DMA AS A METHOD OF MEASURING TOUGHNESS IN INORGANIC POLYMER MATRIX COMPOSITES

D.W. Radford* and P.T. Nivala
Composite Materials, Manufacture and Structures Laboratory, Mechanical Engineering, Colorado State University, Fort Collins, Colorado, USA
* Corresponding author (Donald.Radford@ColoState.edu)

Keywords: geopolymer, inorganic polymer, Nextel 610, DMA

Abstract
Inorganic polymer matrix composites have been fabricated to study the effects of fiber-matrix interface modification, combined with the addition of TiO$_2$ nanoparticles or carbon nanofibers, on the toughness. The primary reinforcement fiber used in this study was Nextel 610. The MEYEB inorganic polymer matrix is of interest as processing involves an initial cure, from the liquid state, at 80°C, followed by a freestanding posture at 250°C, resulting in material use temperatures exceeding 870°C.

Both static bend testing and Dynamic Mechanical Analysis (DMA) were performed, on uni-directional fiber reinforced 3-point bend beam specimens, to evaluate the correlation between the modified interface and the nanofiller additions on the toughness. Specimens were tested, at room temperature and after sequential multi-hour thermal exposures, in air, to a temperature of 760°C.

The resulting measured trends clearly show the effectiveness of the modification of the fiber-matrix interface characteristics, and to a lesser extent the addition of nanofillers, and demonstrate overall mechanical properties improvements are possible. Unfortunately, further investigations are needed to verify the effectiveness of DMA as a method of toughness evaluation.

1 Introduction
The development of fiber reinforced composite materials technology for elevated temperature applications is most often limited by toughness and manufacturability. High temperature polyimide matrix composites have use temperatures approaching 400°C. These polymers have been tailored for resin transfer molding (RTM) and resin infusion molding, both techniques that promise high degrees of manufacturability. Fiber reinforced polyimide engine intake valves have been under investigation, and successful prototypes have been produced using RTM [1–3]. While the potential exists to survive the temperatures of the intake valve using these high temperature polymers, the roughly 800°C requirement for an exhaust valve is clearly out of reach for composites using polyimides as a matrix material.

Based on the successful RTM development of carbon fiber reinforced polyimide intake valve prototypes, liquid geopolymer resin was considered as a candidate material for exhaust valve application. MEYEB FS resin and MEYEB hardener, obtained from the Geopolymiere Institute, were used in attempts to mold ceramic fiber reinforced MEYEB™ matrix composite valves using a RTM approach [4]. The resulting molded valves, as shown in figure 1, demonstrated the potential for RTM as a processing technique for this liquid inorganic polymer resin. The molded composite valves were well wet out and had good shape retention. However, the prototype valves were too brittle to be considered for in-engine testing. Thus, research was initiated to investigate the possible enhancement of the toughness of these ceramic fiber reinforced inorganic polymer matrix composites.

1.1 Inorganic Polymers
“Geopolymer” is the term often used to refer to a class of alumina-silica based inorganic materials which are processed like a polymer that undergoes
polycondensation at low temperatures, but resemble ceramics in the resulting structure and high temperature resistant properties [5,6]. The minerals that constitute this material are readily available. The name “geopolymer” was originated in 1978 during research efforts focused on the development of fire-resistant, non-toxic materials to be used in building structures [7]. This material evolved into a mineral-based binder for use as a high strength industrial cement with significantly shorter cure times than traditional Portland cements [5]. More recently there has been interest in utilizing the high-temperature resistant properties of this material and its low density to replace heavier metallic components in high-temperature applications. The ease of processing fiber reinforced composites with these inorganic polymer binders as the matrix, compared to traditional ceramic matrix composites (CMC’s), also makes them attractive. The samples used in this study were prepared using wet-lay-up techniques, with an initial 1 hour cure at 80°C followed by a freestanding postcure at 250°C for 5 hours. This is in contrast to more typical ceramic matrix composite manufacturing processes, which generally require much higher processing temperatures, usually exceeding 1,000°C [8]. While a substantial amount of research has been published on the cementitious variants of these inorganic polymers, there is limited data available on fiber reinforced composites produced using the thermoset resin-like versions, such as the MEYEB FS resin.

