oligomer. The y-intercept for the three plots varied significantly. It would be logical to equate the modulus of the unfilled crosslinked PTMO with the variable b in equation 6-1. This would reflect the lower limit of the CERAMERs Young's modulus, where the metal alkoxide volume fraction approaches zero. The different rates of increase of Young's

modulus with increasing concentration of the inorganic component in the CERAMERs was attributed to differences in the nature of the surfaces of the inorganic phases which one might expect to impact changes in the elastic modulus of the resin. However, this is all speculative in nature since the actual volume fraction of the inorganic phase is not known. This of course explicitly states that the volume fraction of PTMO is also unknown since the system has been treated as a two phase network.

6.2.3 Small Angle X-ray Scattering Behavior

6.2.3.1 Effect of Metal Alkoxide to PTMO Ratio

The dynamic mechanical behavior of both the titanium and the zirconium CERAMERs along with their mechanical properties indicated there was some microphase separation. Since the TiOPr/PTMO were clear, transparent monoliths the same as the TEOS/PTMO CERAMERs, the dimensions of the phases must be less than ca. 200 nm., which would minimize scattering of visible light. Thus, the SAXS behavior of the TiOPr/PTMO was investigated as a means of determining the dimensions of the phases. The SAXS profiles, plotted as the scattered intensity versus the angular factor s , are presented in Figure 6-11 for the CERAMER compositions TiOPr(X)-PTMO(2K)-25-0.06 where X was 25%, 49%, 54%, 58%, or

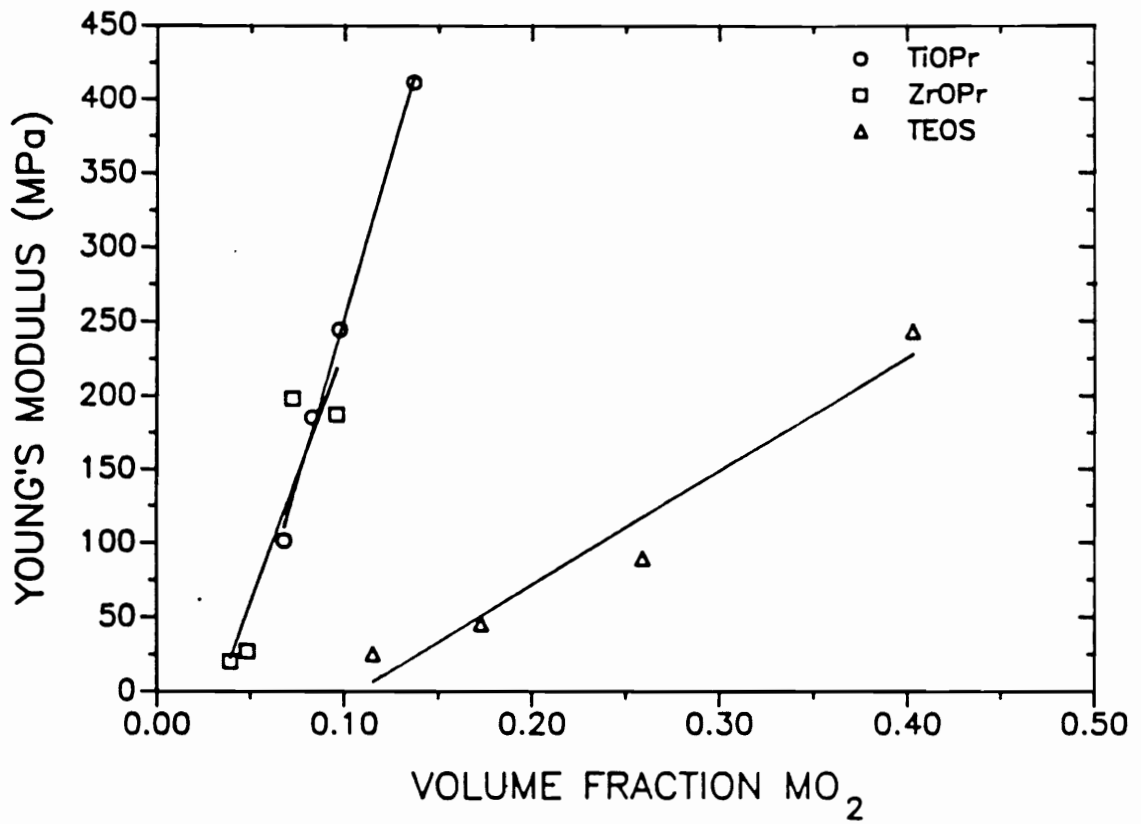


Figure 6-10 Young's modulus as a function of volume fraction of inorganic component

66%. The maxima of the scattered intensity in the SAXS profiles (Fig. 6-11), as previously described (Chapter 4), correlates with a characteristic spacing of two phases of the same electron densities. The characteristic length for the TiOPr(X)-PTMO(2K)-25-0.06 series increases from a value of ca. 7.4 nm to a value of 14 nm as the initial weight fraction of TiOPr was increased from 25% to 66%, respectively.

The SAXS profiles of the ZrOPr(X)-PTMO(2K)-0.0-0.06 series in Figure 6-12 resemble those of the TiOPr/PTMO CERAMERS plotted in Figure 6-11 in terms of their overall shape. The SAXS profile of the composition ZrOPr(57)-PTMO(2K)-0.0-0.06 did not exhibit a distinct maxima which the other compositions with lower levels of ZrOPr did, i.e. 50%, 45% and 35%. However, the size of the characteristic length, as determined from the reciprocal of the s value which corresponds to the maximum scattered intensity of the SAXS profile for the ZrOPr/PTMO hybrid materials, increased from a value of ca. 12 nm to ca. 16 nm as the ratio of ZrOPr to PTMO was increased from 35% to 50% (Fig. 6-12). Thus, the dimensions which correlate with the average spacing between the inorganic phases are somewhat larger for the ZrOPr/PTMO CERAMER ZrOPr(50)-PTMO(2K)-0.0-0.06 compared to the equivalent composition, TiOPr(49)-PTMO(2K)-25-0.06, in the TiOPr/PTMO series of hybrid materials (Fig. 6-11). The SAXS maximum scattered intensities generated by the ZrOPr/PTMO gels were also significantly higher than the maximum scattered intensities determined for equivalent compositions of the TiOPr/PTMO materials.

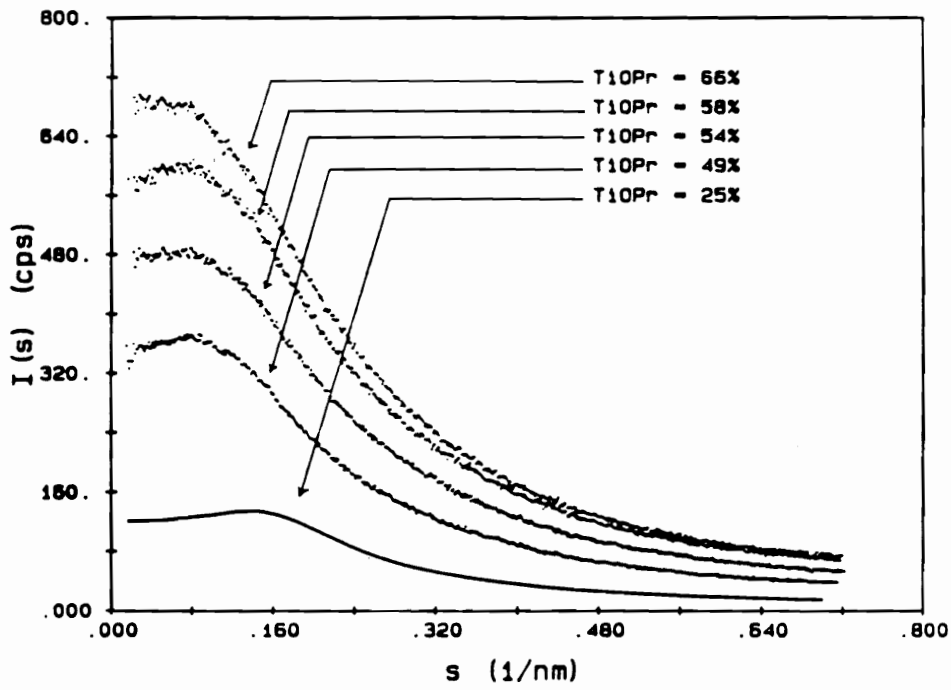


Figure 6-11 SAXS behavior of CERAMERs as a function of TiOPr to PTMO ratio: TiOPr(X)-PTMO(2K)-25-0.06

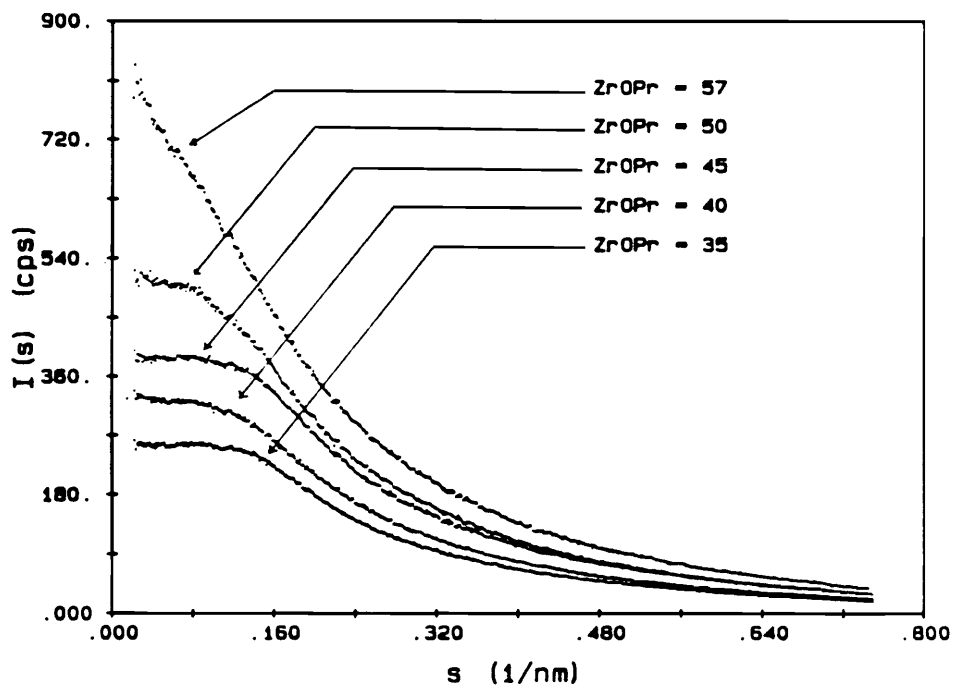


Figure 6-12 SAXS behavior of CERAMERs as a function of ZrOPr to PTMO ratio: ZrOPr(X)-PTMO(2K)-0.0-0.06

The higher intensity of the scattered radiation associated with the SAXS behavior of the ZrOPr/PTMO CERAMERs compared with the TiOPr/PTMO CERAMERs is illustrated in Figure 6-13 along with the SAXS profile for the CERAMER composition TEOS(50)-PTMO(2K)-100-0.014 PSS. The maxima of the SAXS profiles intensified as the reactivity of the metal alkoxide increased. The explanation for the large increase in the SAXS intensities for the CERAMER compositions with the more reactive metal alkoxides can be explained in terms of the structure that causes the scattering. As described earlier, the intensity of the scattered radiation from a SAXS experiment can be described by the relationship:

$$I(s) = 4\pi i_e \langle \Delta \rho^2 \rangle V \int_0^\infty \gamma(r) \frac{\sin(2\pi sr)}{2\pi sr} r^2 dr \quad [4-1]$$

where $\langle \Delta \rho^2 \rangle$ represents the mean square electron density fluctuation, V is the illuminated sample volume, i_e is the Thomson scattering constant for an electron and $\gamma(r)$ is the correlation function which represents a measure of the spatial inhomogeneity in the electron density. The term s as previously described is the angular vector which is given by the expression $2\sin\theta/\lambda$ where θ is one-half the radial scattering angle and λ is the wavelength of the incident x-ray beam. Equation 4-1 illustrates that the intensity of the scattered radiation is directly proportional to the mean square electron density fluctuation of the sample. The mean square

electron density fluctuation of a system for a sharp boundary two phase system is described by the following relationship:

$$\langle \rho^2 \rangle = \varphi_1 \varphi_2 (\rho_1 - \rho_2)^2 \quad [6-2]$$

where φ_1 and φ_2 represent the volume fractions of phase 1 and phase 2 respectively. The terms ρ_1 and ρ_2 are the electron densities of phases 1 and 2, respectively. The validity of this relationship in describing electron density fluctuations within the TiOPr/PTMO and ZrOPr/PTMO CERAMERs depends upon the extent of mixing between phases which will define the thickness of the phase boundaries. It is reasonable to assume the phase boundaries between the inorganic structure and PTMO are sharp if one considers the boundary as the bond between the silicon atom and carbon atom of the propyltriethoxy silane end groups of the functionalized PTMO chains. The electron density of the inorganic structure, however, will be expected to vary as a function of the extent of condensation and the electron density of the metal, i.e. $Zr > Ti > Si$. Thus, the increased scattering by the CERAMERs with ZrOPr compared to TiOPr which is greater than the TEOS/PTMO CERAMERs, is attributed largely to a higher contrast factor provided by the higher electron density in the inorganic phase with increasing atomic weight of the metal.

The overall morphology of the three system does not appear to differ significantly as deduced from the similarity of the three SAXS profiles (Fig. 6-13).

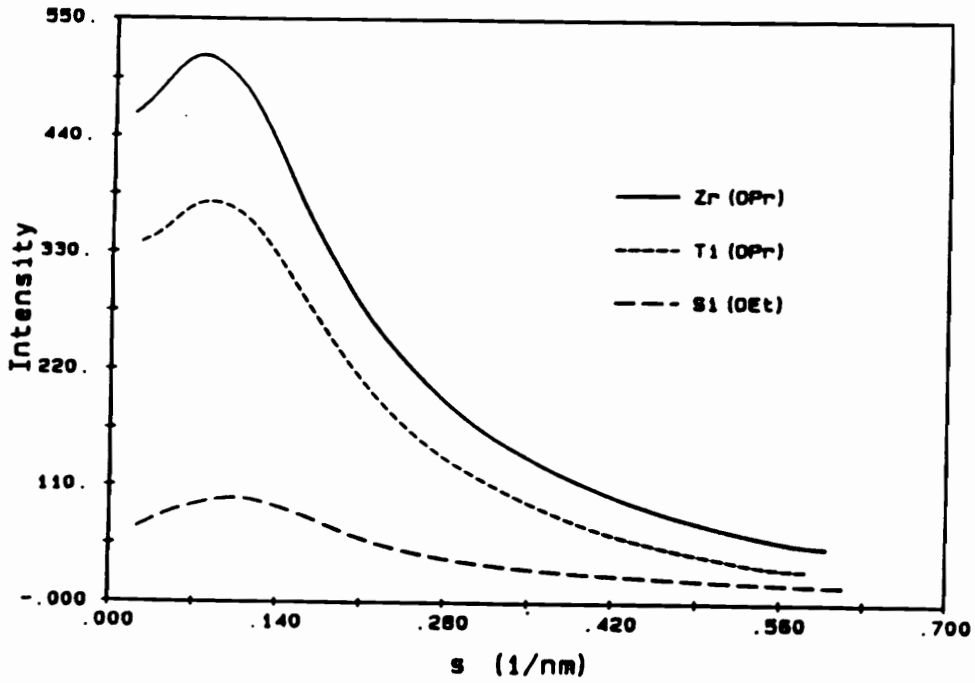


Figure 6-13 SAXS behavior of CERAMERs as a function of metal alkoxide: MO(50)-PTMO(2K)-Y-0.06, where Y is 0, 25, 100 when M is ZrOPr, TiOPr, and TEOS, respectively.

Therefore, the differences in the intensities must be related to the higher electron density of the inorganic structures as previously stated. This assumes that the density of the PTMO phase (δ_1) is constant throughout the different CERAMER compositions. The other factor to consider here is the d spacing which as stated previously is an estimate of the interdomain spacing that was shown in Chapter 4 to vary with the molecular weight of the oligomer. Yet, another contributing factor to the spacing would be the size of the inorganic phase. As the inorganic phase increases in size, the d spacing, as estimated by the reciprocal of the s value, should also increase if the sharp phase boundary assumption is valid and the molecular weight of the oligomers remains constant. The plot of initial weight percent of TiOPr versus d-spacing in Figure 6-14 clearly illustrates the increase in the characteristic length of the TiOPr(X)-PTMO(2K)-25-0.06 CERAMERs as the value of X was changed from 25% to 66%. The intensity of the SAXS profiles increasing with the higher levels of TiOPr in the TiOPr(X)-PTMO(2K)-25-0.06 CERAMERs could be attributed to both an increase in the volume fraction of the metal alkoxide and an increase in the density of the TiOPr phase. An analysis of this for the three CERAMER systems, ZrOPr/PTMO, TiOPr/PTMO and TEOS/PTMO; is presented in Appendix I. It would appear from this analysis that both an increase in the volume fraction of the metal alkoxide and a higher density of the inorganic phase contribute to the higher intensities of the SAXS profiles in Fig. 6-11, 6-12 and 6-13.

