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NOVEL CERAMER MATERIALS BASED ON POLY(PROPYLENE OXIDE) AND TETRAMETHOXYSILANE: COMPARISON OF ACCLAIM™ POLYETHER POLYOL AND JEFFAMINE® AND POLYOXYALKYLENEAMINE AS THE POLY(PROPYLENE OXIDE) SOURCE

Kurt Jordens^a; Garth Wilkes^b

^a Texas Eastman Division, Eastman Chemical Company, Longview, TX, U.S.A. ^b Department of Chemical Engineering, Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, U.S.A.

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NOVEL CERAMER MATERIALS BASED ON POLY(PROPYLENE OXIDE) AND TETRAMETHOXY-SILANE: COMPARISON OF ACCLAIM™ POLYETHER POLYOL AND JEFFAMINE® AND POLYOXYALKYLENEAMINE AS THE POLY(PROPYLENE OXIDE) SOURCE

Kurt Jordens† and Garth Wilkes*

Department of Chemical Engineering
Polymer Materials and Interfaces Laboratory
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061-0211

Key Words: Ceramer, Sol-Gel, Hybrid, Thermomechanical Spectrum, Alkoxide

ABSTRACT

Novel hybrid inorganic-organic network materials were generated through a modified sol-gel process based on poly(propylene oxide) (PPO) and tetramethoxysilane. The PPO sources chosen for study were (a) JEFFAMINE® D2000, an amine terminated PPO oligomer available commercially from the Huntsman Corporation, and (b) ACCLAIM™ 2220N, a polyether polyol available from Lyondell which is a copolymer of ethylene oxide ($\approx 25\%$) and propylene oxide ($\approx 75\%$). Overall, the structure-property relationships of ceramers made from these two oligomers are similar. Among the few differences is the tensile stress-strain behavior. The ACCLAIM™ based ceramers can be

* Author to whom correspondence should be addressed.

† Present address: Texas Eastman Division, Eastman Chemical Company, P.O. Box 7444, Longview, TX 76507-7444.

drawn to higher extents before failure. Also among the discrepancies is the dynamic mechanical behavior in the rubbery region. The ACCLAIM™ based ceramers appear to more closely mimic ideal rubber elasticity behavior, whereas the JEFFAMINE® based materials show less than direct proportionality of the storage modulus to temperature. These differences in behavior are due to the less than ideal functionality of the JEFFAMINE® oligomers, which is -1.94 (ideally 2.0), compared to the ACCLAIM™ oligomer which is greater than 1.99. This lower functionality led to a notable sol-fraction, and likely many dangling ends in the JEFFAMINE® based materials. Other minor differences and many similarities were found from small angle X-ray scattering, differential scanning calorimetry, and thermogravimetry experiments.

INTRODUCTION

Ceramers are among a class of hybrid network materials [1], typically composed of functionalized polymeric or oligomeric species which are reacted into a hybrid inorganic-organic network through the sol-gel reaction. The first ceramer material made in our laboratory in 1985 was based on an oligomeric form of hydroxyl terminated poly(dimethyl siloxane) (PDMS) and tetraethoxysilane (TEOS) [2]. Recently, we synthesized a similar ceramer based on poly(propylene oxide) (PPO) and tetramethoxysilane (TMOS) which was the subject of a previous manuscript [3]. That research explored the structure-property relationships in ceramer materials based on PPO oligomers derived from the family of JEFFAMINE® polyoxyalkyleneamines of the Huntsman Corporation. These JEFFAMINE® materials are generally imperfect in their chemistry, however; the functionality of these “diamines” is actually less than two (Table 1). This non-ideal functionality led to an imperfect ceramer network which would be expected to contain dangling ends and a finite sol-fraction [3]. However, due to a new catalyst and synthetic pathway, PPO oligomers can be made with high functionality (very near 2) and hence, low monol content. Lyondell makes such a family of materials that are newly available, known as the ACCLAIM™ polyether polyols. This allows an interesting comparison of ceramers based on these two PPO oligomers. The focus of this manuscript is to compare the properties of ceramers of similar formulation based on JEFFAMINE® and ACCLAIM™ PPO sources. Other researchers have prepared similar hybrid materials based on JEFFAMINEs® ED2001, ED900, and ED600 which are oligomeric forms of

TABLE 1. Comparison of JEFFAMINE[®] and ACCLAIM[™] Poly(propylene oxide) Oligomers

Material	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	f
ACCLAIM [™] 2220N	≈ 2200	≈ 2420	≈ 1.1	1.99+
JEFFAMINE [®] D2000	1577	1656	1.05	1.94

* Average functionality; i.e., the average number of either hydroxyl (ACCLAIM[™]) or primary amine (JEFFAMINE[®]) end-groups per molecule.

propylene oxide and ethylene oxide copolymers [4-7]. After incorporating lanthanide cations into these hybrids, the resulting luminescent materials have the potential for application as optical devices such as solid state lasers and optical fiber amplifiers. Materials similar to these based on oligomeric forms of poly(ethylene oxide) (PEO) and PPO homopolymers have also been reported and are considered to be solid electrolytes after incorporation of lithium salts [8-12]. These systems have potential application in areas such as batteries and energy and data storage devices.

EXPERIMENTAL

Materials and Synthesis

The ACCLAIM[™] PPO oligomer utilized in this study was provided by Lyondell, and is known as ARCOL[®] R-2744 polyol (ACCLAIM[™] polyol 2220N). It is an ethylene oxide (EO) end-capped PPO diol with a number average molecular weight of ≈ 2200 g/mol (generalized structure shown in Figure 1). The total EO content in the copolymer is approximately 25%, and 85% of the terminal groups are primary hydroxyls. The balance of the termini are secondary hydroxyls resulting from a propylene oxide group. This large portion of primary hydroxyl end-groups causes the EO end-capped oligomer to be more reactive with an isocyanate than a purely PPO oligomer, and the EO component makes the oligomer more hydrophilic in character than pure PPO. As can be seen in Table 1, the functionality of this oligomer is greater than 1.99, which is very close to the ideal case of 2.

The JEFFAMINE[®] PPO oligomer employed in this study was provided by the Huntsman Corporation, and is known as D2000. It is a primary amine ter-

minated PPO oligomer where the “D” stands for difunctional (ideally) and the subsequent number roughly corresponds to the number average molecular weight. The actual functionality of this material is less than 2, as shown in Table 1, where the measured molecular weights and breadth indexes (\bar{M}_w/\bar{M}_n), provided by the manufacturers, are also listed.

Other chemicals used in this study include TMOS (99+%, obtained from Gelest), isocyanatopropyltriethoxysilane, (ICPTES, 95%, Gelest), isopropanol (IPA, reagent grade, obtained from EM Sciences), dibutyltin dilaurate (95%, Aldrich Chemical) and 1 M aqueous HCl solution (Aldrich Chemical).

The synthesis of ceramers based on various JEFFAMINE[®], oligomers has been addressed previously [3]. Briefly, the amine terminated JEFFAMINES[®], are end-capped with an isocyanate silane (ICPTES) to form urea linkages. The silane functionality (specifically, the alkoxy silane end-groups) can subsequently participate in the sol-gel reaction.