1.1 Chemical Structure of the Inorganic Resin

The inorganic polymer can exhibit several different structures characterized by tetrahedral aluminate and silicate units referred to as “aluminosilicates” [5]. The aluminosilicate starting precursors, the AlO4 and SiO4 tetrahedra, are found naturally in the mineral metakaolinite (nominal composition Al2O3·2SiO2) by calcining kaolinite at 700°C to remove chemically attached water [9]. The precursors are polycondensed with alkali activators, either KOH or NaOH, to form structures, which may be amorphous or semicrystalline. These resulting structures are charge-balanced by the addition of alkali metal ions such as sodium and potassium [6]. Three prominent structural units exist, with the base unit referred to as “sialate”, which is an abbreviation for silicon-oxo-aluminate [5,10]:

(1) “sialate” [-Si-O-Al-O-]
(2) “sialate-siloxo” [-Si-O-Al-O-Si-O-]
(3) “sialate-disiloxo” [-Si-O-Al-O-Si-O-Si-O-]

These sialate-based fragments condense together to form larger polymeric structures called polysialate (PS), polysialate-siloxo (PSS), and polysialate-disiloxo (PSDS) [11,12]. The sialate network structure containing the SiO4 and AlO4 tetrahedra units are linked in an alternating fashion by the sharing of oxygen atoms. To balance the negative charge of Al³⁺ in IV-fold coordination, positive ions (Na+, K+, Li+, Ca²⁺, Ba²⁺, NH₄⁺, H₂O) must be present in the structural spaces [5,6]. The structure of the MEYEB inorganic polymer resin used for this study is PS containing potassium ions and is predominantly amorphous. This inorganic polymer polycondenses in just a matter of minutes. The mechanical properties of the matrix appear to be directly related to the silica and alumina ratio, with greater silica leading to higher strength [5,13]. The addition of reinforcing fibers has been shown to substantially improve the strength of the unreinforced material [5,14].

1.2 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis is a technique in which a time variant load is applied to a specimen and the resulting material response is measured. In this way, both the elastic and viscous components of the material response are measured, and an understanding of the internal material energy loss can be generated.

Previous authors have reported on using DMA as a method of assessing toughness in fiber reinforced composites. The effect of fiber-matrix interface strength has been specifically investigated through comparison of the DMA measured energy dissipation, or Loss Tangent, to the energy absorbed by the composite in static testing [15].

In the current research, DMA is performed on unidirectional fiber reinforced bend beam specimens to investigate the correlations between fiber-matrix interface modifications, toughness, and the dynamic properties. The goal is to gain a better understanding of the effects of interface and matrix modification, and of heat treatment temperature on toughness, through the measurement of the variation in storage modulus (E’) and loss modulus (E”).
2 Experimental Procedure

The experimental approach involved 3-point bend testing of uni-directional NEXTEL 610 fiber reinforced MEYEB FS inorganic polymer matrix composite beams, using both conventional static loading, in a mechanical test frame, and dynamic loading in a Metravib VA2000 DMA. The effect of fiber-matrix interface performance was investigated by comparing composites reinforced with NEXTEL 610 fibers that had two different surface conditions, (i) cleaned and (ii) carbon coated. Further, Pyrograf III carbon nanofibers and TiO$_2$ nanoparticles were added, individually, to the matrix of carbon-coated fiber reinforced specimens, at a 1% volume fraction. Uni-directionally reinforced beams were used, as previous research with woven fabric reinforcement resulted in significant complexity in separating mechanisms of failure [4]. The uni-directional fiber reinforced beams tested were nominally 60 mm in overall length, 2 mm thick and 7.5 mm wide. A similar test span was used in both static and dynamic test procedures. All tests were performed at nominally 20°C.