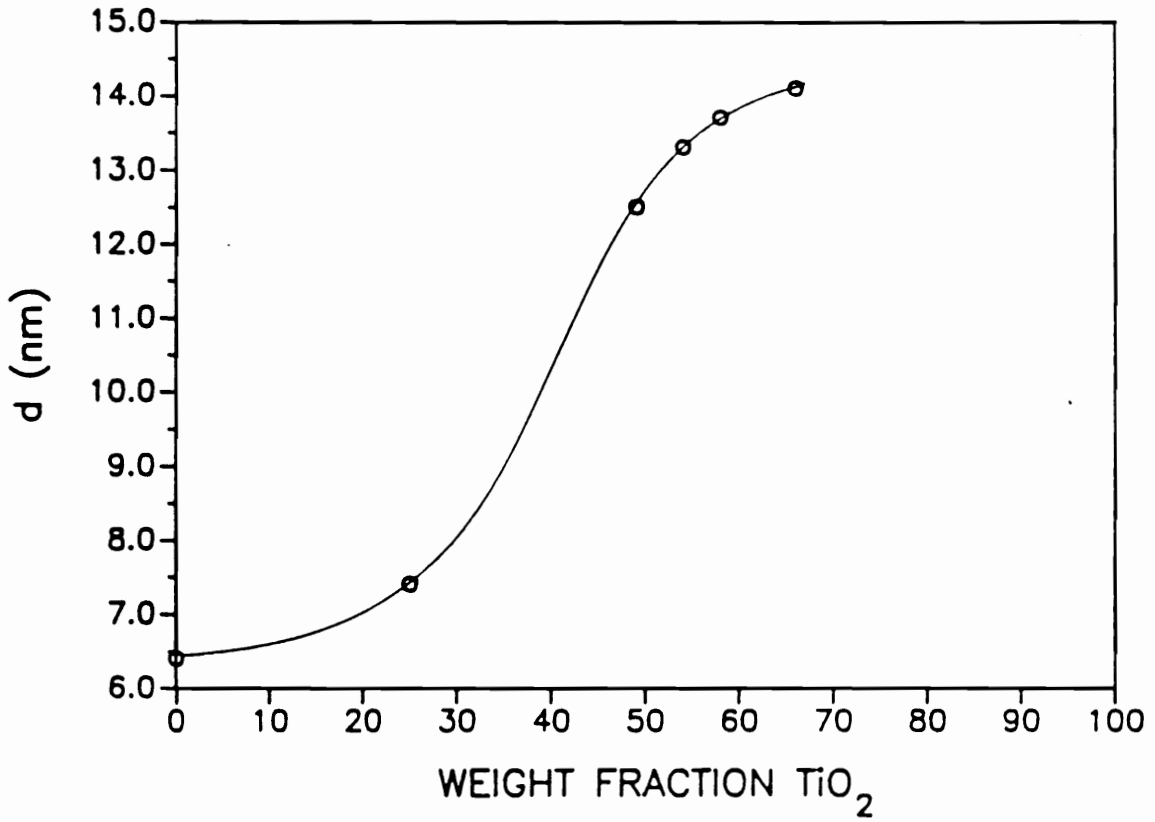


Figure 6-14 Weight fraction of TiOPr as a function of d spacing (SAXS): $\text{TiOPr(X)}\text{-PTMO(2K)}\text{-25-0.06}$.

The CERAMER morphological model which was developed based upon their structure/property behavior has been described in detail for the TEOS/PTMO hybrid materials in this thesis as well as in numerous other publications [18,24,30]. The model, which is illustrated in Figure 6-15, defines the spatial relationships of the structures formed from the sol-gel processing of the inorganic components, i.e. TEOS, TiOPr and ZrOPr and the organic component, i.e. PTMO oligomers. It illustrates the general relationship between the inorganic network and the PTMO segments in terms of varying degrees of mixing as described above. The inverse relationship of the scattering factor s and the characteristic length d was depicted as the spacing between two regimes with a high concentration of the inorganic component on a relative basis. The increase in the characteristic dimension d with the increasing reactivity of the metal alkoxide, i.e. TEOS, TiOPr, and ZrOPr, can be accounted for by the model in terms of the size of the inorganic.

6.2.4 Thermal Analysis

6.2.4.1 Differential Thermal Analysis

The aging of the TEOS/PTMO CERAMERs catalyzed with different acids was described in Chapter 4 of this thesis and as a function of processing conditions in prior publications from this laboratory (18,24,30). The trends observed in most

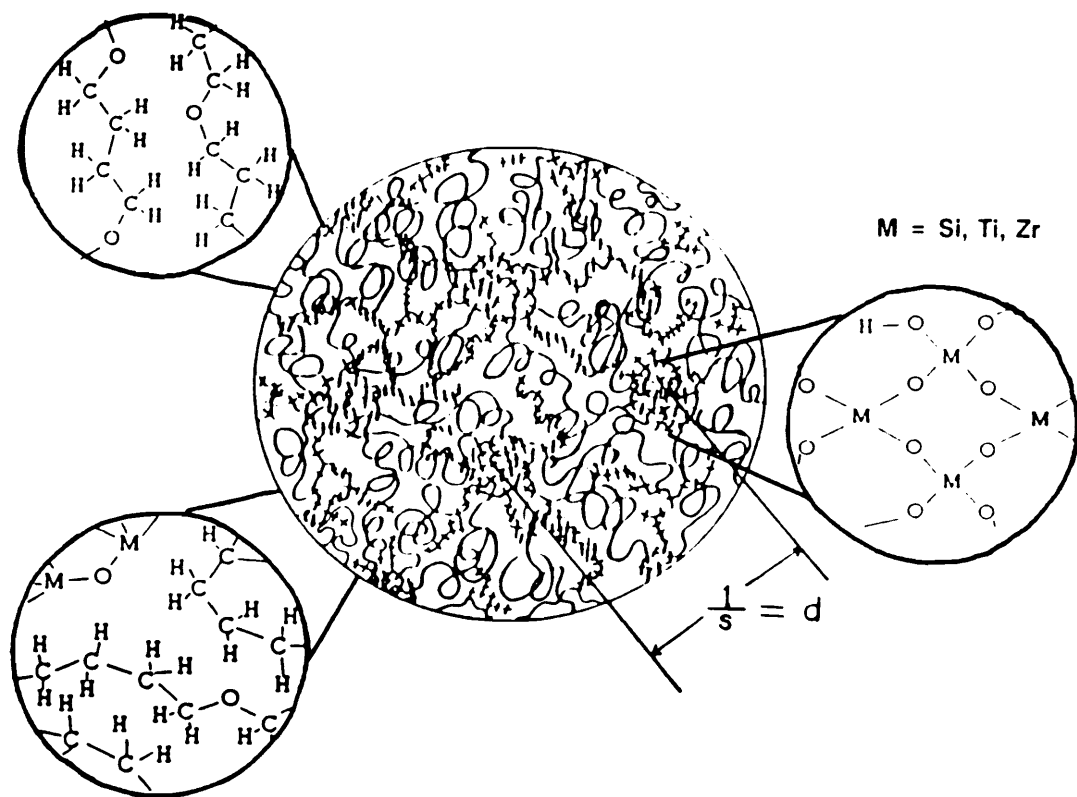


Figure 6-15 Morphological model of CERAMERs as a function of metal alkoxides; i.e. TEOS, TiOPr, or ZrOPr in combination with functionalized PTMO.

of the CERAMERs in terms of aging were attributed to increases in the extent of condensation of reactive hydroxyl groups along with a loss of solvent. These changes in the CERAMERs with time result in a rise in the Young's modulus, a rise in the stress at break, a decrease in the overall percent elongation, and an increase in the maximum scattered intensity measured. The TiOPr/PTMO CERAMERs and ZrOPr/PTMO CERAMERs did not appear to exhibit any dramatic changes in the aforementioned properties with time. There was the typical loss of solvent (clearly noted by odor), but the TiOPr/PTMO and ZrOPr/PTMO CERAMER's overall properties did not display the sensitivity to time exhibited by the CERAMERs based upon TEOS and PTMO.

The TiOPr/PTMO and ZrOPr/PTMO CERAMERs gelled very quickly, ca. 1 to 2 hours, compared to the TEOS/PTMO CERAMERs which required at least 12 to 18 hours for gelation. Thermal gravimetric analysis of the TiOPr(49)-PTMO(2K)-25-0.06 CERAMER composition as a function of heating in the Rheovibron revealed little to no change at temperatures below ca. 320°C (Figure 6-16). Samples of the CERAMER were removed from the Rheovibron after quenching to -150°C and heating at a rate of 1°C to 2°C per minute to 100°C and to 175°C. The only measurable change in weight loss was at the temperature of ca. 420°C. The sample heated in the Rheovibron to 175°C had approximately 3% less overall loss compared to the sample heated to 100°C. This is contrasted by the thermogram of the gelled sample versus one that was quenched to -150°C and

heated to ambient at a rate of ca. 1°C to 2°C per minute. Both these samples had an overall weight loss of ca. 85% and there was no difference in their thermogravimetric behavior in the temperature range of 20°C to 800°C. All the samples after heating to 800°C were a pure white residue which was brittle, but very abrasive. The differences noted in the TGA analysis indicated some changes may have occurred in the inorganic phases as a result of heating the samples to 100°C and 175°C. This is based upon the large loss beginning at ca. 250°C which is most likely due to thermal oxidative degradation of the PTMO.

DSC measurements were made on a series of the TiOPr(X)-PTMO(2K)-25-0.06 CERAMERs, where X was either 25, 50 or 75, to determine if any changes in the gels occurred early after gelation and could be attributed to the sol-gel reactions. Figure 6-17 illustrates there were differences in the DSC profiles for the three formulations described. The T_g of the TiOPr(25)-PTMO(2K)-25-0.06 gel is given on the first thermogram as -74.0°C, which may be slightly lower than the value abstracted from the $\tan \delta$ behavior given in Fig. 6-1, but clearly reflects the high volume fraction of PTMO in the CERAMER. It is important to also note that this T_g of -74.0°C indicates the PTMO chains must not be mixing to any large degree with the inorganic phase, otherwise one would expect the T_g to be higher in temperature. There is upon addition of more TiOPr, e.g. TiOPr(50)-PTMO(2K)-25-0.06 and TiOPr(75)-PTMO(2K)-25-0.06, a decrease in the magnitude of the change in the heat capacity at the T_g as one would predict for a second order transition with

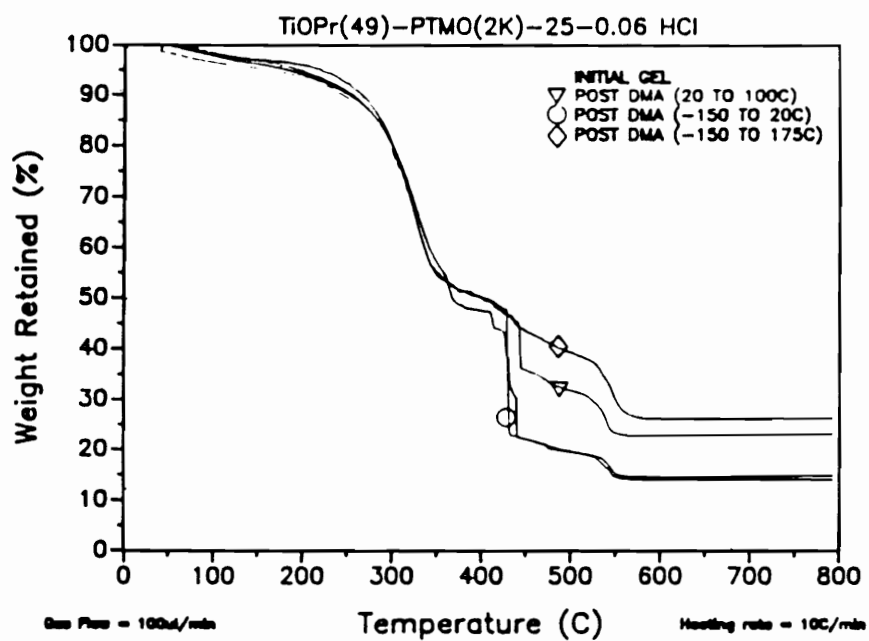


Figure 6-16 Thermal gravimetric behavior of TiOPr(50)-PTMO(2K)-25-0.06 CERAMERs as a function of different heat treatments

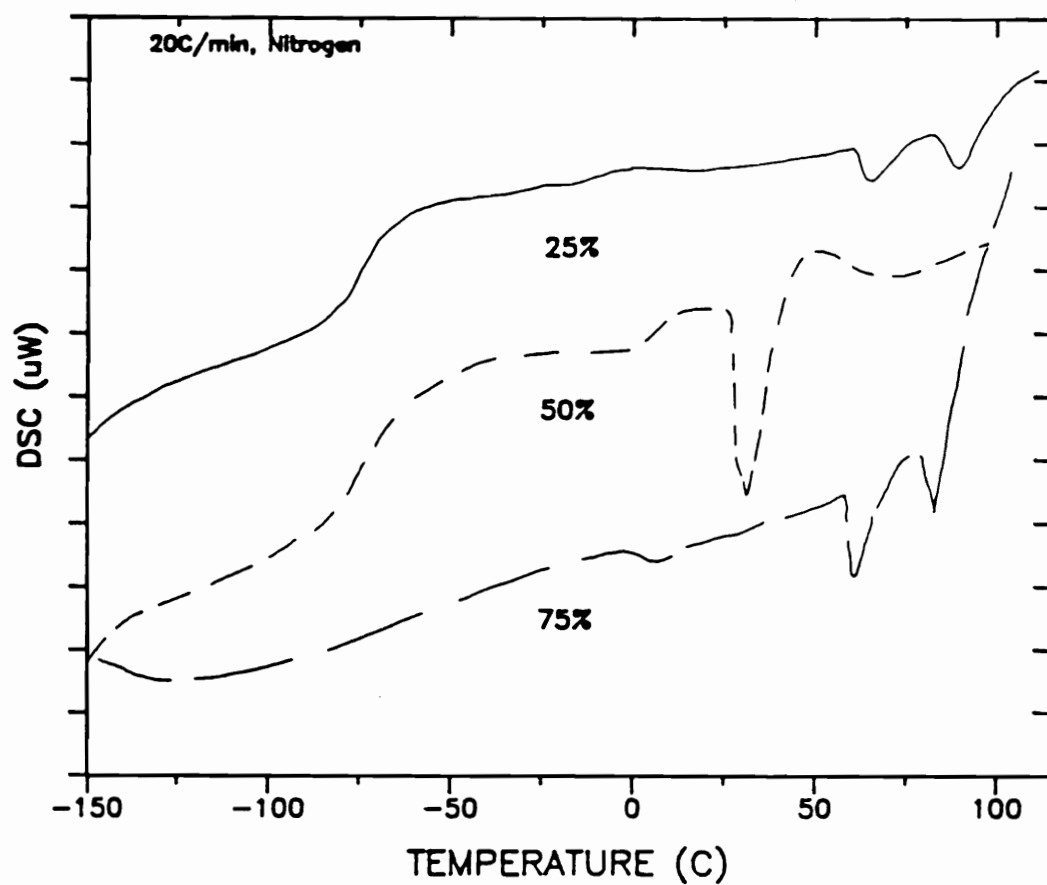


Figure 6-17 DSC analysis of CERAMERS as a function of TiOPr to PTMO ratio: TiOPr(X)-PTMO(2K)-25-0.06 where X is 25, 50 or 75.

the decrease in PTMO volume fraction. There are a number of exotherms associated with the heating of the composition TiOPr(25)-PTMO(2K)-25-0.06, beginning at ca. 60°C and 82°C, which are not present in the DSC trace of the composition TiOPr(50)-PTMO(2K)-25-0.06. The gel TiOPr(50)-PTMO(2K)-25-0.06 does have a single large exotherm which begins at ca. 35°C and another broad exotherm which extends from ca. 48°C to nearly 90°C. The CERAMER composition TiOPr(75)-PTMO(2K)-25-0.06 has a number of exotherms that occur in the same temperature range of the composition TiOPr(25)-PTMO(2K)-25-0.06 but not at the exact same temperatures. The nature of these were investigated using the composition TiOPr(25)-PTMO(2K)-25-0.06 by performing a second run. It must be noted that all the CERAMERs upon heating to 100°C discolor and some develop cracks that indicate some structural changes occur (Recall that the TGA analysis did not reveal significant weight loss below 100°C). Figure 6-18 illustrates differences between the first and second runs of the gel TiOPr(25)-PTMO(2K)-25-0.06 are significant in terms of the upper temperature exotherms only. The lower temperature transition associated with the T_g was not changed by the second heating. The two upper temperature exotherms were, however, eliminated and a large exotherm was measured at ca. 46°C. The third run was not performed on this sample. The nature of these exotherms is not understood, but it was noted that a step increase in the DSC trace occurred in the second heat (Fig. 6-18) of the gel TiOPr(25)-PTMO(2K)-25-0.06 and before the endotherm of the composition

TiOPr(50)-PTMO(2K)-25-0.06 (Fig. 6-17). These results were reproducible, but apparent degradation of the PTMO made it difficult to reheat these materials to 120°C which was the typical maximum. Further studies using TG/Mass spectroscopy or TG/FTIR would be useful in identifying the nature of the changes which occur in the CERAMERs described here.