The synthetic pathway to generating ceramers based on the ACCLAIM[™] materials is more difficult than with JEFFAMINES[®]. The urea formation involved in the functionalization of the JEFFAMINES[®], occurs readily at room temperature. However, due to the hydroxyl termination on the ACCLAIM[™] oligomers, reaction with an aliphatic isocyanate leads to a urethane linkage, which is not readily formed at room temperature. Hence, the reaction involved here, outlined in Figure 1, was carried out at elevated temperature with added catalyst in an inert atmosphere. This was accomplished as follows. The ACCLAIM[™] polyol was first added to a sealed, argon purged flask by syringe, and was heated to 90°C. This was followed by the addition of the liquid catalyst (dibutyltin dilaurate), in an amount of 250 ppm based on the ACCLAIM[™] oligomer. After the temperature stabilized, the isocyanate (ICPTES) was slowly added by syringe. The flask was then left sealed and kept between 80 and 100°C for eight hours. This generates the alkoxy silane functionalized ACCLAIM[™] Species (Figure 1) that can participate in the sol-gel reaction through the alkoxy silane endgroups.

The main chemical distinctions between the functionalized JEFFAMINES[®] and functionalized ACCLAIM[™] materials are the linkages between the alkoxy silane and the PPO are urea and urethane, respectively. Also, the JEFFAMINE[®] are strictly PPO chains whereas the ACCLAIM[™] material is an EO end-capped PPO oligomer. The EO content in the ACCLAIM[™] oligomer renders this material somewhat more hydrophilic than a homopolymer based on PO. Also important to the results of this work is that the molecular weight and

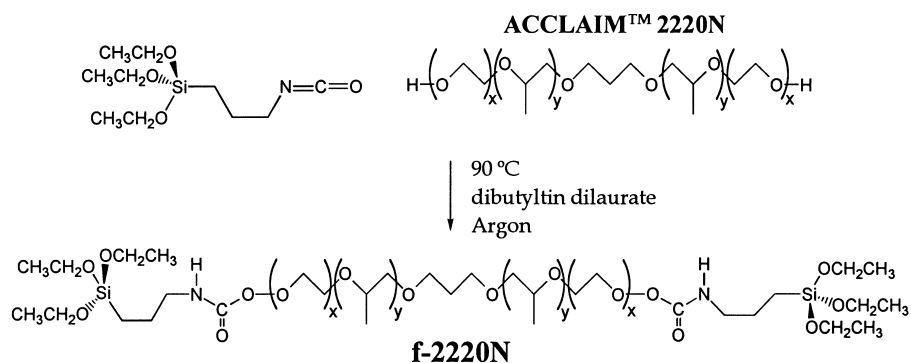


Figure 1. Schematic of the alkoxy silane functionalization of hydroxyl terminated ACCLAIM™ 2220N polyether polyol.

functionality of the original oligomers are different. The ACCLAIM™ material has higher functionality due to the recent improvements in the synthetic pathway (Table 1).

Formation of hybrid networks is then accomplished by employing the functionalized oligomers in the sol-gel reaction. Both the functionalized ACCLAIM™ and JEFFAMINE® materials, with their alkoxy silane end-groups, are able to undergo the sol-gel reaction in the presence of water. Or, as shown in

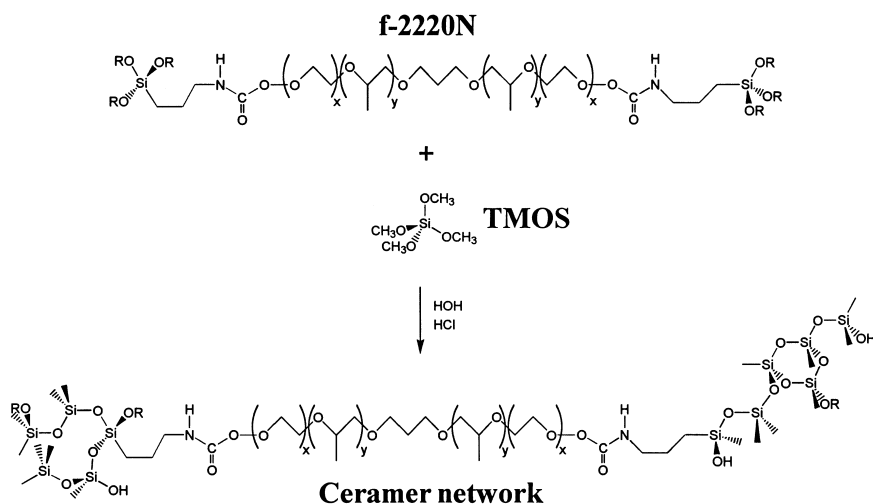


Figure 2. Schematic of the sol-gel reaction of f-2220N with TMOS.

Figure 2 for the case of f-222ON (functionalized ACCLAIM™ oligomer), the functionalized oligomers can coreact with TMOS. The TMOS contributes only inorganic character to the resulting material, as it condenses to form a structure similar to amorphous silicon dioxide. When the sol-gel reaction is carried out at room temperature, however, it is likely to be incomplete and hence, uncondensed groups tend to linger. Therefore, a more polysiloxane-like structure is formed rather than a purely silicate structure.

Once the sol-gel reaction is initiated and allowed to stir for approximately three minutes, the reacting solution is poured into a polystyrene petri dish, covered, rapidly degassed in a vacuum chamber, and allowed to cure for one week at laboratory conditions. After this, the samples are stored under vacuum for at least one day before characterization.

Characterization

All small angle X-ray scattering (SAXS) experiments were performed with nickel filtered, slit collimated CuK α radiation (1.542 Å) [13] produced by a Philips generator, model PW1729. A Kratky camera and a one-dimensional M. Braun position-sensitive detector were used to collect the scattered radiation. Absolute intensities were calibrated through the use of a polyethylene (Lupolen) working standard [13]. The collimating slit had a width of 100 μ m. Parasitic scattering was subtracted from the intensity, however, the contribution from thermal density fluctuations has not been removed. Also, the data were not corrected for slit smearing, however, desmearing of the SAXS curves would not change our conclusions. SAXS data will be presented as absolute intensity versus the magnitude of the scattering vector $s = (2 \sin \theta / \lambda)$, where θ is one-half of the radial scattering angle and λ is the wavelength of the radiation (1.542 Å). Correlation distances were determined as the inverse value of s at the location of the interference peaks.

The differential scanning calorimetry (DSC) experiments were performed on a Seiko DSC 220C with nitrogen purge gas. A heating rate of 20 K/min was employed for all scans, and samples weighed between 5 and 10 mg.

Thermogravimetry (TG) was accomplished with a Seiko TG/DTA under an air purge. A heating rate of 10 K/min was used and samples weighed between 5 and 10 Mg.

A Seiko DMS 210 was utilized for dynamic mechanical spectroscopy (DMS) experiments. Rectangular samples had a gauge length of 10 mm, and were cut such that their cross-sectional area was between 2 and 7 mm². Scans

were started at room temperature, and cooled slowly (1.5-2 K/min) with liquid nitrogen to $\approx -150^{\circ}\text{C}$ while collecting data. After this cooling scan, the sample was allowed to equilibrate back to room temperature, and a heating scan was then started under nitrogen purge gas with a heating rate of 1.5-2 K/min. The data from the heating and cooling scans were then combined to give the thermomechanical spectrum for each sample.

Tensile stress-strain experiments were carried out at lab conditions with an Instron model 4204 equipped with a 1 kN load cell using a crosshead speed of 2.54 mm/min. Dogbone shaped samples were cut with a die from cast films, and had a gauge length of ≈ 10 mm and a width at the gauge of ≈ 2.7 mm. Cross-sectional areas of each sample differed due to variations in the thickness of films which ranged between 0.25 and 0.7 mm. At least eight specimens were tested for each formulation which lead to the statistical averages to be presented.