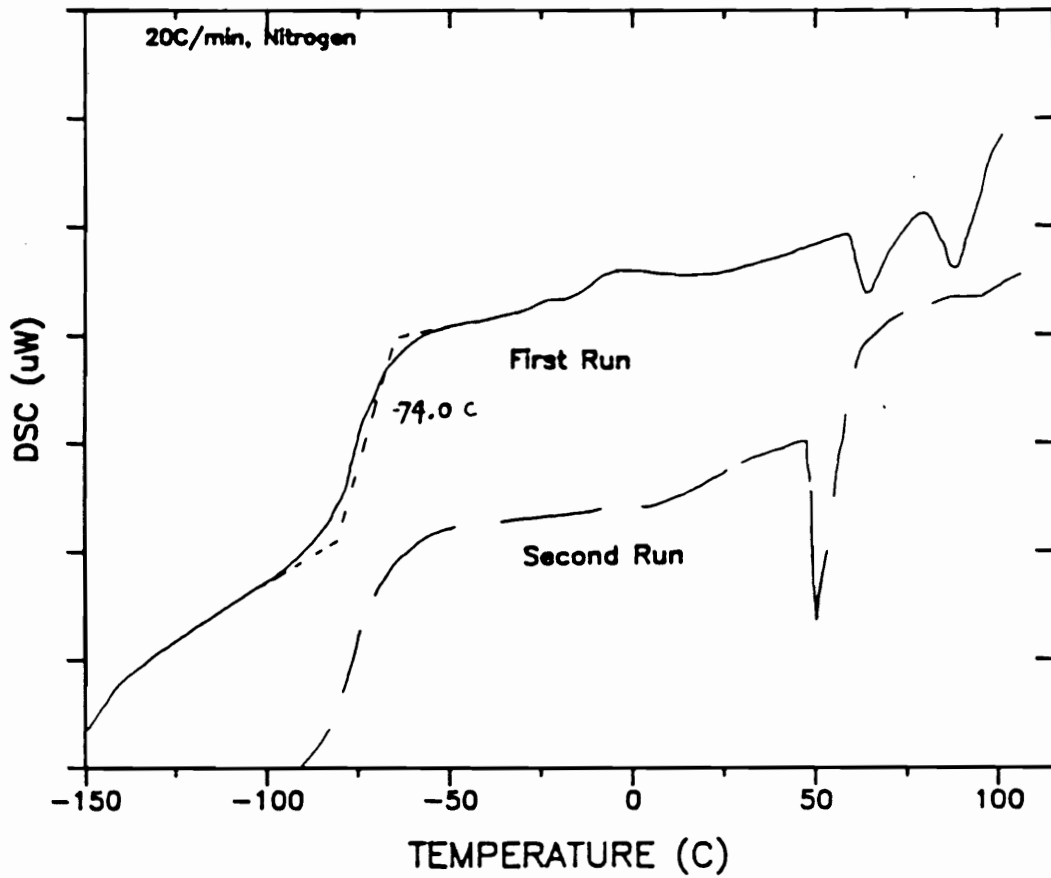


Figure 6-18 Comparison of first and second DSC runs of CERAMER TiOPr(25)-PTMO(2K)-25-0.06.

6.3 CONCLUSIONS

A new generation of hybrid materials have been developed which are based upon the incorporation of titanium tetra-isopropoxide and zirconium tetra-n-propoxide into networks with silane endcapped PTMO oligomers. The loss dispersion behavior of these two new CERAMERs is similar to previously described CERAMERs composed of TEOS and the silane endcapped PTMO oligomers. There were significant differences in the loss dispersion behavior of the TiOPr/PTMO and ZrOPr/PTMO CERAMERs compared to those prepared with TEOS and PTMO. The TiOPr(49)-PTMO(2K)-25-0.06 and ZrOPr(50)-PTMO(2K)-0.0-0.06 networks exhibited a low temperature loss dispersion with a maxima at ca. -70°C compared to the TEOS/PTMO type CERAMERs which had a typical maxima at ca. -10°C to 0°C for the general composition of TEOS(50)-PTMO(2K)-100-0.014 (Chapter 4). This low temperature dispersion which is ascribed to molecular relaxations of the PTMO oligomers reflects the level of interaction between the PTMO and inorganic structures. In the case of the TiOPr/PTMO and the ZrOPr/PTMO CERAMERs the temperature at which the maximum loss dispersion was measured, equaled that of the pure PTMO and thus indicates little mixing between the two phases compared to equivalent compositions of TEOS and PTMO.

The maximum stress ranges from 19 MPa to 40 MPa as the level of titanium isopropoxide (X) was increased from 49% to 66% in TiOPr(X)-PTMO(2K)-25-0.06,

respectively. The Young's modulus increased from 101 MPa to 411 MPa for the same materials. The stress elongation isotherms for the TiOPr/PTMO and ZrOPr/PTMO CERAMERs exhibit a yield point which was not observed in TEOS/PTMO CERAMERs. The ultimate properties of the ZrOPr/PTMO CERAMERs were lower in magnitude than the TiOPr/PTMO CERAMERs of equivalent composition. This is most likely related to the deficiency of water for hydrolysis in the zirconium based CERAMERs. A relationship between the Young's modulus and the ratio of mole fraction of titania to weight of PTMO was demonstrated for the TiOPr/PTMO CERAMERs.

The SAXS behavior of these two new CERAMERs indicated a microphase separated morphology similar in nature to previously described systems based upon TEOS and the silane end capped PTMO. The correlation lengths in these systems ranged from nearly 12 nm. to a maximum of ca. 17 nm. for the TiOPr(49)-PTMO(2K)-25-0.06 and the ZrOPr(57)-PTMO(2K)-25-0.06 CERAMERs, respectively. The morphological model developed for CERAMERs earlier was modified slightly to account for the loss dispersion behavior and mechanical behavior of the TiOPr/PTMO and ZrOPr/PTMO CERAMERs.

The thermogravimetric behavior of the TiOPr/PTMO CERAMER composition TiOPr(49)-PTMO(2K)-25-0.06 showed little change in the low temperature portion (ca. below 320°C) of the weight loss profile as a function of different thermal treatments. There was a larger loss of mass upon heating to 800°C

for samples that were kept at room temperature, ca. 20°C or below, ca -150°C. The weight losses occurring above ca. 420°C were attributed to changes in the inorganic structure. The DSC analysis of a series of TiOPr(X)-PTMO(2K)-25-0.06 gels where X was either 25, 50 or 75, provided support for the DMA results which indicated the T_g was approximately -75°C for the CERAMER containing 50 weight percent TiOPr. There were a number of exotherms identified by the DSC analysis at temperatures greater than ca. 35°C. Reheating the sample TiOPr(25)-PTMO(2K)-25-0.06 eliminated the higher temperature exotherms, but resulted in the loss of heat at a temperature ca. 30°C lower than the other two exotherms.

Overall, the higher reactivity of the TiOPr and the ZrOPr metal alkoxides led to a class of CERAMERs with little to no evidence of aging in terms of the methods used to characterize them. The overall mechanical strength was higher for the TiOPr/PTMO and the ZrOPr/PTMO type CERAMERs than comparable TEOS/PTMO formulations. This could be due to the apparent higher extent of reaction in the TiOPr/PTMO and the ZrOPr/PTMO CERAMERs as concluded from the apparent lack of aging.

CHAPTER 7

POLYIMIDE SOL-GEL DERIVED HYBRID MATERIALS

7.1 INTRODUCTION

The incorporation of polymers with a T_g significantly higher than room temperature (ca. 200°C or higher) into the sol-gel derived hybrid networks referred to as CERAMERs was first accomplished by Noell et. al. in this laboratory [29]. The poly(arylene ether ketone) oligomer (PEK) prepared by Noell et. al. was end capped by reacting isocyanatopropyltriethoxysilane with the amine terminal groups of the oligomers to form urea linkages. The functionalized oligomers were then successfully incorporated into a network with TEOS via a sol-gel process. The high T_g required thermal treatments up to ca. 200°C to achieve a high extent of condensation of the metal alkoxide. The success of Noell et. al. with the PEK induced further efforts to seek other high temperature oligomers which could be combined with metal alkoxides to produce other novel systems. The logical choice was a polyimide, because of its high T_g , ca. greater than 250°C, and its excellent chemical resistance.

The incorporation of high T_g oligomers such as polyimides would provide an excellent thermally stable, abrasion resistant coating. However, in addition to the structure of the polyimide oligomers, the nature of the bond formed by the addition of the metal alkoxide functionality was considered critical in achieving a CERAMER with high temperature stability. The urea linkages of the silane end capped PEK oligomers, were considered more stable hydrolytically and thermally than the urethane linkages formed by addition of isocyanatopropyltriethoxysilane to the PTMO oligomers. However, in the presence of acid which has been the most common catalyst for preparation of CERAMERs, both the urethane and urea linkage would be prone to hydrolytic and thermo-oxidative decomposition at temperatures near the T_g of the polyimide oligomers which were described in Chapter 3 of this thesis. Therefore, a major deal of effort was placed on the characterization of oligomers which were end capped with a alkoxy silane by a number of methods. The most promising was a technique developed by Prof. McGrath and co-workers for the polyimides described in Chapter 3, Section 3.3.4.2, which will be referred to as 6F-AMP. The method, referred to as a transimidization, generated functionalized polyimide oligomers which were successfully incorporated into CERAMERs. The resulting gels were clear monoliths which were not achieved with the other functionalized polyimides. Therefore the major emphasis of this chapter will be these materials.

Another class of polyimide based CERAMERS was developed during a three month summer internship at Dow-Corning. The method of preparation as described in Chapter 3, Section 3.3.4.1, involved the functionalization of polyamic acid precursors followed by direct incorporation into the hybrid network. As will be described in this chapter these materials were unique, but the structure-property relationships would indicate the method involving the polyamic acid was not totally successful.

The organization of this chapter will be slightly different from Chapters 4, 5 and 6. This chapter will be divided into basically three sections, Introduction, Results and Discussion, and Conclusions. However, the Results and Discussion section will be subdivided into two sections which will be devoted to the 6F/AMP polyimide CERAMERS and the polyimide CERAMERS made at Dow-Corning.

7.2 RESULTS AND DISCUSSION

7.2.1 TiOPr/6F-BTDA/BisP/AmPTMOS CERAMERS

The method of preparation of the TiOPr/6F-BTDA/BisP/AMP CERAMERS was provided in detail in Chapter 3. However, a number of interesting observations concerning these materials are worth noting. The polyimides were provided as solutions, usually 10 to 15 wt% in NMP with traces of chlorobenzene. The solutions were quite viscous and dark brown, but clear. Normally the procedure followed was similar to the procedure used for preparation of the TiOPr/PTMO CERAMERS, except no water was added beyond that added as a portion of the acid used in the preparation of the titania sol (Chapter 3, Section 3.2.3). This was determined necessary to assure the polyimide would remain in solution throughout the sol-gel process. The endcap was aminophenyltrimethoxysilane and as such was quite sensitive to any moisture. The exposure of the polyimide (functionalized) to any moisture at ambient conditions resulted in the formation of a precipitate almost instantaneously. Therefore, the procedures followed for preparation of these CERAMERS required the exclusion of water from all steps beyond the formation of the titania sol. Incorporation of these polyimide oligomers into monolithic CERAMERS required the sols to be heated to at least 60°C immediately after blending of the polyimide with the titania sol. Attempts to gel these systems at

ambient conditions were unsuccessful. A white precipitate formed as the bottom of two layers within sealed petri dishes after 1 to 2 days at ambient conditions.

A DSC analysis (Figure 7-1) of the CERAMER composition TiOPr(18)-6F/AMP(13K)-0-0.06 was performed after the hybrid network was gelled at 100°C. The first trace at the top of Fig. 7-1 indicates that the T_g was approximately 145°C and following the first, second, third and fourth runs, which were up to ca. 295°C, the T_g was shifted up to ca. 210°C. The fifth run up to ca. 295°C extended the T_g slightly, but a significant broadening occurred in the DSC trace over the temperature range of ca. 185°C to 275°C. In addition, to the broadening, the magnitude of the transition dropped off significantly with each successive heating to ca. 295°C. The results suggest that the T_g was increasing due to increased crosslinking within the network, however, the evidence is insufficient to draw any further conclusions.

The effect of molecular weight of the 6F/AMP oligomers on the T_g was determined by DSC analysis (Figure 7-2) of the three CERAMERs of composition TiOPr(18)-6F/AMP(X)-0-0.06 where X was either 5000 g/mol, 10000 g/mol or 13000 g/mol. It is important to remind the reader that the molecular weights of these oligomers are estimates only based upon the initial stoichiometry and analysis of endgroups by ^1H NMR. Therefore the molecular weight differences should be viewed as relative and the results as trends rather than absolute. The trends, for example in Fig. 7-2, clearly indicate that the T_g increased for the CERAMER compositions as the molecular weight of the oligomer was increased from an

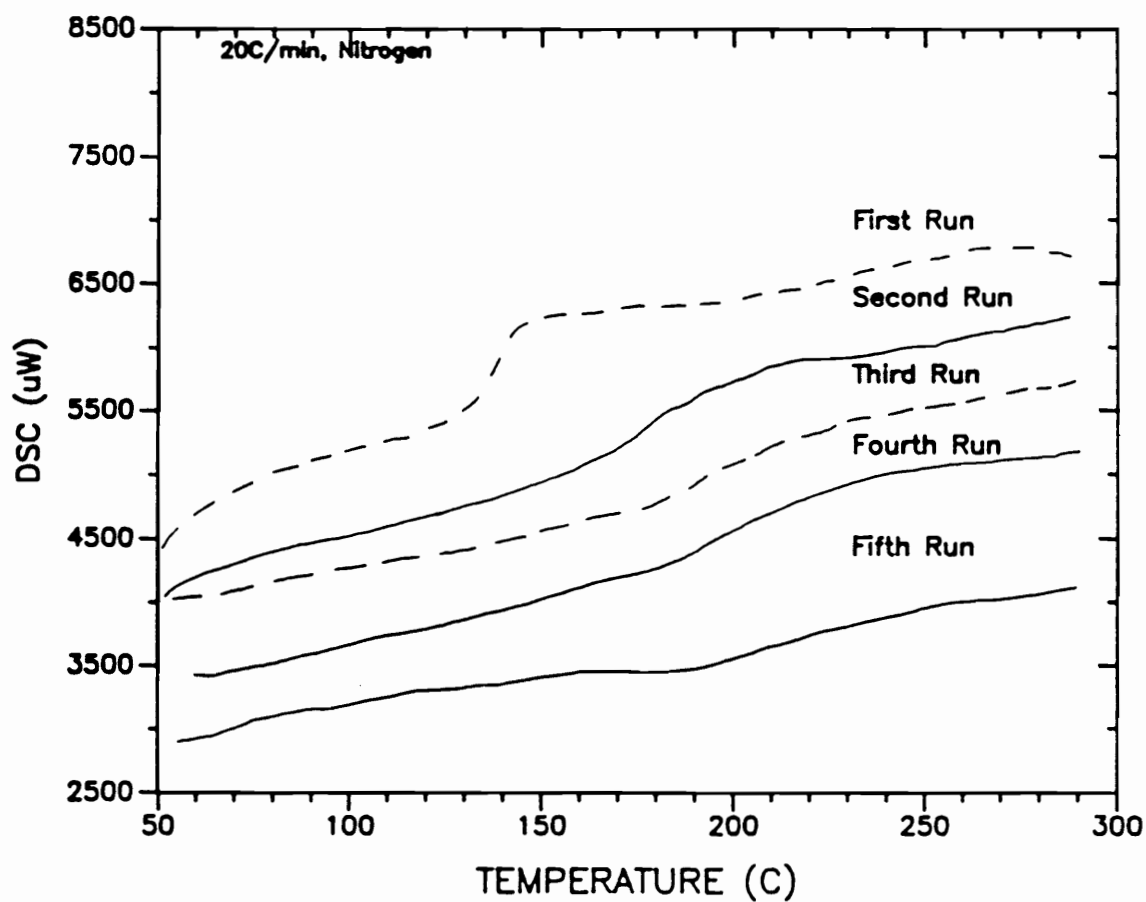


Figure 7-1 T_g of TiOPr(18)-6F/AMP(13)-0-0.06 CERAMERs as a function of cycling to 295°C.

apparent low of ca. 5000 g/mol to a high of ca. 13000 g/mol. All three samples had been heated to 250°C at a rate of approximately 1°C to 2°C per minute prior to the DSC analysis. The T_g indicated of ca. 221°C in Fig.7-2 was for the composition containing the 5000 g/mol oligomer of 6F/AMP. There is a slight shift of T_g by ca. 30°C to 40°C to higher temperatures as the molecular weight of the oligomer was increased from ca. 5000 g/mol to 13000 g/mol.

The T_g was confirmed by analysis of the composition TiOPr(18)-6F/AMP(13K)-0-0.06 with the SEIKO Thermo Mechanical Analyzer in a compression mode. The profile of the samples' deflection under a 1 gm load is illustrated in Figure 7-3. There was a small step at ca. 70°C to 80°C for which no explanation is yet known, but is considered insignificant compared to the overall profile. The major deflection occurred at ca. 270°C as indicated. The two traces, first and second runs, reflect the response of a sample which was gelled at 100°C and then heated slowly, ca. 1°C to 2°C per minute, to 250°C prior to analysis. The results indicate there is a difference of approximately 20°C between the first and second runs. Thus, the T_g of these materials with a level of ca. 18 weight percent TiOPr added is in the range of ca. 225°C to 270°C depending upon the molecular weight of the oligomer and the method of analysis. It appears that the T_g of the system is approximately 270°C as indicated by the discontinuity in the profile of all three compositions which occurs near 270°C.

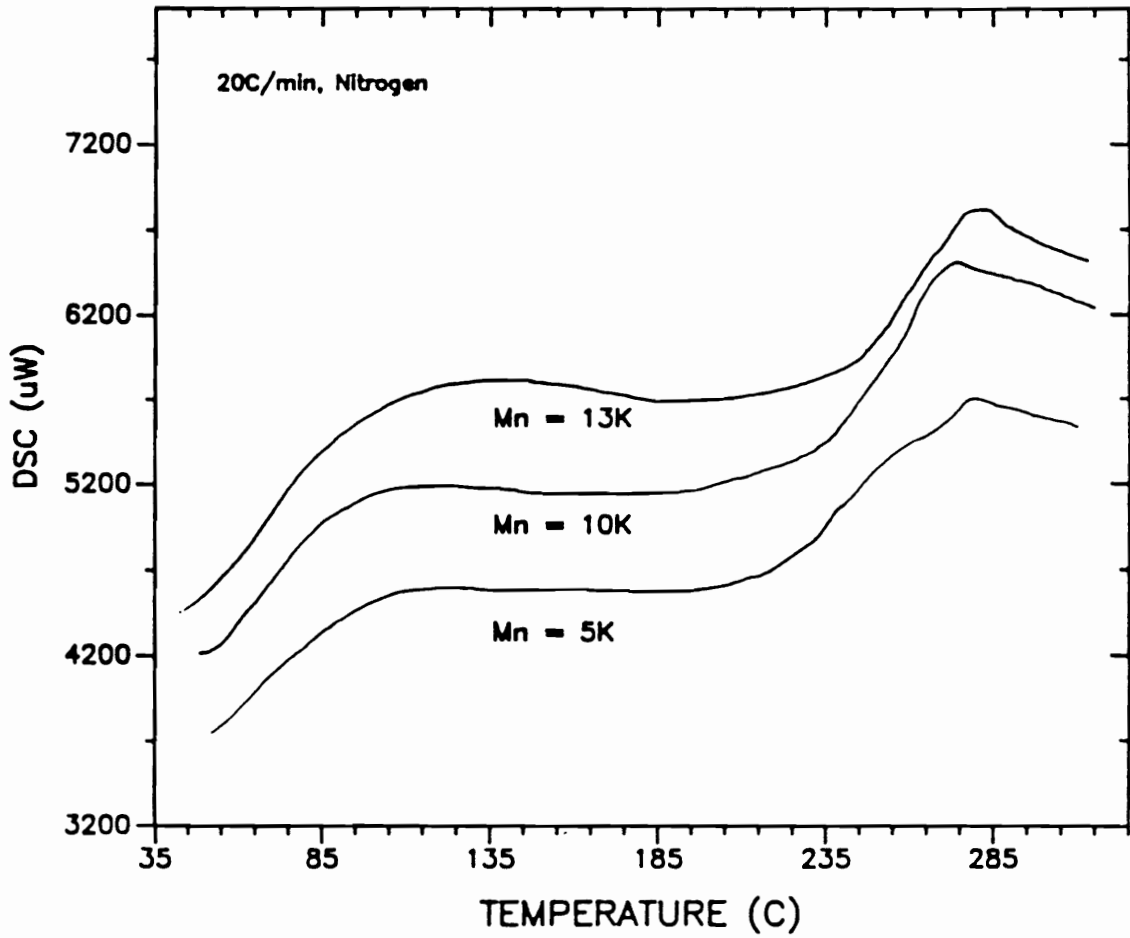


Figure 7-2 T_g of TiOPr/6F/AMP CERAMERs as a function of M_n .

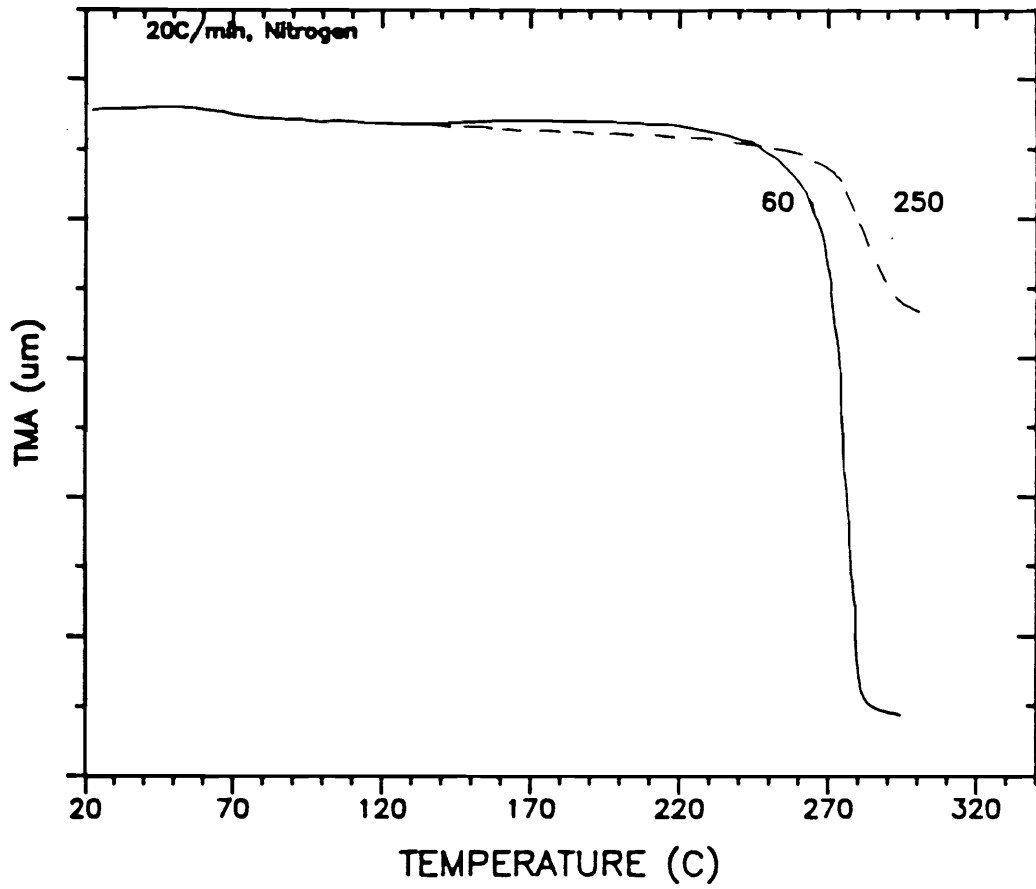
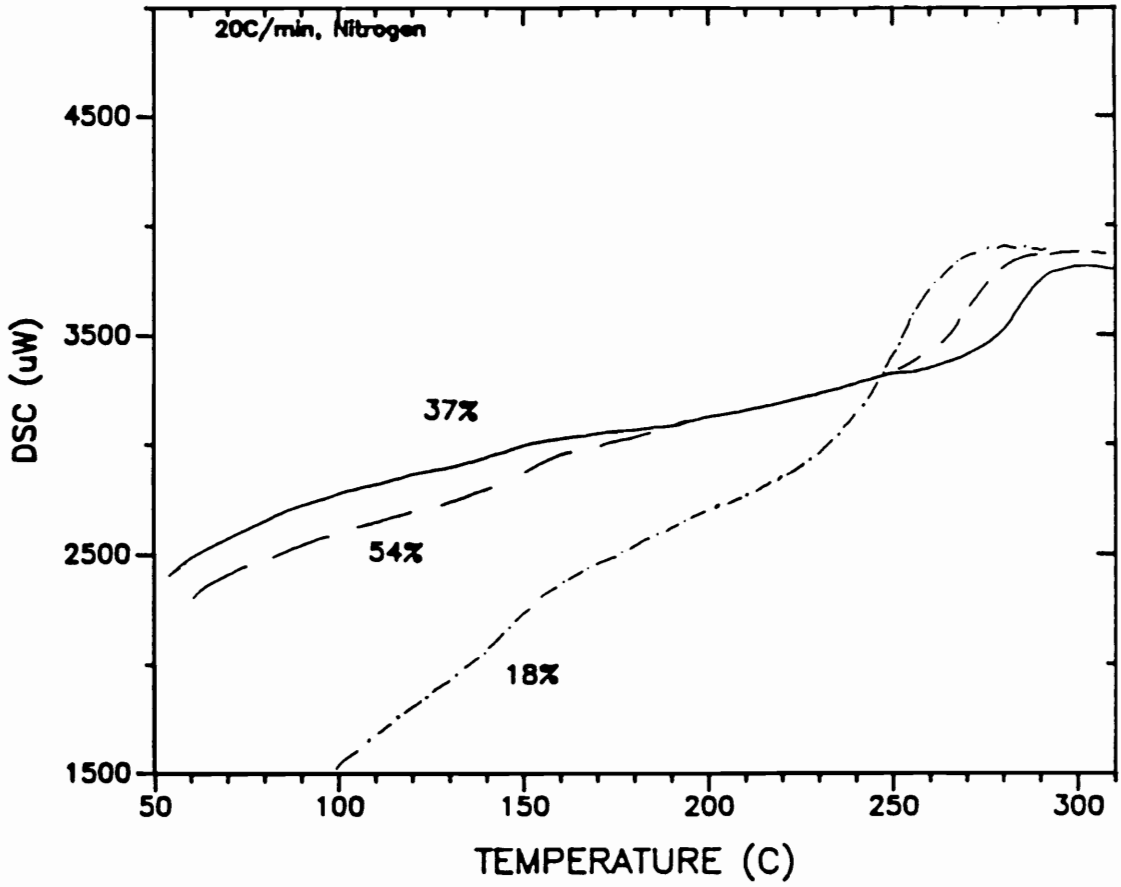


Figure 7-3 Thermal mechanical analysis of TiOPr/6F/AMP CERAMERS.

The effect of the ratio of the metal alkoxide to the 6F/AMP was investigated at three different levels of the TiOPr, 18%, 37% and 54%. The DSC traces in Figure 7-4 which represent the CERAMER compositions TiOPr(X)-6F/AMP(5K)-0-0.06 where X was 18%, 37% or 54%, reflect the thermal transitions of samples following a post cure to 275°C prior to analysis at a rate of 1°C to 2°C per minute. The T_g of the CERAMER composition TiOPr(X)-6F/AMP(5K)-0-0.06 increased from ca. 250°C to 284°C as the TiOPr level was increased from 18% to 54% (Fig. 7-4). However, the T_g increased from ca. 270°C for the composition TiOPr(18)-6F/AMP(5K)-0-0.06 to the highest value of nearly 284°C for composition TiOPr(37)-6F/AMP(5K)-0-0.06 which would be expected based upon the higher inorganic content. Yet, the T_g actually decreased with the addition of more TiOPr beyond the 37% level to 54%. This trend would not be predicted based on the weight loss behavior of the TEOS/PTMO CERAMERS described in Chapter 4, and, thus the decrease in the T_g was attributed to a degradation process such as chain scission.

The curing behavior of the hybrid system TiOPr(54)-6F/AMP(5K)-0-0.06 was examined by DSC and TGA in an attempt to explain the illogical drop in T_g with the higher level of TiOPr. The DSC of a sample gelled at 100°C is depicted in Figure 7-5 along with the DSC profiles of the sample gelled at 100°C and then heated to 175°C or to 275°C. The sample after gelation in an oven at 100°C had a rather broad nondescript DSC trace, whereas following the thermal treatment to 175°C, a clear transition which was attributed to the T_g is now visible in the middle trace (Fig.



Heating rate = 20°C/min.
N₂ purge gas at 50 μ l/min.

Figure 7-4 DSC behavior as a function of the TiOPr to 6F/AMP ratio: TiOPr(X)-6F/AMP(5K)-0-0.06 where X was 18%, 37% or 54%.

7-6). The final treatment to 275°C shifts the T_g higher by approximately 40°C from ca. 150°C (middle DSC trace) to 248°C (bottom DSC trace). The samples were extremely brittle at this stage of the thermal treatments. The TGA profile of the CERAMER composition TiOPr(54)-6F/AMP(5K)-0-0.06 exhibited practically no weight loss prior to ca. 150°C following gelation at 100°C. However, it began to lose weight at a rapid rate near the T_g ca. 248°C and again near 437°C. The first loss could possibly be attributed to the sample losing solvent and to a small extent some of the end products which result from condensation of the metal alkoxides as a result of the sample undergoing a glass transition. The higher temperature loss at ca. 437°C would appear to be related to degradation of the polyimide structure based on the relatively high percent weight decrease.

The thermal stability of the CERAMER TiOPr(54)-6F/AMP(5K)-0-0.06 was compared to the CERAMERs with composition TiOPr(X)-6F/AMP(5K)-0-0.06, where X was either 18% or 54%. The results of analysis by TGA of the three compositions are illustrated in Figure 7-6 as a plot of weight loss versus temperature. Using a weight loss of 5% as the onset of degradation, the temperature associated with this weight loss decreased approximately 70°C when the level of TiOPr added was increased from 18% to 54% (Fig. 7-6). The overall weight loss profiles are quite similar for the samples containing 37% and 54% TiOPr, in that following the rapid rate of loss from ca. 430°C to ca. 600°C, the rate of weight loss up to 900°C was quite low. The sample containing TiOPr(18)-6F/AMP(5K)-0-0.06 did not follow the

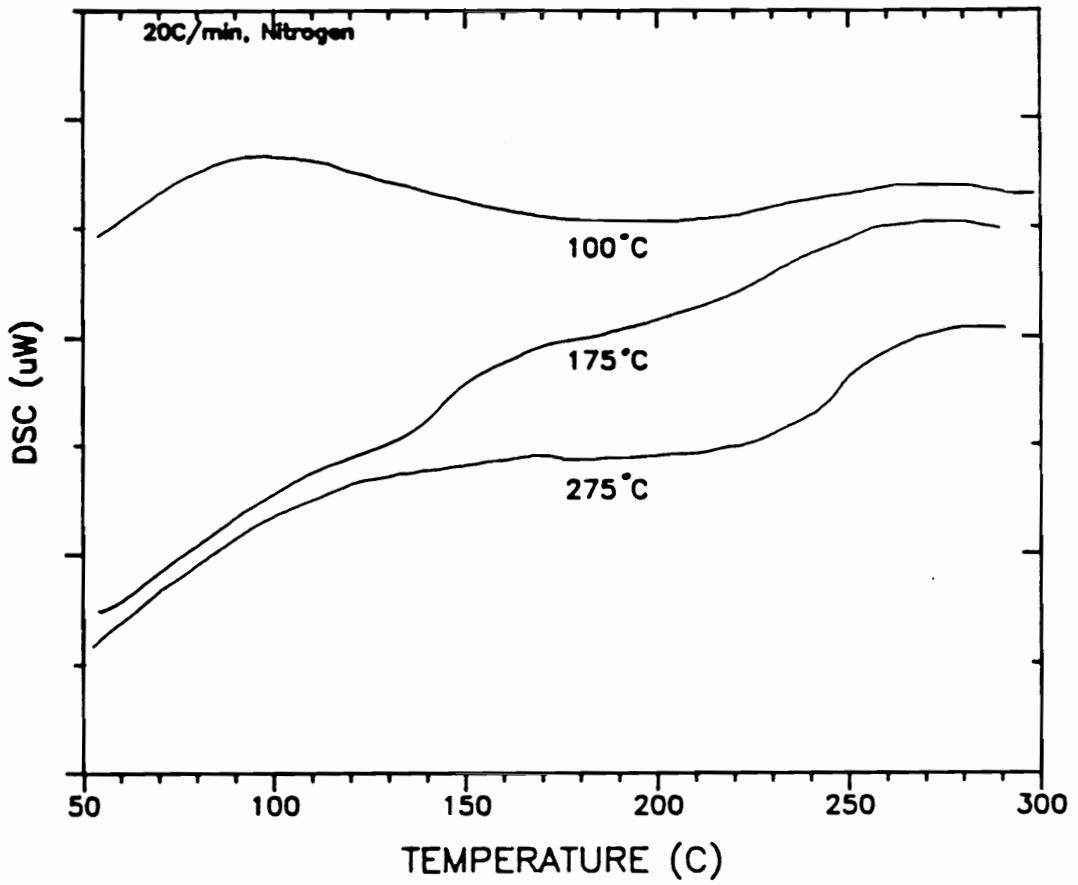


Figure 7-5 DSC of TiOPr/6F/AMP CERAMERS.

same trend above 600°C where the rate of weight loss was quite high. The final weight of each sample did not follow any trend that one would predict based upon the weight fraction of TiOPr. The sample with 54% TiOPr had a lower final weight than the sample containing 37% TiOPr initially. These trends and those described previously i.e. lower onset of degradation and lower T_g , are not what one would expect for a system in which the level of the inorganic component was increasing. The only explanation that can be offered with the current information is that chain scission occurs at the higher levels of TiOPr due to the increased levels of acid added to the system. Other polyimide oligomers, which had backbone structures similar to the 6F/BTDA/AMP oligomers, i.e. the 6F/BTDA molecule and either the Bis A or the Bis P, exhibited different thermal stabilities which were related to the structure of the end-cap, i.e. isocyanatopropyltrimethoxysilane, nadic anhydride or aminophenyltrimethoxysilane. The thermograms in Figure 7-7 represent three different polyimide structures which were all based upon the 6F/BTDA and Bis A oligomer whose synthesis was described in Chapter 3. The oligomer with amine endgroups, which were the result of the stoichiometric ratio of the anhydride to the diamine, was thermally stable upto ca. 517°C using N₂ as the purge gas. The addition of nadic anhydride to the amine terminal group followed by hydrosilylation of the vinyl group, as described in Section 3.3.4.2 of Chapter 3, reduced the thermal stability of the polyimide oligomer by ca. 130°C to 390°C. However, the addition of isocyanatopropyltrimethoxysilane to the amine terminated polyimide, which would

generate a urea linkage for each amine reacted, reduced the thermal stability of the polyimide by only 60°C to ca. 450°C. There are other factors that could have contributed to the lower thermal stability of these endcapped polyimide oligomers such as residual catalysts or other contaminants associated with the endcapping reactions. The results, however, do suggest that the nature of the end group strongly influences the thermal stability of the polyimide oligomer.