Nomenclature

Due to the numerous variables explored in this work, a simplified system of nomenclature has been employed so that samples can be easily differentiated. This will be illustrated by the following example:

f-2220N(50) TMOS(50) 2/1/0.02

The f-2220N represents alkoxy silane end-functionalized ARCOL[®] R-2744 polyol (ACCLAIM[™] polyol 2220N). The functionalized JEFFAMINE[™] oligomer is referred to as f-D2000 in place of the f-2220N. The value of (50) implies that the functionalized oligomer was employed in the sol-gel reaction in a proportion of 50 wt%, relative to TMOS only. The TMOS(50) represents 50 wt% tetramethoxysilane, and the 2/1/0.02 represents the molar ratio of water/ alkoxy silane/HCl employed during the sol-gel reaction. Note that the moles of alkoxy silane groups used in this ratio are derived from the TMOS and the functionalized both oligomers for a given formulation.

RESULTS AND DISCUSSION

The general behavior of the ACCLAIM[™] based ceramers will first be addressed, since the general behavior of the JEFFAMINE[®] based ceramers has

been reported in the previous manuscript [3]. This will be followed by a direct comparison of ceramers of similar formulation based on functionalized ACCLAIM™ and JEFFAMINE® oligomers.

ACCLAIM™ Based Ceramers: General Behavior

Influence of TMOS Content on ACCLAIM™ Based Ceramers

The SAXS profiles for ceramers based on f-2220N with varied TMOS contents are displayed in Figure 3. Several trends can be noted in this plot. Firstly, as the TMOS content increases from 0 wt% to 25 and 50 wt%, the estimated correlation length (manifested as a peak in the SAXS profile) increases from 53 Å to 64 Å and 70 Å, respectively. This peak corresponds to a phase separated structure, one phase being rich in PPO (which is the continuous phase) and the other being rich in the inorganic component. If the PPO chains are assumed to be the same size in each ceramer (occupy roughly the same pervaded volume), then increasing the TMOS content would be expected to increase the size of the inorganic domains, thereby increasing the correlation length accordingly. This same trend was previously observed for ceramers based on poly(tetramethylene oxide) (PTMO) with titanium isopropoxide as the metal alkoxide source [14].

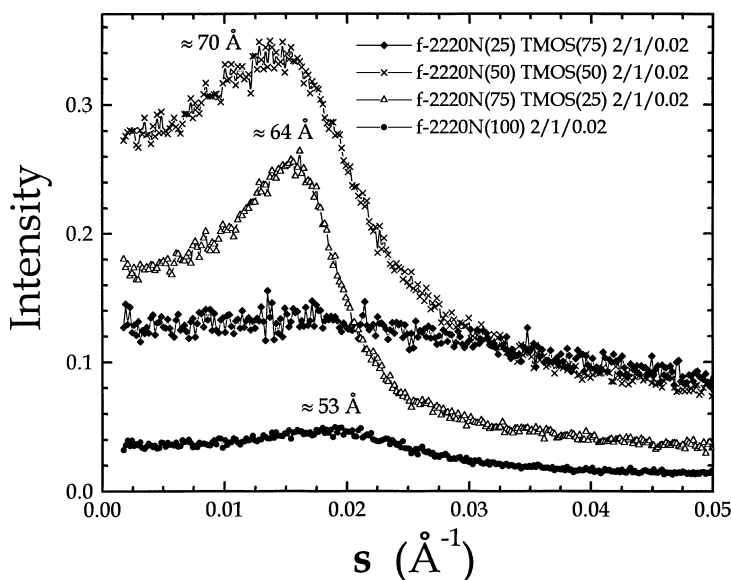


Figure 3. SAXS profiles for ceramers of varied TMOS content based on f-2220N.

However, increasing the TMOS content to 75 wt% leads to a SAXS profile with no clear interference peak. Hence, this material has no obvious correlation length evidenced from the raw data. The morphology of this material is quite different from the lower TMOS containing ceramers. The connectivity between the silicate phase is much greater, which is likely the continuous phase for this sample. Similarly, connectivity between inorganic domains was observed by transmission electron microscopy for a ceramer based on PTMO (≈ 2000 g/mol) and 80% TEOS [14]. The f-22ON(25) TMOS(75) sample was extremely brittle and uniform films could not be produced due to the excessive shrinkage and cracking caused by evaporation of the byproduct water and alcohols. Further analysis of the SAXS data showed that this material also did not display fractal character (self-similarity). In contrast, mass fractal character had been observed for high TMOS containing JEFFAMINE® based ceramers [3], although those materials were prepared with double the water content compared to the present ACCLAIM® based ceramers.

Another notable trend is that the integrated intensity varies with TMOS content, or in other words, the invariant is a distinct function of TMOS content. This is also an expected result [3] however, the explanation requires a brief discussion of the scattering power and the invariant. The invariant, Q_s , can be expressed as [13]:

$$Q_s = \int_0^{\infty} s \cdot I(s) ds \quad (1)$$

for slit-smear absolute intensity $I(s)$. The invariant is proportional to the mean square fluctuation in the electron density $\langle \Delta\rho^2 \rangle$ (or scattering power) which, for a two phase system displaying sharp phase separation with each phase of uniform electron density, the following simplified mathematical relationship holds:

$$\langle \Delta\rho^2 \rangle = \phi_{PPO} \cdot \phi_{sil} \cdot (\rho_{PPO} - \rho_{sil})^2 \propto Q_s \quad (2)$$

By employing this equation we are assuming that the ceramers are two phase systems, composed of a PPO-rich phase of volume fraction ϕ_{ppo} , and electron density ρ_{ppo} , and a separate silicate-rich phase of volume fraction $\phi_{sil} = 1 - \phi_{ppo}$, and electron density ρ_{sil} . With the value of $(\rho_{ppo} - \rho_{sil})^2$ remaining constant,

$\langle \Delta\rho^2 \rangle$ reaches a maximum at $\phi_{\text{ppo}} = \phi_{\text{sil}} = 0.5$. Hence, we would expect the integrated intensity of the SAXS profiles to be a maximum for a sample which has a silicate volume fraction of 0.5. This appears to be in agreement with the data of Figure 3, where the maximum integrated intensity occurs for the f-2220N(50) TMOS(50) ceramer (50 wt% TMOS). However, the 50 wt% TMOS content reflects the weight fraction of liquid TMOS in the formulation prior to the sol-gel reaction, and the condensation reaction leads to a loss of mass as by-product water and alcohols. Hence, the silicate content in the final ceramer is certainly not the same as the initial TMOS content in the formulation. The weight fraction of silicate for several ceramers can be estimated from thermogravimetry (Figure 4), and these results are listed in Table 2. Note that the value of silicate content estimated from thermogravimetry is a weight fraction, and ϕ_{sil} in Equation 2 reflects a volume fraction. Estimating the silicate content in this fashion leads to a value of 51 wt% silicate for the f-2220N(25) TMOS(75) ceramer. Since this value is the closest to $\phi_{\text{ppo}} = \phi_{\text{sil}} = 0.5$, one might expect that the integrated SAXS intensity should be the greatest for this material. This is not the case as noted above, where the f-2220N(50) TMOS(50) ceramer appears to have the greatest

TABLE 2. Glass Transition, Estimated Silicate Content, and Correlation Length Data for Various Acclaim™ and JEFFAMINE® Ceramers of the 2/1/0.02 Formulation

Sample	T_g (°C)	silicate content† (wt.%)	correlation length‡ (Å)
f-2220N(100)	-55	10	53
f-2220N(75) TMOS(25)	-43	19	64
f-2220N(50) TMOS(50)	-10	34	70
f-2220N(25) TMOS(75)	-§	51	<i>none observed</i>
f-D2000(100)	-57	13	45
f-D2000(75) TMOS(25)**	-46	22	<i>none observed</i>
f-D2000(50) TMOS(50)	-23	36	61

* Determined from DMS experiments as the midpoint (on the *log-scale*) of the drop in storage modulus across the glass transition.

† Estimated from char yield measured by thermogravimetry.

‡ Slit-smeared SAXS result.

§ Not measured.

** 4/1/0.04 formulation.

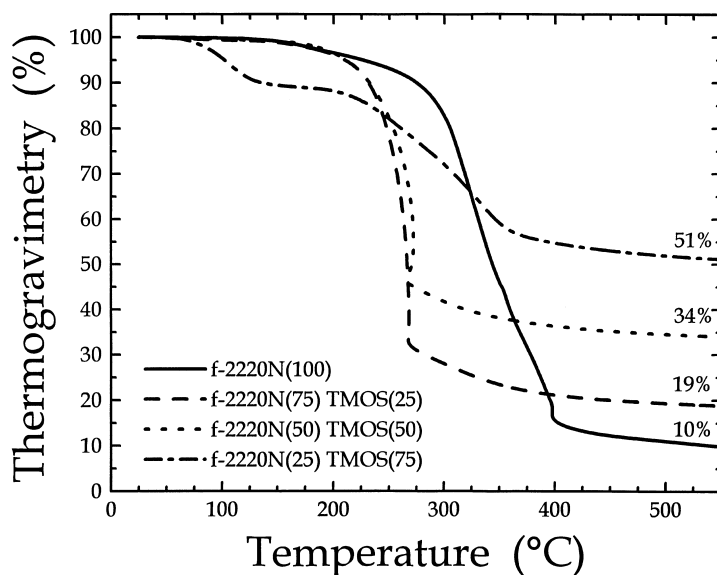


Figure 4. Thermogravimetry scans of f-2220N based ceramers of varied TMOS content.

integrated intensity. However, the thermogravimetrically estimated value of 51 wt% also does not reflect the true amount of polysiloxane (or silicate) in the ceramer before the thermogravimetry scan, as the sol-gel reaction can occur as the material is heated during this measurement. The alkoxy and silanol groups of the polysiloxane phase can continue to condense as the temperature is increased, thereby, leading to weight loss of this phase [15]. This proposal is supported by the TG scan for this ceramer as seen in Figure 4, where there is a substantial weight loss (≈ 10 wt%) which occurs in the region of 50 to 150°C. Since no degradation is expected in this low temperature range, the observed weight loss is evidence of further reaction due to the release of volatile water and alcohol. Accounting for this, the estimated silicate content for this ceramer now becomes ≈ 58 wt%. Such a result, however, still dictates that this sample is closest to ϕ_{sil} , = 0.5.

The TMOS content also drastically influences the dynamic mechanical behavior of the f-2220N based ceramers, as seen in Figure 5. First consider the storage modulus data for the ceramer with no added TMOS, the f-2220N(100) material. This sample has the sharpest glass transition, which occurs at, $\approx -55^\circ\text{C}$, within a temperature window of -70 to 0°C . The storage modulus shifts from

≈ 4 GPa in the glassy state (a typical value for an organic glass) to ≈ 3 MPa in the rubbery state (a typical value for a rubber or elastomer). This three order-of-magnitude reduction in the storage modulus across the glass transition is characteristic of amorphous, high molecular weight organic polymers and lightly crosslinked amorphous organic networks. However, for the f-2220N(75) TMOS(25) ceramer, the glass transition is increased slightly to $\approx -43^\circ\text{C}$ and broadened (occurs over the temperature range of -70 to 30°C). The storage modulus in the glassy state is similar to that of the TMOS-free ceramer, however, the change in the storage modulus across the glass transition for this sample is about 2.5 orders-of-magnitude.

Hence, the storage modulus in the rubbery state is somewhat higher than the nonTMOS containing ceramer. Finally, the f-2220N(50) TMOS(50) ceramer possesses the broadest (temperature window of -70 to 80°C) and highest glass transition, near -10°C . Again, the storage modulus in the glassy state for this material is similar to the other two samples, in this case almost 10 GPa, but the drop across the glass transition is only two orders of magnitude. Hence, the major effect of increasing the TMOS content is to increase and broaden the glass transition, and increase the storage modulus in the rubbery state. In this manner, the influence of TMOS is similar to the influence of a reinforcing filler on an elastomer [16]. This is not surprising since the TMOS reacts to form a rigid, inorganic, silicate-like phase. These trends have also been observed for the JEFFAMINE[®] based ceramers [31, as well as other similar ceramer materials based on PTMO and TEOS [15, 17, 18], and poly(vinyl acetate) and TEOS [19, 20].

An interesting point to note is that the modulus in the rubbery plateau (which is located between, ≈ 0 and 200°C for the f-2220N(100) ceramer) actually increases slightly with temperature. This is due to a combination of the rubber elastic effect and an increase in the crosslink density as the sample reacts further above room temperature. For an ideal elastomer, the equilibrium Young's modulus E is given by [21]:

$$E = 3N_v kT = \frac{3\rho RT}{M_c} \quad (3)$$

(N_v) is the number of crosslinks per volume, k is Boltzmann's constant, ρ is the density of the material at the absolute temperature T , R is the universal gas constant, and M_c is the molecular weight between crosslinks. Although Equation 3 is derived for ideal networks with functionality of four, and also the dynamic mechanical experiment provides storage modulus data (E') and not equilibrium modulus data, the proportionality to the absolute temperature is expected to be a

reasonable approximation (i. e., the rubber elastic effect). In fact, dynamic mechanical experiments have proven to provide data which is compliant with equilibrium swelling experiments for similar ceramers based on PTMO and TEOS (although the authors employed a slower heating rate of 0.75 K/min in their DMS experiments) [22]. It can be seen from this equation that the modulus would also increase as the crosslink density increases (N_v). This is the second possible explanation for the behavior observed in Figure 5, since these materials were cured at room temperature and the reaction may continue when higher temperatures are reached during the dynamic mechanical experiment. The true source of this observed modulus increase is easily deciphered by the cyclic DMS experiment in Figure 6. During the first heating scan, the storage modulus increases due to both the rubber elastic effect (T increasing) and further reaction (N_v increasing). After annealing at 150°C for an hour, the storage modulus data for the subsequent cooling and second heating scans coincide. The data for these two subsequent steps have the same shape as that predicted by ideal rubber elasticity (proportionality to temperature), also included in this plot as a dark line. Hence, the first heating step displays the combined effects of rubbery elasticity and increased crosslink density, while the rubber elastic effect alone is active for the two subsequent steps. Similar, but not exactly the same behavior has been

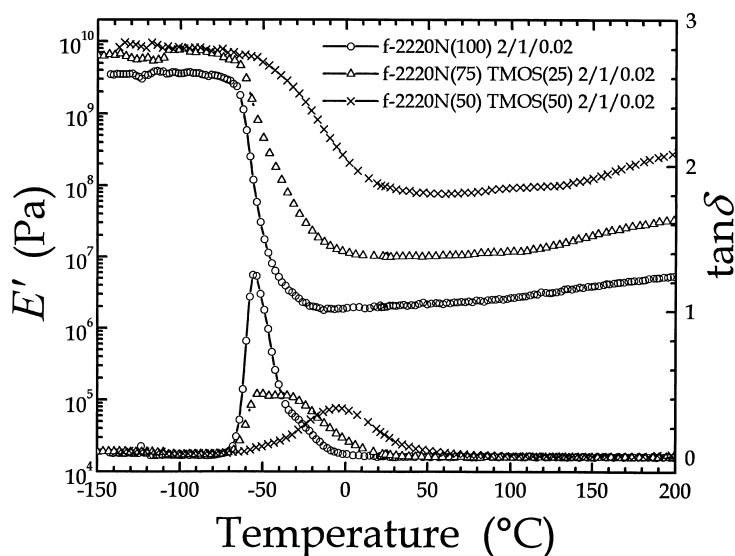


Figure 5. Thermomechanical spectra of f-2220N based ceramers of varied TMOS content.