The results of the thermal analysis of these materials suggest that the polyimide was incorporated into the sol-gel derived network of which the inorganic component was predominantly titania based. However, the mechanical properties of these hybrid materials did not allow one to subject them to analytical techniques such as DMA or stress-elongation measurements i.e. their dimensions were non-uniform and the samples were very brittle. The small angle x-ray scattering behavior of these samples which were prepared in monolithic and transparent forms (which were, as stated previously, dark amber to brown in color) revealed a number of features that support the thermal analysis results. The SAXS profiles in Figure 7-8 which represent the scattered intensity as a function of s the angular quantity which is equal to $2 \sin \theta / \lambda$ where θ is one-half the radial scattering angle as defined by Bragg's law and λ is the wavelength of the incident irradiation (refer to Chapters 4 and 5), are quite similar in their general features. It is important to note that the dimensions of the samples were quite non-uniform in thickness and therefore the SAXS profiles in this section represent trends only. The CERAMER composition

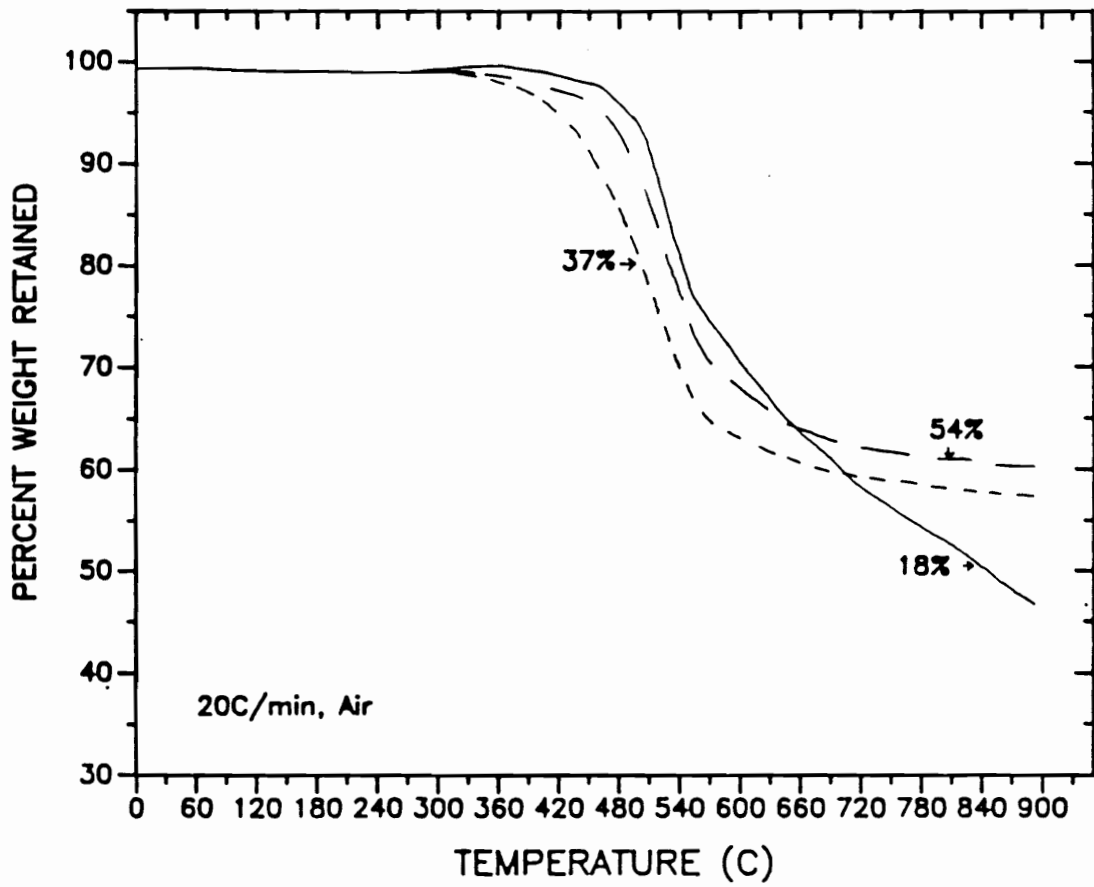


Figure 7-6 TGA of TiOPr/6F/AMP CERAMERS.

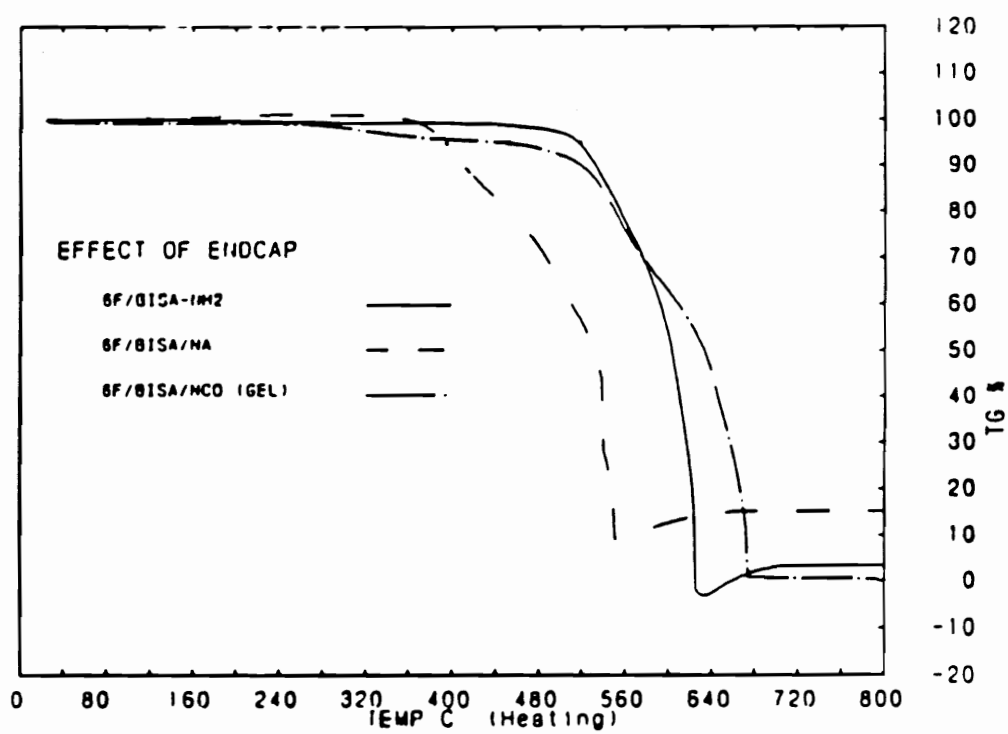


Figure 7-7 TGA of 6F/BisA oligomers as a function of end group.

TiOPr(18)-6F/AMP(10K)-0-0.06 was evaluated by SAXS as a function of the curing temperature. The sample was initially kept at 60°C for three days to gel, followed by a cure at 100°C for an additional three days. The next step involved a slow heat to 150°C where it was held for 20 minutes. The sample was analyzed by SAXS and then heated to the next temperature of 270°C. The SAXS behavior of the same gel was determined a second time. The final thermal treatment was to 325°C. Thus in this case the relative intensity of the three SAXS profiles in Figure 7-8 can be compared directly since sample thickness was not a factor. The maximum intensity of the CERAMER TiOPr(18)-6F/AMP(10K)-0-0.06 increased as the sample was heat treated at increasingly higher temperatures over the range of 150°C to 325°C. The d spacing or characteristic length of approximately 15 nm did not change with heating (Fig. 7-8). The increase in the maximum intensity of the SAXS profiles in Fig. 7-8 suggests that the morphology of the TiOPr/6F/AMP resembles that of the other TiOPr containing CERAMERs as well as the TEOS and ZrOPr containing hybrid materials.

The characteristic length or psuedo Bragg spacing of the CERAMERs described in Chapter 4 of this thesis was shown to increase with the molecular weight of the oligomer by SAXS. Figure 7-9 illustrates the same trend for the composition TiOPr(18)-6F/AMP(X)-0-0.06 where X was 5000 g/mol, 10000 g/mol or 13000 g/mol. The characteristic length increased from ca. 7.3 nm to 16 nm for the CERAMERs prepared with the 5000 g/mol and 13000 g/mol oligomers respectively.

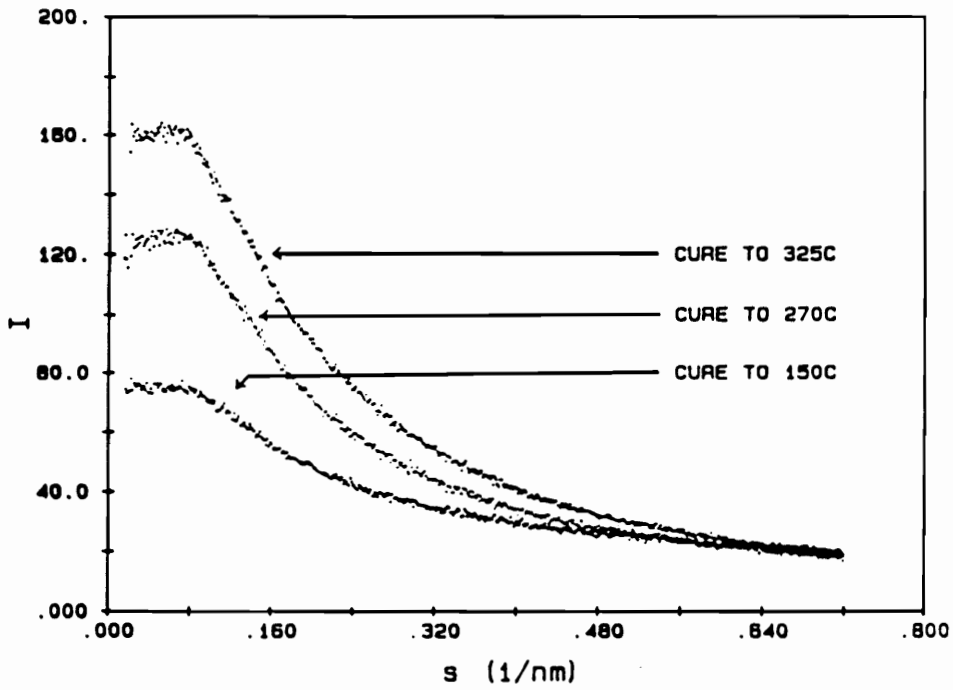


Figure 7-8 SAXS behavior of TiOPr/6F/AMP CERAMERs as a function of thermal cures: TiOPr(18)-6F/AMP(10K)-0-0.06.

The difference between the 10000 g/mol and 13000 g/mol oligomer was not great, but did increase with molecular weight. Recall, that the molecular weight distribution of these polyimides were not determined. Also, just to reemphasize an earlier statement, the relative intensities of these three materials cannot be compared due to the heterogeneity in sample dimensions. However, the SAXS results in Fig. 7-9 do demonstrate a correlation of the characteristic length with the d-spacing.

It was also shown that the characteristic spacing in the TEOS/PTMO, TiOPr/PTMO and ZrOPr/PTMO hybrid systems increased with the level of the metal alkoxide. That is, as the weight fraction of the metal alkoxide was increased, the maximum scattering intensity shifted to smaller s values. The same trend was found in the TiOPr/6F/AMP CERAMERs as seen in Figure 7-10. The d spacing for the three SAXS profiles corresponding to compositions TiOPr(X)-6F/AMP(5K)-0-0.06 where X was 18%, 37% and 54%, was 7.9 nm, 8.3 nm, and 8.7 nm, respectively. Once more, however, the relative intensities of the three materials do not follow a trend one would predict, based upon the relative volume fractions of the metal alkoxide and the polyimide. Yet, the shift of the maximum scattering intensity to smaller s values is clear.

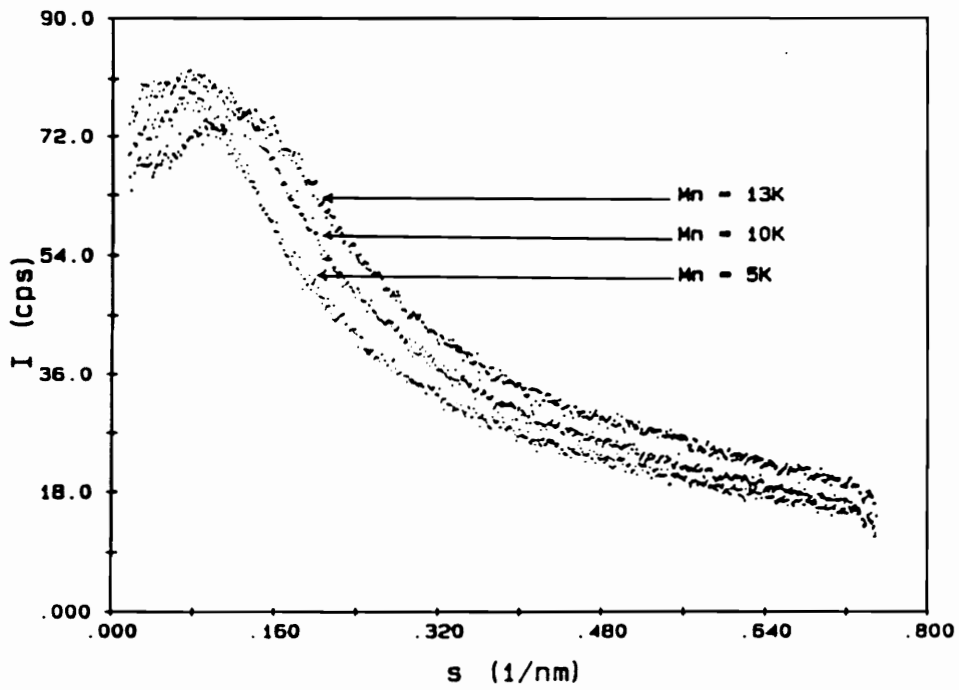


Figure 7-9 SAXS behavior of TiOPr/6F/AMP CERAMERs as a function of M_n .

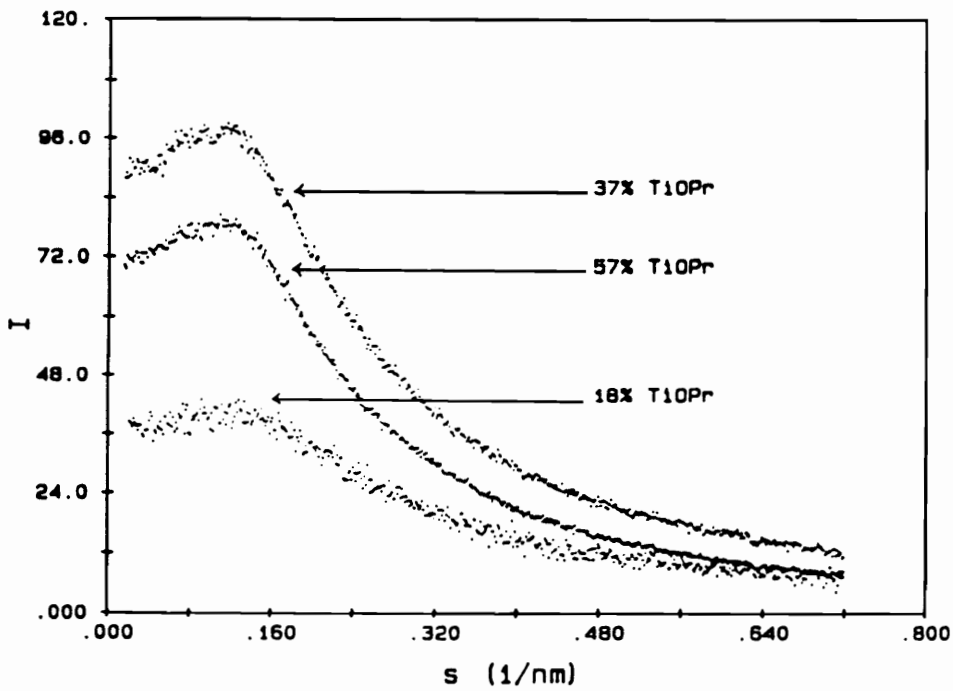


Figure 7-10 SAXS behavior of TiOPr/6F/AMP CERAMERS as a function of TiOPr level: TiOPr(X)-6F/AMP(10K)-0-0.06.

7.2.2 TEOS/Siloxane Copolyimide CERAMERs

The previous section was devoted to the analysis of a series of polyimides which were incorporated into hybrid inorganic/organic networks by a sol-gel process which was water deficient. The solubilities of the polyimides limited the use of metal alkoxides which would condense with minimal amounts of moisture. The other approach to the incorporation of polyimides into the sol-gel derived networks investigated was the coreaction of polyamic acids, which had been functionalized with aminophenyltrimethoxy silane, with TEOS. The information provided in this section was obtained during a summer internship at Dow-Corning. The release of these results for inclusion within this thesis was approved Dr. Russell King of Dow-Corning.

The polyamic acid described in this section was a 5000 g/mol oligomer based upon BTDA and bis-aminopropyltetramethyldisiloxane. As described in Sections 3.3.2.5 and 3.3.4.3 of this thesis, the oligomers were end capped with aminophenyltrimethoxy silane and then combined with the desired weight of prehydrolyzed TEOS. The hybrid materials were gelled at 60°C under a N₂ atmosphere followed by step programmed heating to 250°C. The complete details are described in Section 3.3.4.3 of Chapter 3. All of the samples were monolithic following gelation at 60°C. Normally the samples were sectioned into smaller pieces for the final stages of curing to temperatures of ca. 250°C. The extent of conversion

of the polyamic acid as well as the sol-gel reactions were monitored by FTIR, which are not available for publication. However, the key features of the FTIR were the disappearance of the amic acid peaks at ca. 1610 cm^{-1} and the appearance of the imide peaks at ca. 1753 cm^{-1} and ca. 1810 cm^{-1} .

7.2.2.1 Dynamic Mechanical Behavior

The dynamic mechanical behavior of a series of the BTDA/disiloxane polyimides was evaluated in shear at a frequency of 1 Hz. The storage modulus as a function of the temperature is illustrated in Figure 7-11 for the composition TEOS(X)-DMSX(5K)-100-0.04 HCl where X was increased in increments of 10% from 20% to 80%. The storage modulus in shear (G') was approximately 1 to 2 GPa at temperatures below ca. 30°C as one would expect for a network in its glassy state. The T_g of the CERAMER composition TEOS(20)-DMSX(5K)-100-0.04 was approximately 150°C as indicated by the distinct drop in G' . The storage modulus of the composition TEOS(20)-DMSX(5K)-100-0.04 was approximately two orders of magnitude lower in the rubbery regime, which is characterized by temperatures above the T_g , than the initial value which represented the glassy state modulus. As the level of TEOS was increased from the low of 20% to the high of 80% the drop in G' was practically eliminated at the highest ratio of TEOS to the polyimide oligomer. The T_g increased along with the storage modulus in the rubbery regime as the level

of TEOS was increased which are the same trends observed in TEOS/PTMO CERAMERS.