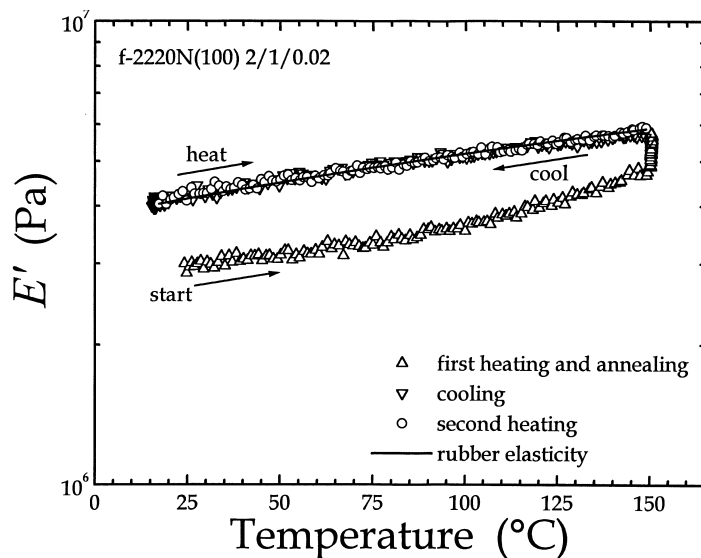


Figure 6. A cyclic dynamic mechanical experiment for f-2220N(100).

noted for the JEFFAMINE[®] based ceramers [3], which will be compared to the ACCLAIM[™] based ceramers later.

The influence of increasing TMOS content on the glass transition behavior of these ceramers is analogous to the JEFFAMINE[®] based ceramers discussed in our earlier report [3]. Briefly, the physical and chemical environment in which the PPO chain segments inhabit dictate their glass transition behavior. This molecular environment is best interpreted through the dynamic $\tan \delta$ data. The f-2220N(100) ceramer possesses one major, sharp relaxation peak in the $\tan \delta$ data at $\approx -55^\circ\text{C}$. This corresponds to the glass transition of a phase rich in PPO (pure high molecular weight, homopolymeric PPO has a reported dilatometric glass transition between -78 and -73°C) [23-26], which has little constraints imposed upon it by the silicate phase. Note that this silicate phase in this sample is located solely at the PPO chain ends, as no TMOS was added to this formulation. The small shoulder in the $\tan \delta$ data, just above the main relaxation, has been tentatively assigned to the relaxation of segments at the interface between the silicate and the PPO-rich phases [3]. These segments would be more constrained than those in the bulk PPO phase (where their behavior is similar to homopolymeric PPO) due to their direct connection to the rigid silicate, and hence would relax at a higher temperature. An analogous shoulder has been observed for similar ceramers based on polybutadiene [27] and as will be shown

later, a small related peak is present for the JEFFAMINE[®] f-D2000(100) ceramers.

With the addition of TMOS to the ACCLAIM[™] based ceramers, the silicate component can impose additional constraints upon the PPO segments, particularly at locations other than solely the chain ends. Therefore, adding TMOS tends to decrease the relative intensity of the $\tan \delta$ peak at $\approx -55^\circ\text{C}$ associated with the homopolymeric like PPO phase, while introducing relaxation phenomena at higher temperatures associated with the more highly constrained segments [28]. This can be seen in Figure 5 for the f-2220N(75) TMOS(25) ceramer, where the low-temperature peak ($\approx -55^\circ\text{C}$) in the $\tan \delta$ data is reduced considerably in magnitude compared to the f-2220N(100) ceramer. This is accompanied by an increase in the magnitude of the higher temperature relaxation, the relaxation which is merely a shoulder to the main glass transition for the f-2220N(100) material. Hence, the $\tan \delta$ data for the f-2220N(75) TMOS(25) ceramer appears somewhat bimodal in shape, where both relaxation phenomena are similar in magnitude. The relaxation phenomenon occurring at higher temperature may again be associated with the constrained PPO segments at the interface between the silicate and bulk PPO phase. The addition of 25 wt% TMOS leads to a larger silicate content and hence a higher concentration of constrained interfacial material, and therefore a larger magnitude of the higher temperature relaxation process. For the material with 50 wt% TMOS, one broad relaxation phenomenon is observed in the $\tan \delta$ data. The whole relaxation spans from ≈ -60 to $\approx 80^\circ\text{C}$, and the peak of this relaxation occurs at $\approx -5^\circ\text{C}$. The broadness reflects the wide distribution of molecular environments inhabited by the PPO segments, some regions being highly constrained, and some being less constrained. Similar environments have been described for PTMO segments in a related ceramer material [28].

The TMOS content also influences the tensile stress-strain (σ_o - ϵ) behavior for these ceramers. The f-2220N(100) ceramer was too soft and weak for tensile testing with the Instron. The mechanical properties of this material are like that of gelatin, and as such the samples were crushed during the gripping process. The σ_o - ϵ data for all ceramer materials which were able to be tested in the Instron are shown in Figure 7. Presently, the reader's attention is drawn to the data of the f-2220N(50) TMOS(50) 2/1/0.02 and f2220N(75) TMOS(25) 2/1/0.02 samples in this plot. The variation in mechanical properties with TMOS content for these two formulations can be easily seen; the f2220N(50) TMOS(50) 2/1/0.02 material has a much higher modulus (E'), stress at break (σ_b , location denoted by the symbol x), and toughness than the f-2220N(75) TMOS(25) 2/1/0.02 sample (Table 3). This is expected, since the reacted TMOS

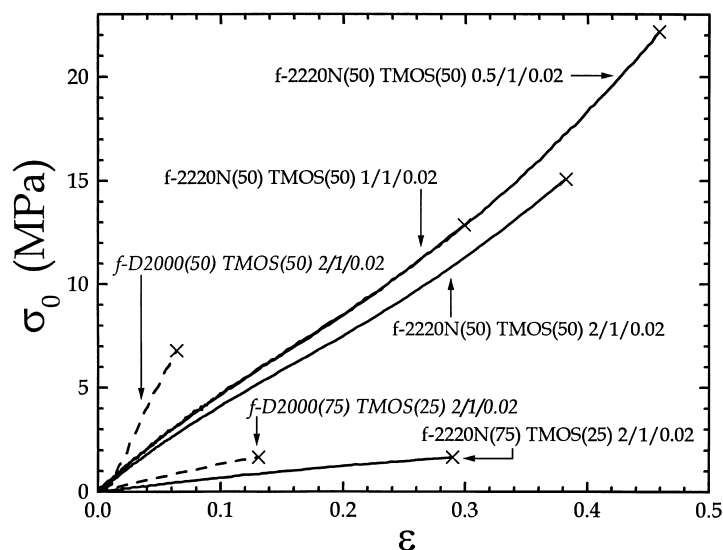


Figure 7. Tensile σ_0 - ϵ data for various ACCLAIM™ and JEFFAMINE® based ceramers. One curve for each formulation is plotted which was the best representative of the statistical results.

forms a polysiloxane structure which acts as a reinforcing filler for the soft PPO. It should be noted that the data for the f-2220N(75) TMOS(25) ceramer is within the noise region of the load cell employed, evidenced by the slight vibrations in the stress data. For this reason the reported parameter values for this sample are provided with caution.

TABLE 3. Tensile Stress-Strain Parameters for Various Ceramers

Formulation	E (MPa)	σ_b (MPa)	ϵ_b	toughness (MJ/m ³)
f-2220N(50) TMOS(50) 2/1/0.02	46.8 ± 2.8	15.1 ± 1.9	0.38 ± 0.03	2.9 ± 0.6
f-2220N(50) TMOS(50) 1/1/0.02	51.3 ± 2.3	13.1 ± 1.3	0.30 ± 0.03	1.98 ± 0.36
f-2220N(50) TMOS(50) 0.5/1/0.02	48.5 ± 2.7	21.8 ± 4.9	0.46 ± 0.07	4.7 ± 1.6
f-2220N(75) TMOS(25) 2/1/0.02*	6.9 ± 0.3	1.61 ± 0.29	0.29 ± 0.06	0.26 ± 0.1
f-D2000(75) TMOS(25) 2/1/0.02	12.7 ± 0.9	1.65 ± 0.39	0.13 ± 0.03	0.12 ± 0.05
f-D2000(50) TMOS(50) 2/1/0.02	108 ± 20	4.3 ± 2.0	0.05 ± 0.02	0.10 ± 0.07

* Data is into the noise region of the load cell for this sample and hence is suspect.

Influence of Water Content on f-2220N(50) TMOS(50) Ceramers

The three SAXS curves of Figure 8 illustrate the variation in the morphological structure of f-2220N(50) TMOS(50) ceramers with water content, in the range of 0.5/1/0.02 to 2/1/0.02. All curves are similar, possessing a clear correlation length. However, the exact location of the peak does depend mildly on the water content; the correlation length increases slightly with increasing water content from 63 Å to 65 Å and 70 Å for the range probed. Recalling that the ACCLAIM™ oligomer contains $\approx 25\%$ EO units, it is expected to be more hydrophilic than the JEFFAMINE® oligomer. Hence, the observed trend may be a result of an improvement in the overall “solvent quality” of the reaction medium with increasing water concentration. Such an effect would cause the chains to expand, or rather increase the end-to-end distance of the oligomer chains in the reacting solution. Subsequent condensation and formation of the network would effectively confine the chains to this expanded end-to-end distance, thereby leading to the observed trend.

The water content shows no significant effect on the thermomechanical spectra for these materials however, as seen in Figure 9. All three samples in this plot display a broad glass transition (onset $\approx -70^\circ\text{C}$, end-point $\approx -70^\circ\text{C}$ by the $\tan \delta$ data) with a peak at $\approx 0^\circ\text{C}$. The storage modulus in the glassy state is ≈ 10 GPa

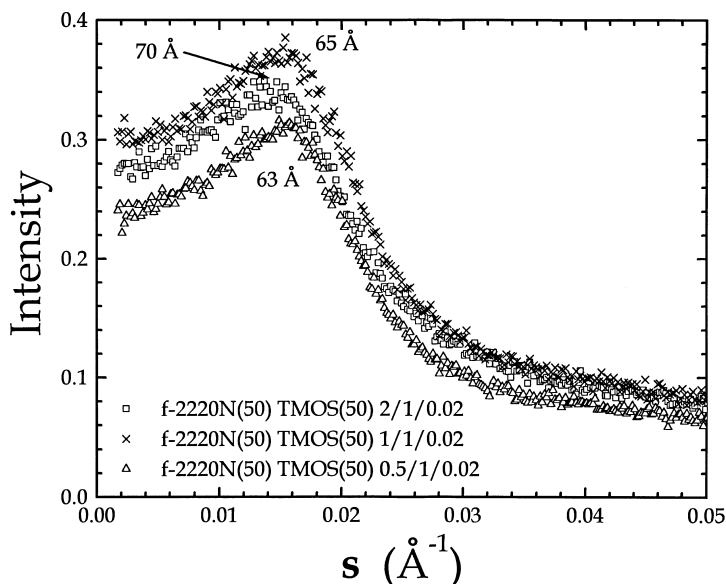


Figure 8. SAXS curves for f-2220N(50) TMOS(50) ceramers of varied water content.

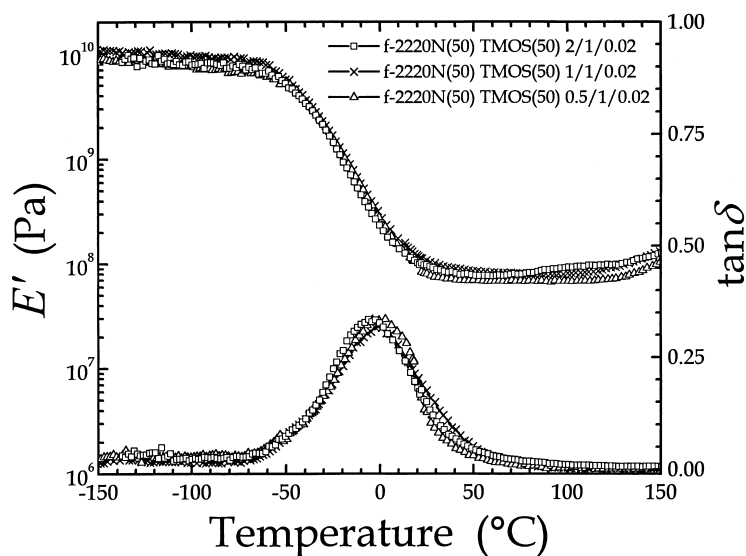


Figure 9. Thermomechanical spectra for f-2220N(50) TMOS(50) ceramers of varied water content.

for all three materials, and drops two orders of magnitude across the glass transition into the rubbery state.

The σ_o - ϵ curves of the f-2220N(50) TMOS(50) ceramers show a slight variation with water content (compare the 2/1/0.02, 1/1/0.02, and 0.5/1/0.02 formulations of Figure 7), however no direct relationships exist for the range probed in this study. All σ_o - ϵ curves for the ACCLAIMTm based ceramers with 50 wt% TMOS show the same basic S-shape, similar to previously reported ceramers based on PTMO and TEOS [17]. The 2/1/0.02 formulation of the present study displays the lowest statistical value of E (Table 3) among the samples, however all the other tensile parameters for this material are intermediate to the 0.5/1/0.02 and 1/1/0.02 formulations. The values of E may not be statistically different for these varied water formulations, however, as all three are within 10% of each other. This aside, the 1/1/0.02 material appears to be the stiffest (highest E) and least tough. The water deficient material (0.5/1/0.02) has the largest values of σ_o , ϵ_b (strain at break), and toughness.

Comparison of JEFFAMINE[®] and Acclaim[™] Based Ceramers

Tensile Stress-Strain Behavior

The greatest distinction between the two ceramer families lies in the mechanical properties, specifically the tensile σ_o - ϵ , behavior. While the σ_o - ϵ data for the ACCLAIM[™] based ceramers were thoroughly discussed in the previous section, the JEFFAMINE[®] based ceramers were quite inferior in this respect. The sample-to-sample variation within a given JEFFAMINE[®] based formulation was rather great (as seen in the magnitudes of the standard deviations in Table 3), and these materials generally had values ϵ_b less than 0.15. The shape of the σ_o - ϵ curves was linear within this limited extent of strain, like that of a Hookean spring, as opposed to the more “S-shaped” curves of the ACCLAIM[™] materials. Representative σ_o - ϵ curves for the fD2000(75) TMOS(25) 2/1/0.02 and f-D2000(50) TMOS(50) 2/1/0.02 ceramers are included in Figure 7 which allows easy comparison of them with the ACCLAIM[™] based ceramers. Similar to the JEFFAMINE[®] based ceramers, low values of ϵ_b and linear σ_o - ϵ , data were also observed for ceramers, based on PDMS and TEC6 [29, 30]. The distinction in the σ_o - ϵ behavior between the JEFFAMINE[®] and ACCLAIM[™] based ceramers is a direct result of the difference in the functionality between the two original oligomers. The ACCLAIM[™] oligomer is superior with a very high functionality of greater than 1.99, whereas the JEFFAMINE[®] oligomer has an estimated functionality of 1.94 (Table 1). Lower functionality generally leads to more dangling ends in the final network material, which explains the variance in the σ_o - ϵ behavior.