The loss behavior of these materials is represented in Figure 7-12 as a series of plots of the $\tan \delta$ versus temperature for the compositions TEOS(X)-DMSX(5K)-100-0.04 where X was either 20%, 30%, 40%, 50%, 70% or 80%. Note that the loss behavior of the CERAMER with the lowest level of TEOS had a maxima at ca. 150°C and little to no evidence of loss dispersions at any other temperatures using a frequency of 1 Hz. The next higher level of TEOS, 30%, however, had a relatively large loss dispersion starting at ca. 20°C and extending to ca. 200°C. The next two CERAMERS of composition TEOS(X)-DMSX(5K)-100-0.04 where X was 50% and 70%, exhibited practically no loss dispersions up to ca. 200°C, where the samples with 70% TEOS exhibited a maxima in the $\tan \delta$. The CERAMER with the highest ratio of TEOS to polyimide resembled the sample of composition TEOS(30)-DMSX(5K)-100-0.04 in its loss behavior, i.e. a rather large loss dispersion characterized the samples at low temperatures, ca. below 100°C, followed by a maxima near ca. 150°C. However, the composition TEOS(80)-DMSX(5K)-100-0.04 also had a second maxima near 250°C. Indeed, closer examination of the $\tan \delta$ behavior of the samples containing greater than 20% TEOS reveals a loss dispersion which occurs near 250°C. The occurrence of this dispersion at or near the maximum temperature to which the samples were exposed during the curing process was interpreted as due to a possible release of entrapped solvent and/or the release of condensation by

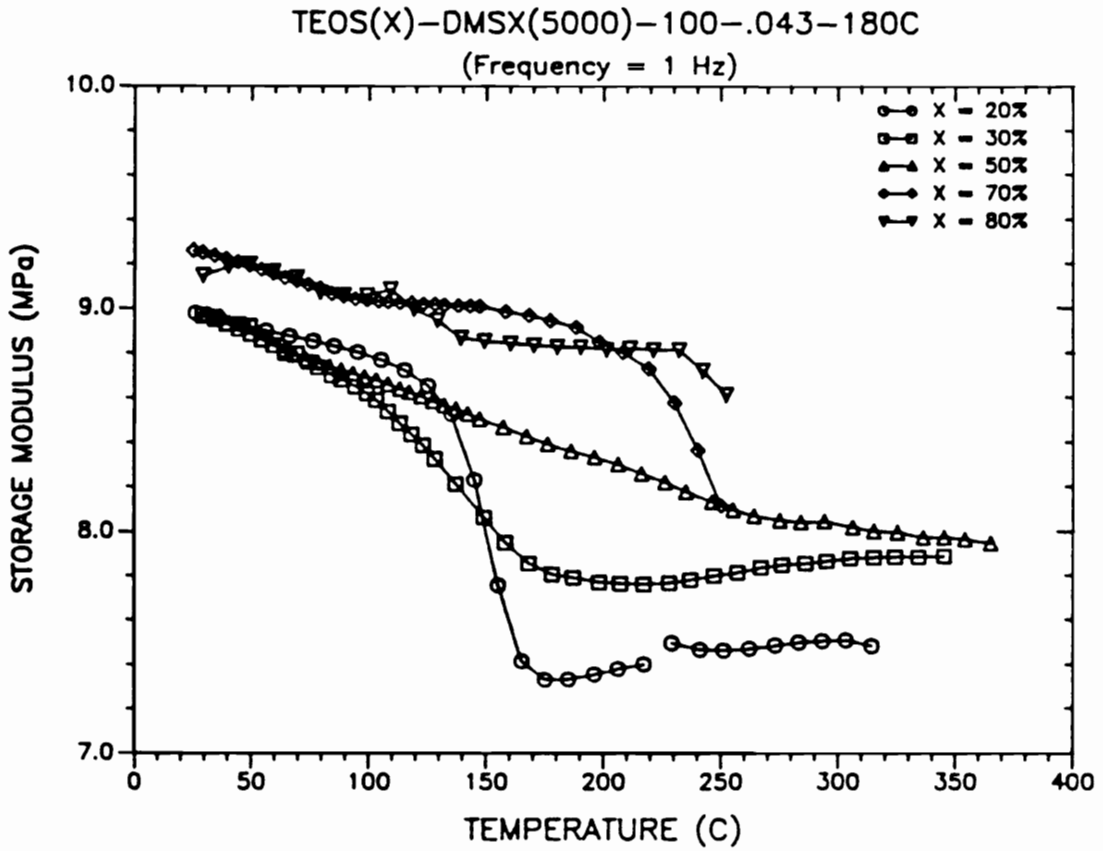


Figure 7-11 Storage modulus (G') of TEOS/DMSX CERAMERs as a function of TEOS: TEOS(X)-DMSX(5K)-100-0.04. Frequency = 1 Hz.

products. The result of subjecting the sample of composition TEOS(50)-DMSX(5K)-100-0.04 to a second DMA analysis is illustrated in Figure 7-13 as a plot of the storage modulus, the loss modulus and the $\tan \delta$ as a function of temperature. The storage modulus increased only slightly in the rubbery regime, ca. above 175°C, during the second analysis, yet it should be noted that during the initial analysis the sample was heated to 280°C which was ca. 30°C higher than the cure temperatures. There was no evidence of degradation of the sample following the initial analysis, however, during the second run the sample fractured at a temperature of approximately 270°C. The $\tan \delta$ of the CERAMER for the first and second run revealed little to no change between the first and second runs. However, the loss modulus reveals a rather significant drop followed by a sharp increase and again a decrease beginning at ca. 190°C (Fig. 7-13). This was attributed to the formation of a crack in the sample.

7.2.2.2 Isothermal Weight Loss

The isothermal weight loss of these materials was examined at a temperature of 250°C in a air circulating oven. The weight loss profiles of the CERAMER compositions TEOS(X)-DMSX(5K)-100-0.04, where X again varied from 20% to 80% in increments of 10%, are depicted as a function of time in Figure 7-14. The most dramatic change occurs after ca. 24 to 48 hours for most of the samples. The

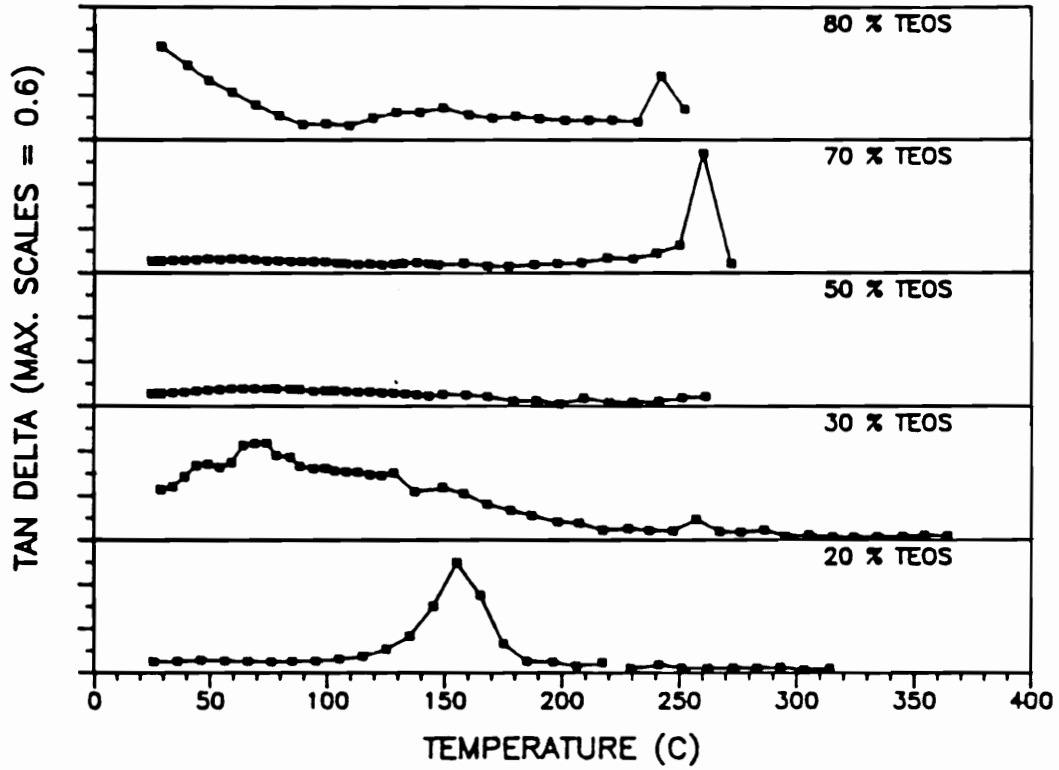


Figure 7-12 Tan δ of TEOS/DMSX CERAMERS as a function of TEOS: TEOS(X)-DMSX(5K)-100-0.04. Frequency = 1 hz.

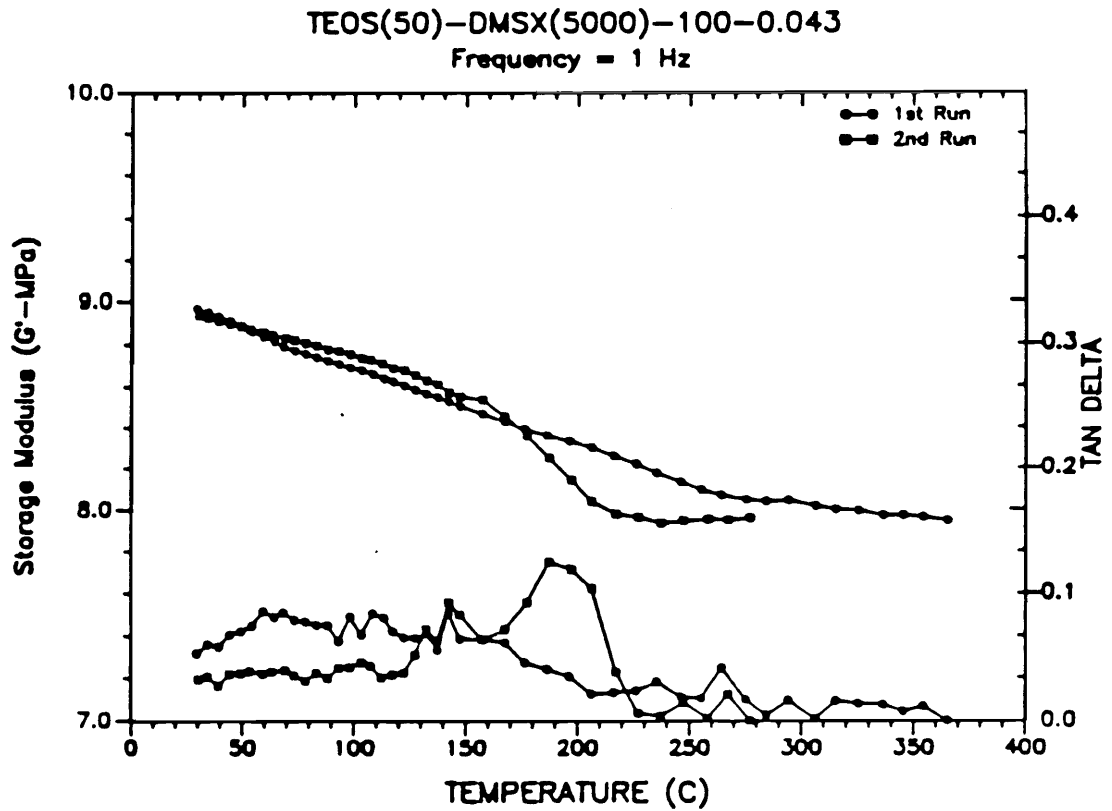


Figure 7-13 Comparison of first and second run in DMA for a CERAMER of composition TEOS(50)-DMSX(5K)-100-0.04. Frequency = 1 hz.

CERAMERs with greater than ca. 50% TEOS decomposed severely such that the samples were mere fragments at the end of the 100 hours. The isothermal weight loss behavior of these samples suggest that the loss dispersions at ca. 250°C in Fig. 7-12 were most likely due to outgassing of volatile components which it is believed reduce the network's structural integrity via degradation of the PTMO oligomers.

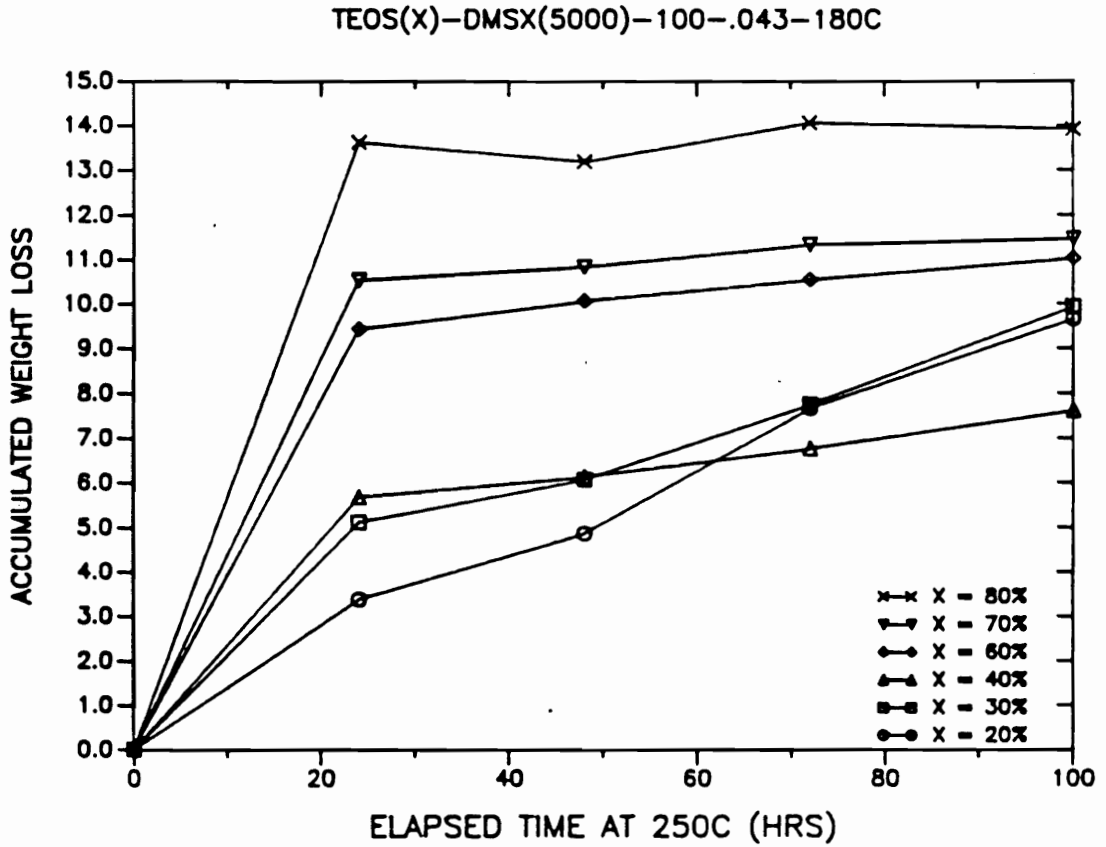


Figure 7-14 Isothermal weight loss of CERAMERs as a function of TEOS at a temperature of 250°C. TEOS(X)-DMSX(5K)-100-0.04, where X was varied from 20% to 80%.

7.3 CONCLUSIONS

The formation of a novel class of hybrid inorganic/organic networks was achieved by the cocondensation of either a polyimide or a polyamic acid, which were appropriately functionalized, and a metal alkoxide. The general structure property relationships of the polyimide containing CERAMERs were only partially characterized in part due to difficulty in obtaining uniform monolithic samples and in part due to limitations of the chemistry. However, monolithic polyimide based samples which were transparent were successfully prepared by the procedures described in Chapter 3 of this thesis. The first series of hybrid metal alkoxide/polyimide networks which were prepared by the direct incorporation of functionalized polyimide oligomers exhibited good thermal stability up to temperatures of ca. 450°C under a N₂ purge. However, as the level of titanium tetraisopropoxide was increased above the level of 54 weight percent, the thermal stability of this class of CERAMERs decreased as indicated by the T_g and the thermal weight loss behavior. The T_g of the TiOPr/6F/AMP CERAMERs increased from ca. 270°C to 284°C when the level of TiOPr was raised from 18% to 37%, but decreased to 248°C when the TiOPr was increased to 54%. The cause of this decrease is not understood at this time. The T_g of the composition TiOPr(37)-

6F/AMP(10K)-0-0.04 was systematically increased as a function of curing temperature from ca. 150°C to a high of 284°C.

The SAXS behavior of these materials was similar to that of the TiOPr/PTMO CERAMERs and the TEOS/PTMO CERAMERs. The maximum in the SAXS scattering intensity as a function of scattering angle was attributed to microphase separation in this class of CERAMERs. The maximum intensity increased as the curing temperature was increased. The d spacing increased with the molecular weight of the polyimide oligomer and the weight fraction of TiOPr. This behavior, i.e. changes in the SAXS behavior in conjunction with the increase in T_g as a function of higher cure temperatures, suggest that the metal alkoxide was incorporated into a hybrid network with the polyimide. Similar trends were reported for the TEOS/PEK CERAMERs described by Noell et. al. [29]. Thermal weight loss studies indicate that the thermal stability of these hybrid systems are dependent upon the nature of the particular silane end group used to functionalize the oligomers. The order of stability appeared to be aminophenyltrimethoxysilane > isocyanatopropyltrimethoxysilane > hydrosilylation of nadic anhydride. However, there are other factors to consider in terms of both the synthetic procedures and the level of acid catalyst employed in the sol-gel process which will ultimately determine the thermal stability of these materials.

The dynamic mechanical behavior of the hybrid inorganic/organic networks formed by the cocondensation of the aminophenyltrimethoxy silane end capped

polyamic acid and TEOS was determined at a frequency of 1 Hz. The storage modulus (shear) increased in the rubbery regime as the ratio of TEOS to functionalized polyamic acid was increased. The $\tan \delta$ behavior of these materials typically showed a minor peak near ca. 250°C which by isothermal weight loss studies was attributed to degradation of the polyimide oligomer.

CHAPTER 8

CONCLUSIONS

AND

RECOMMENDATIONS FOR FUTURE RESEARCH

8.1 SUMMARY

The completion of this dissertation represents the accomplishment of a number of goals. First, the use of a polymeric acid catalyst was successfully implemented and in conjunction with other catalysts it was demonstrated that the acid strength was more crucial than the means of introducing it to the system. That is, the monomeric form of PSS was apparently as effective as a catalyst as the polymer in the sol-gel process. This leads one to the logical extension that a polymeric acid catalyst could be employed in conventional sol-gel processes as a possible rheology modifier.