Small Angle X-Ray Scattering Behavior

The SAXS profiles for various ceramers made from both JEFFAMINE[®] and ACCLAIM[™] sources are shown in Figure 10. As can be seen in this plot, the ceramers made without TMOS (the f-2220N(100) and f-D2000(100) samples) have very similar SAXS patterns. Both possess a clear correlation length, however the ACCLAIM[™] based ceramer has a larger spacing of 53 Å compared to the 45 Å spacing of the JEFFAMINE[®] based material. This discrepancy is believed to be due to two factors; firstly, the ACCLAIM[™] oligomers are slightly higher in molecular weight (compare 2200 to 1577 g/mol). Secondly, as mentioned before, the ACCLAIM[™] oligomer is a copolymer containing EO. The molecular weight of EO per repeat unit is less than that of propylene oxide. Hence the contour length of the EO containing oligomer would be longer than

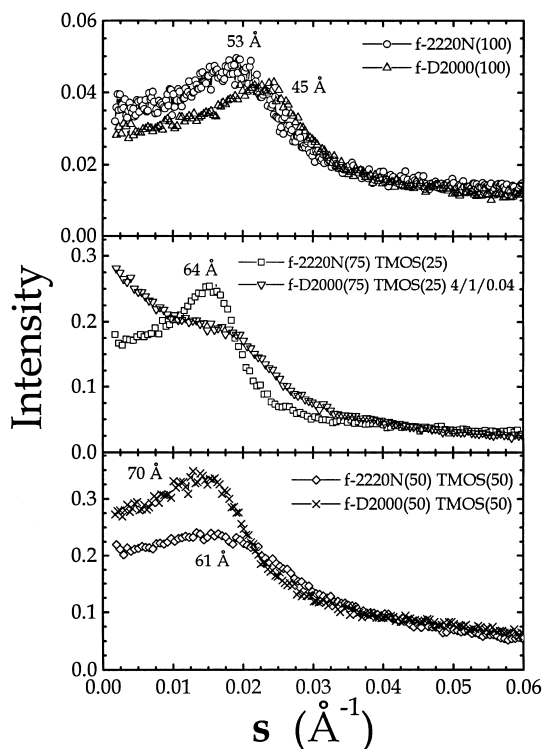


Figure 10. SAXS profiles for JEFFAMINE[®] and ACCLAIM[™] based ceramers with varied TMOS content. No TMOS (top); 25 wt% TMOS (center); 50 wt% TMOS (bottom).

that of a purely propylene oxide oligomer of identical molecular weight. These factors can easily account for the slightly larger correlation length in the ACCLAIM[™] based ceramer.

The ceramers containing 25 wt% TMOS cannot be compared as fairly as the other materials since the f-D2000(75) TMOS(25) 4/1/0.04 material was synthesized with twice the water and acid concentration as the f-2220N(75) TMOS(25) 2/1/0.02 sample.

Acknowledging this fact, it can be seen from Figure 10 that the ACCLAIM[™] based ceramer possesses a clear correlation length at 64 Å, while the JEFFAMINE[®] based sample has no clear peak, but rather has a shoulder. As discussed in detail in a previous report, the f-D2000(75) TMOS(25) 4/1/0.04 sample has mass fractal character, or dilation symmetry (fractal dimension of ≈ 2.7). This implies that the material has the property that it is not space filling

or of uniform density in three dimensions (which would correspond to a fractal dimension of 3.0). Hence, the polysiloxane structure is slightly “open” compared to a uniform, three-dimensional solid.

Comparing the two 50 wt% TMOS containing ceramers leads to the observation that the ACCLAIM™ based material has a larger long spacing of 70 Å compared to the 61 Å spacing of the JEFFAMINE® material. The explanation of this is the same as that for the two non-TMOS ceramers; the slightly higher contour length of the oligomeric ACCLAIM™ materials compared to the JEFFAMINE® oligomers can account for the discrepancy. Therefore, the size of the silicate domains in each 50 wt% TMOS sample are not necessarily different, as the oligomer alone can account for the difference in long spacing. This is supported by the fact that the variance in the long spacing for the 50 wt% TMOS containing materials is ≈ 9 Å, which is roughly the same as the nonTMOS samples which differ by ≈ 8 Å.

The f-2220N(50) TMOS(50) 2/1/0.02 sample shows a sharper or more narrow correlation peak than the f-D2000(50) TMOS(50) 2/1/0.02 material. This is likely due to sharper phase separation in the f-2220N(50) TMOS(50) material. The sharper phase separation is partly a result of the higher molecular weight 2220N oligomer.

Dynamic Mechanical Behavior

The comparison of the thermomechanical spectra for the ACCLAIM™ and JEFFAMINE® based ceramers is shown in Figure 11. The similarities between the ceramers made from both oligomers are apparent in this plot. First considering the non-TMOS containing ceramers, both the f-2220N(100) and f-D2000(100) materials have essentially the same main glass transition at -55°C . Just above the main glass transition, the f-2220N(100) sample shows a shoulder in the $\tan \delta$ data, whereas the fD2000(100) material displays an additional small peak in this region. These post- T_g relaxations were discussed above, and were assigned to the segments at the interface between the bulk PPO phase and the silicate phase. The fact that the f-2220N(100) sample has just a shoulder and the f-D2000(100) sample has a small peak is likely due to the slightly different chemistry at the silicate-bulk PPO interface. In the f-D2000(100) material these interfacial segments are likely composed of urea groups and propylene oxide units, however, in the f-2220N(100) material the interfacial segments would be composed of urethane and ethylene oxide units. Hence, these slightly different moieties are potentially responsible for the slightly different relaxation behavior. Note that in the previously mentioned study on butadiene-based ceramers, the

dynamic mechanical $\tan \delta$ data displayed a shoulder just above the main glass transition, and this material also possessed urethane groups between the silicate and bulk rubbery phase [27].

Another notable difference in the dynamic mechanical data is that the ACCLAIM™ based ceramers, have a lower value of the storage modulus in the rubbery state than the JEFFAMINE® ceramers. This is believed to be due to the higher molecular weight of the ACCLAIM™ oligomer, which can be rationalized by recalling Equation 3. The value of M_c for the ceramers is expected to approximately correspond to the molecular weight of the original oligomers, (or perhaps more precisely the functionalized oligomers). Hence, the D2000 oligomer, which has a number average molecular weight of ≈ 1577 g/mol (Table 1), would be expected to produce a ceramer with a higher rubbery modulus than the 2220N oligomer of ≈ 2200 g/mol as observed in Figure 11.

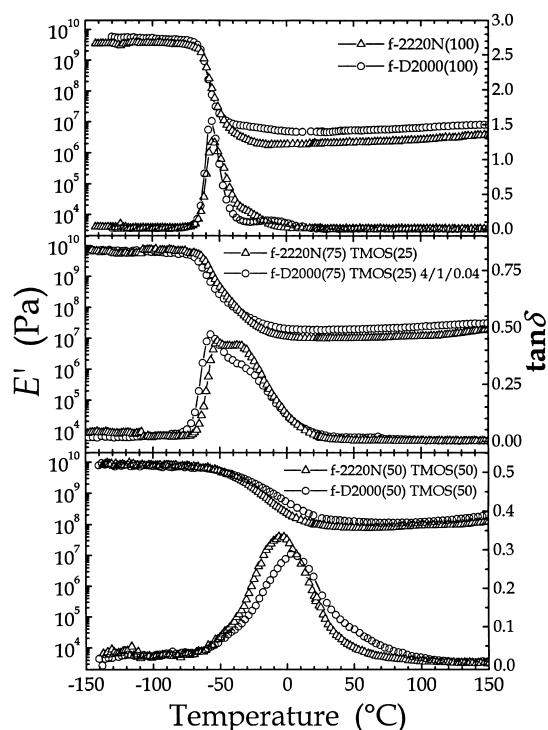


Figure 11. Thermomechanical spectra for JEFFAMINE® and ACCLAIM™ based ceramers of varied TMOS content. No TMOS (top); 25 wt% - TMOS (center); 50 wt%. -TMOS (bottom).

This is true for the TMOS containing ceramers as well; the D2000 based materials always have a higher storage modulus above the glass transition than the corresponding (equal TMOS containing) 2220N based samples.

As previously discussed and shown in Figure 6, the f-2220N(100) 2/1/0.02 ceramer complies with ideal rubber elasticity once it has been annealed at an elevated temperature. This was evidenced by the coinciding of the storage modulus data upon cooling and second heating with the line representing ideal rubber elasticity. However, the f-D2000(100) ceramer did not correspond perfectly with the dictates of ideal rubber elasticity during the cooling and subsequent heating steps [3]. This was attributed to the imperfect chemistry of the D2000 oligomers, specifically to the network imperfections (dangling chains) which it would generate. Because of these defects, non-equilibrium effects on the modulus may be present at the lower temperature portion of the cyclic experiment for the JEFFAMINE[®] ceramer, which would translate to higher values of E' than would be predicted from equilibrium elasticity. The improved functionality in the ACCLAIM[™] oligomer generates a ceramer material which more closely obeys the relationship to temperature predicted by ideal rubber elasticity theory.

The 25 wt% TMOS ceramers have very similar thermomechanical spectra, despite the differences in their SAXS patterns and the fact that the f-D2000(75) TMOS(25) 4/1/0.04 was generated with twice the water and acid content as the f-2220N(75) TMOS(25) 2/1/0.02 material. Both show a peak in the $\tan \delta$ data corresponding to bulk PPO phase at $\approx -50^\circ\text{C}$, and a second peak or relaxation just above it, of nearly equal strength. Again, this second, higher temperature relaxation would correspond to the interfacial segments, between the bulk PPO and silicate phases.

The materials containing 50 wt% TMOS are also very similar in their thermomechanical spectra. Both possess one broad relaxation in the $\tan \delta$ data, centered at $\approx 0^\circ\text{C}$. Although the JEFFAMINE[®] based material appears to have shoulders in the $\tan \delta$ data at $\approx -50^\circ\text{C}$ and 100°C [3], no such shoulders are apparent in the ACCLAIM[™] ceramer.

Differential Scanning Calorimetry

Figure 12 contains the DSC traces for the various ceramers made from both JEFFAMINE[®] and ACCLAIM[™] oligomers. Confirming the observations from the DMS data, the DSC data for the JEFFAMINE[®] and ACCLAIM[™] based ceramers of similar formulation are nearly identical. For the two samples that contain no TMOS, a clear glass transition is noted at $\approx -55^\circ\text{C}$, the same value

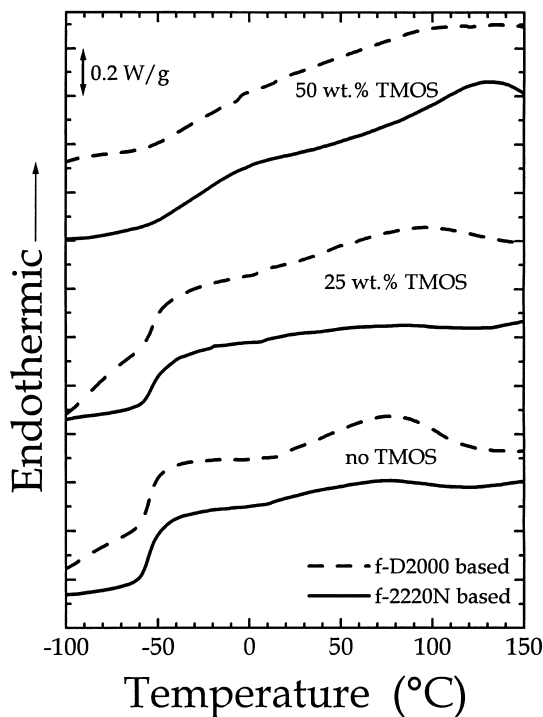


Figure 12. Differential scanning calorimetry scans for JEFFAMINE[®] and ACCLAIM[™] based ceramers of varied TMOS content.

which is observed mechanically. Also note that the change in the heat capacity across the glass transition, ΔC_P (or perhaps better labeled the change in heat flow, since absolute heat capacities were not measured), is roughly the same for both samples. Although the value of ΔC_P is generally a function of chemistry, the JEFFAMINE[®] and ACCLAIM[™] oligomers are similar enough to lead to roughly the same ΔC_P in these ceramers (which also have roughly the same mass fraction of each oligomer in them). The two ceramers containing 25 wt% TMOS show a slightly increased and broadened glass transition at: $\approx -50^\circ\text{C}$. This is a few degrees lower than that observed mechanically at 1 Hz (as the midpoint of the drop in the storage modulus). The value of ΔC_P for these two materials is again approximately the same, but is less than the ΔC_P for the non-TMOS containing ceramers. This is expected since ΔC_P is proportional to the mass of material undergoing the glass transition, and the relative mass of the PPO component is decreasing with increasing TMOS content (relative to the total sample mass). Finally, the glass transition is most broad and highest for the 50 wt% TMOS

materials, centered at $\approx -30^\circ\text{C}$. The true location of the glass transition is difficult to locate for these high TMOS content samples.

CONCLUSION

For the novel ceramer materials synthesized in this study based on ACCLAIM™ EO end-capped PPO oligomers and tetramethoxysilane, the following conclusions can be drawn:

- Increasing the TMOS content led to an increase in the correlation length due to an increase in the size of the silicate domains. However, the highest TMOS content ceramer [f-222ON(25) TMOS(75)] did not possess a correlation length by SAXS.

- Increasing the TMOS content also led to an increased and broadened glass transition temperature, similar to the JEFFAMINE®, based ceramers.

E' in the rubbery region for f-222ON(100) displays a direct proportionality to absolute temperature, obeying the dictates of ideal rubber elasticity. The analogous JEFFAMINE® based ceramer did not behave as closely to rubber-elastic theory. This is most likely due to the lower functionality of the initial JEFFAMINE® oligomer which would lead to increased network imperfections.

- The influence of water concentration on the final properties of ACCLAIM™ based ceramers is minor. This trend was also noted for JEFFAMINE® based ceramers.

- The largest distinction between the ACCLAIM™ and JEFFAMINE® based ceramers is the σ_0 - ϵ behavior. The JEFFAMINE® materials displayed “Hookean spring” (linear) behavior, and broke at small strains (ϵ_b less than 0.15). The ACCLAIM™ materials displayed an “S-shaped” stress-strain curve similar to typical elastomers, and broke at considerably higher values of strain (≈ 0.4). The improved functionality of the ACCLAIM™ oligomer is again believed to be responsible for this result.

Aside from the σ_0 - ϵ behavior, the ACCLAIM™ and JEFFAMINES® based materials behaved in a similar manner in the SAXS, DSC, TG, and DMS experiments.

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