The second goal of this dissertation was to extend the current understanding of the structure/property relationships of CERAMERs by the substitution of TEOS with other metal alkoxides. It was shown that a chelating ligand such as ethylacetoacetate was useful in reducing the reactivity of metal alkoxides such as aluminum tri-n-butoxide and titanium tetra-iso-propoxide for incorporation into the inorganic/organic hybrid networks. However, it was demonstrated there was a high sol fraction in the aluminum tri-n-butoxide system which was attributed to a self condensation reaction of the ethylacetoacetate. The elimination of the ligands led to the production of a new class of CERAMERs based upon TiOPr/PTMO and ZrOPr/PTMO. The substitution of TiOPr or ZrOPr for TEOS in the TEOS/PTMO CERAMERs led to materials with improved mechanical properties. Young's modulus increased most likely due to a higher T_g . As demonstrated in Chapters 4 and 6 and Appendix I, the mechanical properties of the CERAMERs correlate closely with the level of the inorganic phase in a manner similar to a filled composite. The general structure/property relationships of the CERAMERs based upon PTMO and a single metal alkoxide do follow certain trends:

1. The elastic modulus increases as the ratio of metal alkoxide to PTMO is increased, the molecular weight of the PTMO oligomer is reduced, the reactivity of the metal alkoxide is increased, and the ratio of water to alkoxide is increased.

2. The loss dispersions associated with the PTMO phase are reduced by raising the level of metal alkoxide, raising the reactivity of the metal alkoxide, reducing the molecular weight of the PTMO oligomers and increasing the ratio of water to alkoxide and age of the gel.
3. The maximum intensity of scattered x-ray radiation at small angles (SAXS) increases with the level of metal alkoxide, reactivity of metal alkoxide, extent of reaction, and the ratio of water to metal alkoxide.
4. The propensity of both TiOPr and ZrOPr to self condense (1) would exclude the PTMO chains from the pore structure of the inorganic phase in TiOPr/PTMO and ZrOPr/PTMO CERAMERs. Thus, there appears to be less mixing between phases as determined by analysis of the SAXS behavior in conjunction with mechanical properties.

The replacement of PTMO oligomers with high T_g materials does alter the overall morphology of CERAMERs. The broad rather sharp T_g in the TiOPr/PI CERAMERs is distinctly different from the TEOS/PTMO CERAMERs. This supports the earlier findings of Noell et. al. [29]. The thermal stability of CERAMERs can be extended to temperatures greater than ca. 400°C by the use of improved synthetic methods and thermally stable end capping reagents that provide the necessary trimethoxysilane functionality. The overall thermal stability of

CERAMERs based upon polyimides was shown to be dependent upon the chemical structure of the end group.

8.2 RECOMMENDATIONS FOR FUTURE RESEARCH

8.2.1 EFFECT OF pH

The effect of the acid catalyst selected for preparation of the TEOS/PTMO CERAMERs was significant in terms of the extent of reaction and thus the overall mechanical properties of the hybrid structures. This led to preliminary investigations into base catalyzed systems similar in nature to those used by Mark et. al. []. The preliminary results which will not be included here are worth mentioning in terms of their differences. The substitution of an acid catalyst with ethylamine in the TEOS/PTMO systems described in Chapter 4 resulted in the formation of a hybrid structure that first and foremost exhibited SAXS behavior that was quite uncharacteristic. The overall profile was quite narrow and the intensity was an order of magnitude greater than comparable acid catalyzed systems. The only problem with these results was they were not reproduced. This in conjunction with follow-up experiments indicated that the pH of the solution, which was not determined, was critical in determining the rate of gelation for the base catalyzed systems. Indeed,

the results of Coltrain et. al. [38] would tend to confirm this observation. The level of water, level of catalyst, acidity (or basicity, depending upon ones preference) and the ratio of alkoxide to catalyst are all factors that have not been adequately studied for the CERAMERs. It is reasonable to assume that investigations of this nature might be expected to lead to a formulation with better mechanical properties and possibly less aging. This statement is based upon the fact that the range of acid concentrations evaluated with PSS catalyzed CERAMERs revealed no significant changes in the properties, i.e. mechanical, SAXS behavior. This would indicate that the current levels of acid do not represent catalytic quantities, that is too much catalyst has been used. This can be best determined by monitoring the pH of these reactions.

The viscosity of the PSS catalyzed CERAMERs in the initial stages of reaction appeared to be much higher than that of comparable formulations catalyzed with HCl. This behavior which was not investigated to any extent, could prove to be useful in terms of applications such as fiber drawing or spin coating. An approach one might take would be to evaluate different molecular weights of the PSS type catalysts and different ratios of sulfonic acid per mole of poly(styrene sulfonic acid).

8.2.1 POLYIMIDES

The polyimide CERAMERs described in Chapter 7 were thermally stable under dynamic conditions upto temperatures of greater than 400°C. The limit of these materials at this point would appear to be in the efficiency of the end-capping reactions. The recent developments by Prof. McGrath's group with the transimidization reactions are the most promising and if possible should be pursued. The transimidization end-capping reactions provided functionalized polyimides that could be incorporated into monolithic structures. The limitations of materials prevented further characterization of the mechanical properties of these CERAMERs. The endcapping reagent aminophenyltrimethoxysilane is no longer commercially available and the 6F-BTDA is too expensive for practical evaluation in these systems. The aminophenyltrimethoxysilane could most likely be synthesized, but possibly the hydrosilylation reaction should be investigated further as an alternative. The use of mixtures of anhydrides was suggested by Professor McGrath as an alternative for 6F-BTDA for increasing the solubility of the polyimides.

Preliminary investigations by a summer NSF Fellow Erik Falk revealed some interesting possibilities of using the CERAMER formulations for matrix materials of composite structures. TEOS/PTMO CERAMER formulations based upon the 2000 g/mol and 2900 g/mol oligomers were combined with carbon fibers both in single strand and woven fiber forms. The morphological evaluation of these materials by

SEM demonstrated that relatively good adhesion developed between the carbon fibers and the CERAMER, but that it was highly dependent upon the catalyst and the pretreatment of the fibers (as one would predict). The approach one might consider as a follow-up on this study is to evaluate matrix resins with a higher T_g than PTMO and higher molecular weight. The higher modulus material, such as the polyimide or PEK CERAMERs would be more representative of a high performance composite in terms of modulus and thermal and chemical stability. The higher molecular weight of the oligomer would reduce the relative amount of by products associated with the sol-gel process which is the largest negative in terms of using these materials in composites.

APPENDIX I

The dynamic mechanical behavior as well as the SAXS behavior support the existence of a two phase system and as shown in Chapters 4 and 6 there are distinct differences in the mixing between the organic and inorganic phases. The objective of this appendix is to demonstrate how the analysis of the mean square electron density fluctuation of the CERAMERs based upon either TiOPr, ZrOPr or TEOS reacted with functionalized PTMO can provide some insight into the density of the phases formed. This can in turn be used to evaluate the relationship between mechanical properties and the level of metal alkoxide incorporated into the networks. One must be cautioned however, as to the relative simplifications which have been applied in this analysis and the need for development of models to test their validity.

The SAXS intensity was given earlier in the following form:

$$I(s) = 4\pi i_e \langle \Delta \rho^2 \rangle V \int_0^{\infty} \gamma(r) \frac{\sin(2\pi sr)}{2\pi sr} r^2 dr \quad [4-1]$$

where $\langle \Delta \rho^2 \rangle$ represents the mean square electron density fluctuation, V is the illuminated sample volume, i_e is the Thompson scattering constant for an electron and $\gamma(r)$ is the correlation function which represents a measure of the spatial inhomogeneity in the electron density. The term s as previously described is the

angular vector which is given by the expression $2\sin\theta/\lambda$ where θ the Bragg angle is one-half the radial scattering angle and λ is the wavelength of the incident x-ray beam. The mean square electron density fluctuation for a two phase system with sharp boundaries was given by Equation 6-2:

$$\langle \rho^2 \rangle = \varphi_1 \varphi_2 (\rho_1 - \rho_2)^2 \quad [6-2]$$

where φ_1 and φ_2 represent the volume fractions of phase 1 and phase 2 respectively. The terms ρ_1 and ρ_2 are the electron densities of phases 1 and 2, respectively. The electron densities of each phase, i.e. PTMO (ρ_1) and TiOPr (ρ_2), can be calculated according to the simple relationship:

$$\rho_1 = \frac{\delta_1 e}{\text{mol.wt.}} \quad [I-1]$$

where δ_1 is the density of TiO_2 , e represents the electrons per mole of TiO_2 , and mol. wt. is the molecular weight of TiO_2 . Thus, there is one unknown which must be determined. There are basically two different approaches that were used to estimate the density of the TiO_2 as it exists with the CERAMER network. The idea here was to create an envelope that would encompass the range of densities anticipated from the sol-gel process. The first of the two empirical relationships developed, was arbitrarily defined as the Series model and is given by the following:

$$\delta = \varphi_1 \delta_1 + \varphi_2 \delta_2 \quad [\text{I-2}]$$

where φ represents the volume fraction of each phase and δ represents the density of each phase. Thus, this relationship implies that the CERAMER is a two phase system for which the total density is the sum of the densities of the individual phases. The validity of this assumption was not tested, but in light of the structure-property relationships described appears to be reasonable for these materials as demonstrated in Chapters 4 and 6. The other boundary of the envelope is given by the "Parallel" model:

$$\frac{1}{\delta} = \frac{\varphi_1}{\delta_1} + \frac{\varphi_2}{\delta_2} \quad [\text{I-3}]$$

where the terms are the same as given above for equation I-2. The solution to this equation involves the use of a density for the PTMO phase of 1 g/cm³ which was determined experimentally for the 2000 g/mol oligomer of PTMO. The objective here was to create an envelope that would encompass the range of densities anticipated from the sol-gel processing of the various metal alkoxides. In Chapter 6 a correlation between Young's modulus and "volume fraction" of metal oxide was demonstrated for the three different CERAMER types, i.e. TEOS/PTMO, TiOPr/PTMO and ZrOPr/PTMO. It was recognized that many bulk properties, i.e.

Young's modulus, diffusion rate, dielectric loss factor, etc., of a multiphase material are related to the properties of the individual phases. The manner in which the phases interact with each other is often described as being either in series or in parallel. A plot of the calculated total bulk property versus volume fraction of a phase using the two different models, i.e. series and parallel, provides one with a lower limit and an upper limit, respectively. The actual bulk properties will lie within these theoretical limits. Thus, this approach was pursued for the CERAMERs with the realization that the density of the individual phases would require a treatment as defined in this appendix. It is recognized, however, that density itself does not normally behave in such a manner as the series and parallel models would predict. Yet, the definition of a range of densities based upon the bulk density of the CERAMER is believed to be reasonable by this author.

The total bulk density of the CERAMERs was determined by Archimedes principle on materials which were dried to constant weight. The volume fraction of the TiO_2 was expressed in terms of the volume fraction of the PTMO and then one simply solves the equations in terms of the density of TiO_2 . The resultant relationship is then substituted into equation I-2 and using a routine known as TK Solver, the quadratic equation variables are determined. The other variable, the mean square electron density of each CERAMER composition, was determined by first performing a background subtraction and then analyzing the smeared data using Equation 6-1. The method of background subtraction was developed by Bonart and

uses Porod's law to determine the level of background scattering [97]. The method assumes a constant value of $I(s)$ as s , the scattering vector approaches infinity. The value of $I(s)$ at large values of s are then uniformly subtracted from the entire scattering profile. The experimentally determined values of density are tabulated along with the calculated values of the mean square electron density and volume fractions for the TiO_2/PTMO CERAMERs in Table I-1. The values for the ZrOPr/PTMO and TEOS/PTMO CERAMERs which were calculated using the Series model are listed in Tables I-2 and I-3, respectively. The values calculated using the Parallel model are listed in Tables I-4, I-5, and I-6 for the TiOPr/PTMO , ZrOPr/PTMO , and TEOS/PTMO CERAMERs, respectively.

There are significant differences in the calculated volume fractions of the inorganic structure for the TiOPr/PTMO CERAMERs and the ZrOPr/PTMO CERAMERs compared with the TEOS/PTMO CERAMERs which correlates well with the trend one would predict based upon the density differences between the three metal alkoxide forms as stated earlier. The calculated density, ca. 2.34 g/cm^3 to ca. 2.88 g/cm^3 , of the TiO_2 phase in the TiOPr/PTMO CERAMERs appears quite reasonable based upon the density of ca. 2.6 g/cm^3 to 3.2 g/cm^3 reported by Mr. Vidhu Nagpal (private communication) for TiO_2 prepared in dilute alcoholic solution from titanium tetraethoxide. These values are close to the density range of ca. 2.9 g/cm^3 to 3.2 g/cm^3 reported by Fegley, Barringer and Bowen [98] for TiO_2 prepared by the sol-gel process in an alcoholic solution. Thus, the lower densities

Table I-1 Calculated volume fractions of TiO_2 and PTMO for CERAMERs by the Series model: $\text{TiOPr}(\text{X})\text{-PTMO}(2\text{K})\text{-25-0.06}$.

TiOPr (wt%)	$\langle \rho^2 \rangle^\dagger$ $\times 10^{-2}$	δ g/cm^3	φ_1	φ_2	δ_2 g/cm^3
25	2.67	1.07	0.95	0.05	2.34
49	6.31	1.20	0.88	0.12	2.66
54	8.75	1.26	0.87	0.13	2.85
58	8.82	1.33	0.84	0.16	2.88
66	8.88	1.46	0.72	0.28	2.63

† Units are $(\text{mol-e-cm}^{-3})^2$

$$\rho_2 = 38 \cdot \delta / 79.8988 = 0.475602 \delta_2$$

Table I-2 Calculated volume fractions of ZrO_2 and PTMO for CERAMERs
by the Series model: $\text{ZrOPr}(\text{X})\text{-PTMO}(2\text{K})\text{-}0.0\text{-}0.06$.

ZrOPr (wt%)	$\langle \rho^2 \rangle^\dagger$ $\times 10^{-2}$	δ g/cm^3	φ_1	φ_2	δ_2 g/cm^3
35	5.86	1.14	0.95	0.05	3.70
40	6.68	1.22	0.90	0.10	3.11
45	8.68	1.23	0.89	0.11	3.30
50	9.36	1.29	0.87	0.13	3.28
57	12.0	1.21	----	----	----

† Units are $(\text{mol-e-cm}^{-3})^2$

$$\rho_2 = 56 * \delta / 123.2188 = 0.454476 \delta_2$$

Table I-3 Calculated volume fractions of SiO₂ and PTMO for CERAMERs
by Series model: TEOS(X)-PTMO(2K)-100-0.014 PSS.

TEOS (wt%)	$\langle \rho^2 \rangle^\dagger$ $\times 10^{-2}$	δ g/cm ³	φ_1	φ_2	δ_2 g/cm ³
40	1.11	1.15	0.76	0.24	1.63
50	1.35	1.23	0.64	0.36	1.63
60	1.21	1.32	0.46	0.54	1.59
70	0.81	1.42	0.25	0.75	1.57

[†] Units are (mol-e-cm⁻³)²

$$\rho_2 = 30.0 \cdot \delta / 60.0843 = 0.499298 \delta_2$$

Table I-4 Calculated volume fractions of TiO_2 and PTMO for CERAMERs by the Parallel model: $\text{TiOPr}(\text{X})\text{-PTMO}(2\text{K})\text{-25-0.06}$.

TiOPr (wt%)	$\langle \rho^2 \rangle^\dagger$ $\times 10^{-2}$	δ g/cm^3	φ_1	φ_2	δ_2 g/cm^3
25	2.67	1.07	0.88	0.12	2.26
49	6.31	1.20	0.71	0.29	2.35
54	8.75	1.26	0.66	0.34	2.52
58	8.82	1.33	0.57	0.43	2.40
66	8.88	1.46	0.47	0.53	2.46

† Units are $(\text{mol-e-cm}^{-3})^2$

$$\rho_2 = 38 \cdot \delta / 79.8988 = 0.475602 \delta_2$$

Table I-5 Calculated volume fractions of ZrO_2 and PTMO for CERAMERs
by the Parallel model: $\text{ZrOPr(X)}\text{-PTMO(2K)}\text{-}0.0\text{-}0.06$.

ZrOPr (wt%)	$\langle \rho^2 \rangle^\dagger$ $\times 10^{-2}$	δ g/cm^3	φ_1	φ_2	δ_2 g/cm^3
35	5.86	1.14	0.80	0.20	2.61
40	6.68	1.22	0.70	0.30	2.50
45	8.68	1.23	0.70	0.30	2.67
50	9.36	1.29	0.64	0.36	2.78
57	12.0	1.21	----	----	----

† Units are $(\text{mol-e-cm}^{-3})^2$

$$\rho_2 = 56 \cdot \delta / 123.2188 = 0.454476 \delta_2$$

Table I-6 Calculated volume fractions of SiO₂ and PTMO for CERAMERs
by Parallel model: TEOS(X)-PTMO(2K)-100-0.014 PSS.

TEOS (wt%)	$\langle \rho^2 \rangle^\dagger$ $\times 10^{-2}$	δ g/cm ³	φ_1	φ_2	δ_2 g/cm ³
40	1.11	1.15	0.64	0.36	1.59
50	1.35	1.23	0.51	0.49	1.61
60	1.21	1.32	0.36	0.64	1.60
70	0.81	1.42	0.20	0.80	1.59

[†] Units are (mol-e-cm⁻³)²

$$\rho_2 = 30 \cdot \rho / 60.0843 = 0.499298 \rho_2$$

calculated by the methods outlined in this appendix are plausible if one considers the effect of incomplete condensation on the density.

The volume fractions determined by these methods were then used to evaluate the influence of the inorganic phase on the Young's modulus of the samples. Figure I-1 depicts a plot of the Young's modulus as a function of the volume fraction of TiO_2 in the CERAMERs $\text{TiOPr}(X)\text{-PTMO}(2K)\text{-}25\text{-}0.06$ when X varied from 25% to 66%. The symbols reflect the calculated values while the line is based upon fitting the data to a power law function given by:

$$E = E_1 + E_2 \varphi_2^x \quad [\text{I-4}]$$

where E is the Young's modulus of the CERAMER, E_1 is the Young's modulus of the CERAMER prepared by the sol-gel process using only the end capped PTMO, E_2 is the Young's modulus of the inorganic phase, and φ_2 is the volume fraction of the inorganic phase. The value given by the power law term, $E_2 \varphi_2^x$, is used to represent the contribution of the inorganic phase to the total elastic modulus of the CERAMER and thus, provide an estimate of the magnitude of the modulus of the inorganic phase. The values for the terms E_2 , φ_2 and x are given in Table I-7 for each of the three CERAMER systems based upon PTMO, i.e. TiO_2 , ZrO_2 , and SiO_2 , and for both the Series model and Parallel model. The plots of the Young's modulus versus volume fraction of the metal alkoxide are given for the ZrOPr/PTMO and

TEOS/PTMO CERAMERs in Figures I-2 and I-3 respectively. The extension of the current data base to volume fractions of 1.0 for the inorganic phases would appear tenuous at best for TiO_2 and ZrO_2 , but does provide one with an interesting illustration of one aspect of the structure/property relationships of these novel hybrid materials. The TEOS/PTMO CERAMERs studied provide a broader range in terms of the volume fraction of metal alkoxide within the network. It appears that as the volume fraction of SiO_2 approaches the value of 0.7, the simple power law relationship is no longer sufficient for predicting the Young's modulus. One can rationalize this in terms of the phase inversion discussion offered in Chapter 4 with respect to the changes in the overall intensity of the SAXS as a function of TEOS in TEOS/PTMO CERAMERs. It was stated that the loss in the overall intensity of the SAXS profile with increasing levels of TEOS was due to a possible transition from the two phase system where PTMO was the continuous phase to one in which the silicate structure was continuous. This of course, might be expected to also hold true for the TiOPr /PTMO CERAMERs and the ZrOPr /PTMO CERAMERs.

The conclusions one might draw are that the analysis (as shown in this appendix) of the mean square electron density fluctuation of the CERAMERs based upon one metal alkoxide and functionalized PTMO oligomers can provide some insight into the density of the phases. This can in turn be used to evaluate the relationship between mechanical properties and the level of metal alkoxide incorporated into the networks. One must be cautioned again as to the

Table I-7 Values for elastic modulus of inorganic phase formed by sol-gel process in CERAMERs.

	Series		Parallel	
Metal Alkoxide	$E_2^\dagger$ MPa	x	$E_2^\dagger$ MPa	x
TiO ₂	7733	1.97	1023	1.76
ZrO ₂	4344	1.91	330	1.63
SiO ₂	251	1.6	168	1.6

[†] Elastic modulus calculated by a power law line fitting routine.

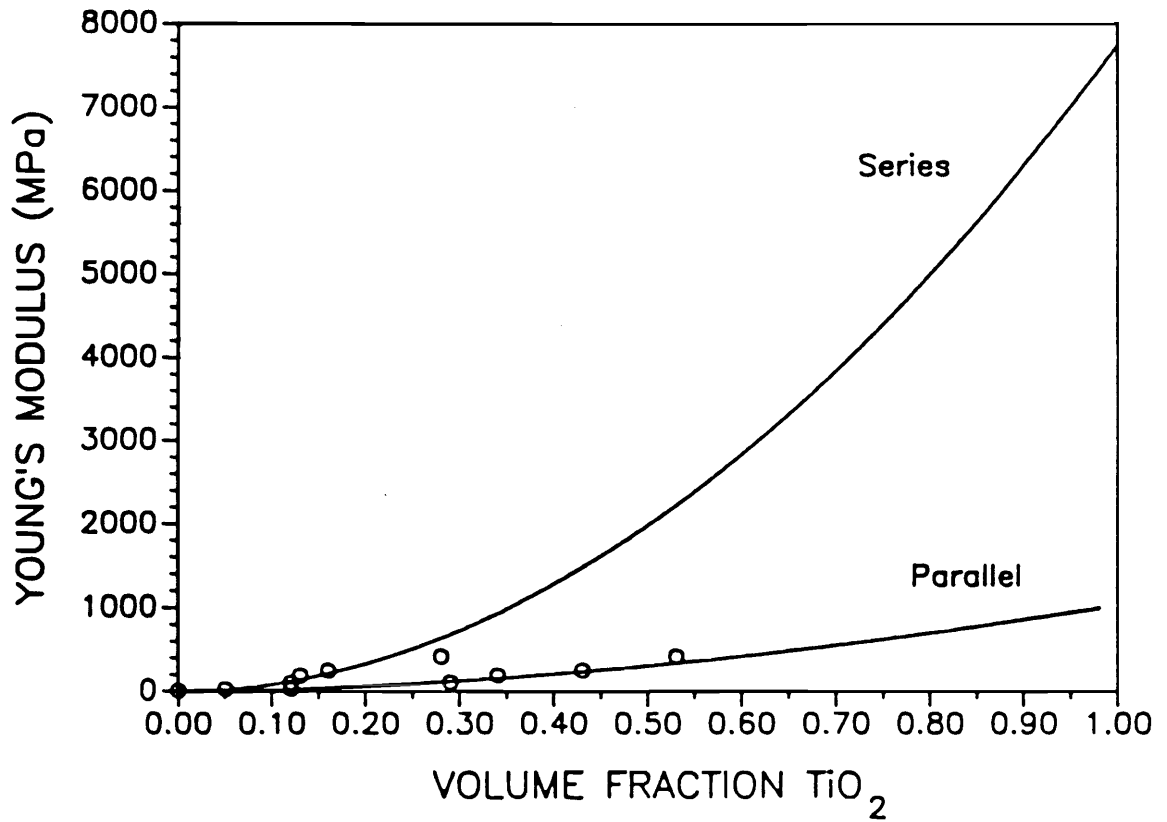


Figure I-1 Young's modulus of CERAMER as a function of calculated volume fraction of TiO_2 : TiOPr(X)-PTMO(2K)-25-0.06.

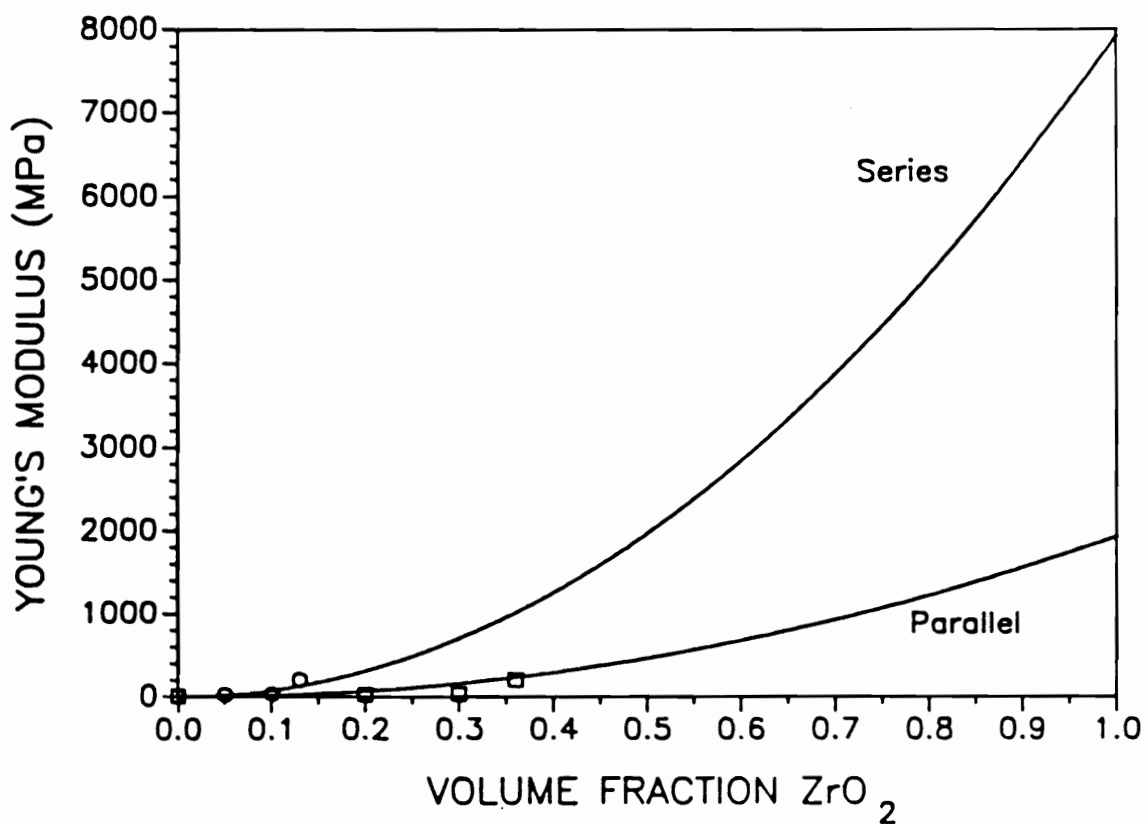


Figure I-2 Young's modulus of CERAMER as a function of calculated volume fraction of ZrO_2 : $\text{ZrOPr(X)}\text{-PTMO(2K)-0.0-0.06}$.

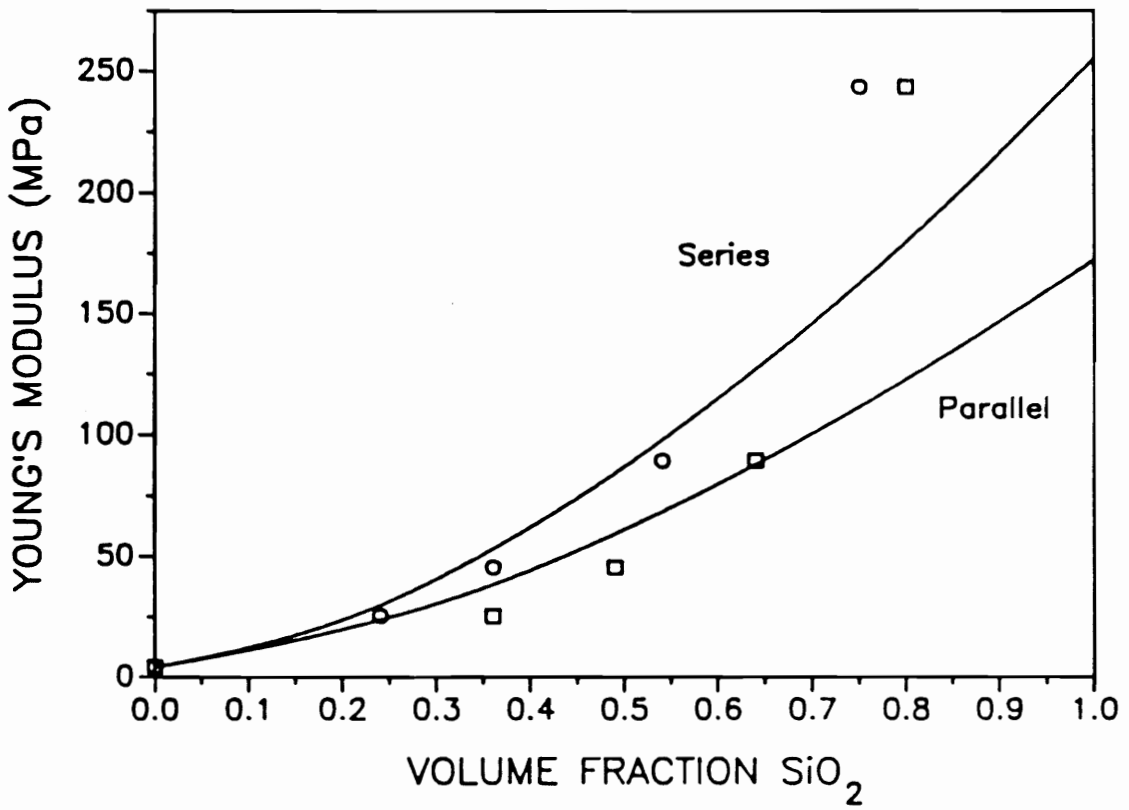


Figure I-3 Young's modulus of CERAMER as a function of calculated volume fraction of SiO_2 : TEOS(X)-PTMO(2K)-100-0.014 PSS.

simplifications and assumptions which were made in this appendix. A more detailed analysis would be critical to the application of this analysis beyond that of a method for predicting trends. The one interesting trend observed in this analysis is that the density of the inorganic phase rises as the apparent level of mixing between the inorganic phase and the PTMO chain segments decreases. This statement requires one to review the dynamic mechanical results presented in Chapters 4 and 6. It was clearly demonstrated that the TEOS/PTMO systems exhibited a lower density by this analysis and a greater extent of mixing (as determined from the broad loss dispersions in the dynamic mechanical response) compared to either the TiOPr/PTMO CERAMERs or the ZrOPr/PTMO CERAMERs. The densities of the inorganic structures of the TiOPr/PTMO and ZrOPr/PTMO CERAMERs are nearly a factor of two greater than those of the inorganic phase within the TEOS/PTMO CERAMERs which is largely a factor of the higher atomic weight of the metals, but less mixing would also be a contributing factor. A normalization of the Young's modulus as a function of the volume fraction of metal alkoxide for the three systems is depicted in Figure I-4. It is clear that the TiOPr/PTMO and ZrOPr/PTMO CERAMERs are quite similar to each other and significantly different than the TEOS/PTMO CERAMERs. Thus, this analysis appears to reflect trends one might predict based upon the components of these novel hybrid inorganic/organic networks.

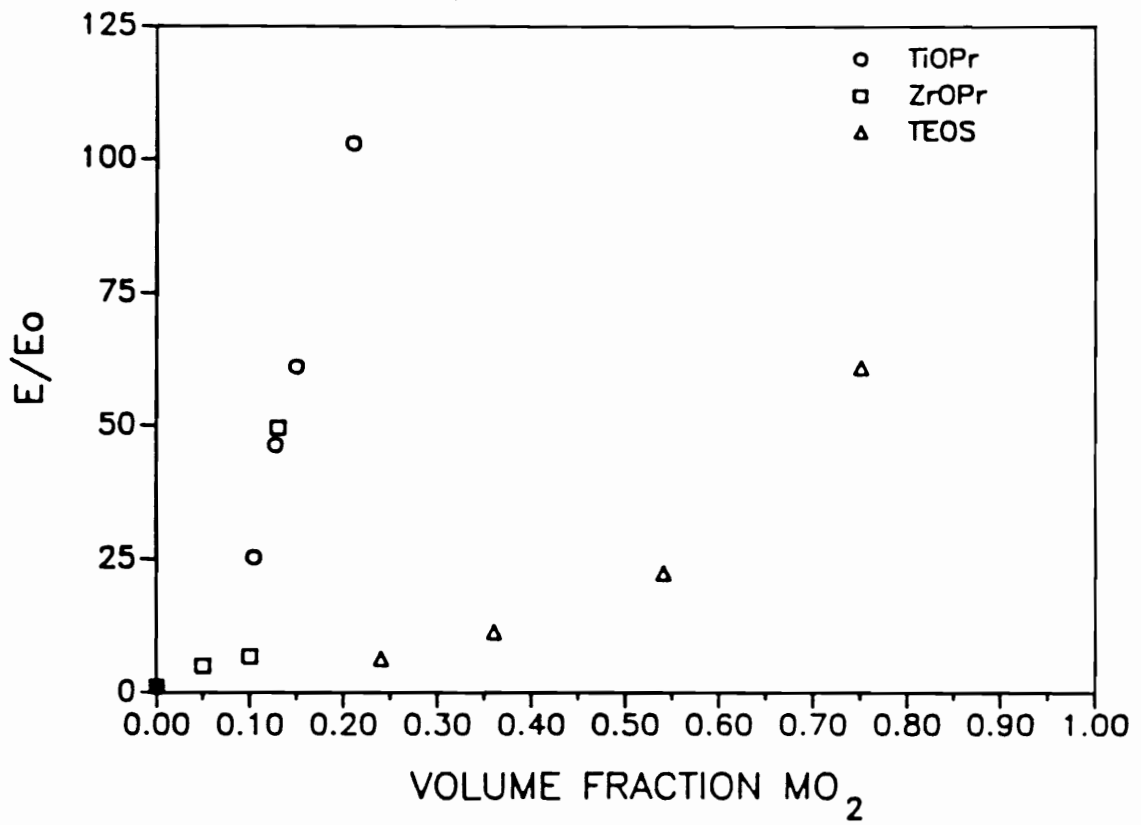


Figure I-4 Normalized Young's modulus of CERAMER as a function of calculated volume fraction of metal alkoxide.

Vita

Anthony B. Brennan, the sixth child of nine children of Henry and Marion Brennan was born January 1, 1952 in Saranac Lake, New York. He was raised in Natural Bridge, New York, graduated from the Carthage Central High School in 1970 and Jefferson Community College in 1972 with an Associate in Arts and Sciences degree. He married Miss Kathryn Carole Norland on August 10, 1974 and graduated with a Bachelor of Science degree in Chemistry from SUNY at Potsdam in May of 1975. In 1977, after receiving a Master of Science degree from Rochester Institute of Technology and one year as a Visiting Instructor, he began an industrial career in materials science at Rocky Mountain Orthodontics in Denver, Colorado. Shortly after the birth of his first child on January 17, 1980, Meaghan Alexe; and numerous developments in dental bonding resins, the pursuit of aesthetically acceptable orthodontic devices led him to Coors Ceramics Company and eventually a position as Senior Research Scientist at Coors Biomedical Company. His main areas of research were in non-shrinking, high temperature epoxies and non-shrinking moldable ceramics. A second child, Henry Michael, was born to Anthony and Kathryn on December 7, 1983. A continuing desire to understand fundamental properties of polymeric materials led him to Virginia Polytechnic Institute & State University in 1987 to pursue a Ph.D. under the guidance of Professor Garth L. Wilkes. After the defense of this dissertation, he will join the Materials Science and Engineering Department at the University of Florida.

A handwritten signature in cursive script that reads "Anthony Brennan". The signature is written in dark ink and is positioned to the right of the main text block.

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