2.1 Materials

The as-received NEXTEL 610 fibers have a polymer sizing to protect them from abrasion damage prior to incorporation into a matrix. To investigate the effectiveness of interfacial strength modification, the as-received fibers were treated in two different ways. In both cases the fiber tow was heated to 700°C. In one case the atmosphere was air, resulting in a “cleaned” fiber surface, free of any coating, while in the other case the atmosphere was nitrogen (N$_2$), resulting in a carbon coating from the converted polymer. The as-received fibers are pink, indicative of the polymer sizing, the fiber heat treated in air is bright white, and the fibers treated in nitrogen range from dark gray to black in color. Visual differences are shown in figure 2. The carbon coating is predicted to result in a composite with reduced interfacial bond strength, and therefore, increased toughness, as long as the carbon layer remains intact, at the fiber-matrix interface.

The nanomaterials used in the fabrication of the composite specimens included Pyrograf®-III PR 19 XT-PS carbon nanofibers and Altair TiNano 40 Series titanium dioxide (TiO$_2$) nanoparticles.

Fig. 2. Nextel 440 fibers (a) as-received, (b) after 700°C in air, and (c) after 700°C in N$_2$

The carbon nanofibers are very fine, highly graphitic, low cost, tubular nanomaterials with an average diameter of approximately 150 nm and a length ranging from approximately 50 to 200 μm [16]. The nanofiber consists of a chemically vapor deposited carbon layer on the surface of a graphitic tubular core fiber [16]. The PS grade nanofiber is produced by pyrolytically stripping the as-produced fiber to remove polyaromatic hydrocarbons from the fiber surface [16]. The XT designation indicates a debulked, powder-like form with a bulk density ranging from 0.016 to 0.048 g/cm$^3$ [16]. The inorganic polymer resin must be stored at a temperature of ~18°C or below. Once mixed with the supplied hardener, it has a room temperature useable pot-life of about 30 minutes. Nanofibers were added to the resin prior to the addition of the hardener. Dispersion was performed using a Thinky ARE-250 Mixer, set to 2,000 RPM, for a period of 5 minutes. The resin with the dispersed nanofibers was placed back into cold storage until required for specimen preparation, at which time a specified amount was brought to room temperature and manually mixed with hardener. The resin was mixed with the hardener at a ratio of 5:1 by weight.

2.2 Composite Specimen Preparation

Uni-directional fiber reinforced composite beams were produced in the stainless steel die set shown in figure 3. Each of the 8 cavities is nominally 200 mm long and 7.5 mm wide, which results in a molded sample long enough to be cut into three test specimens. The specimens used in the static bend testing were nominally 2.5 mm thick, while the DMA specimens were approximately 1.9 mm thick. The differences were related to differences in required bend test configurations.
The stainless steel die set was treated with a PTFE-based mold release. A predetermined amount of liquid resin was poured into each cavity of the die along with a corresponding pre-measured amount of the fiber tow, to achieve a nominal fiber volume fraction of 50%. ‘T’-bars were then placed in the slots and the complete die placed in a laboratory hot press for consolidation. A preliminary cure cycle of 1 hour at 80°C was performed while pressure was maintained in the hot press. Upon completion of the 80°C cure, samples were removed from the die and postcured, in air, for 5 hours at 250°C. This was the starting condition for the evaluation. The resulting matrix material is capable of withstanding temperatures in excess of 870°C. Each of the molded samples was then cut into three, nominally 60 mm long, bend beam specimens using a diamond saw. Composite specimens looked quite different from each other depending on the fiber treatment and nanofiller addition. Representative Nextel DMA bend specimens are shown in figure 4, illustrating the difference in color of the specimens using fibers with a cleaned surface versus those with a carbon coating, as well as the effect of the nanofiller additions on the appearance. Nextel reinforced inorganic polymers with the fiber surface cleaned result in white specimens after the initial cure at 80°C and 5 hour postcure at 250°C. The carbon-coated Nextel fiber composites have a light gray color, which is unchanged by the addition of the TiO₂, while the addition of 1% Pyrograf III carbon nanofibers results in a composite specimen with a much darker shade of gray.

Specimens were tested after each stage of an incremental elevated temperature heat treatment. Heat treatments were cumulative, including 430°C for 5 hrs, 540°C for 5 hrs, 650°C for 8 hrs, 760°C for 5 hrs, and a final heat treatment at 870°C for 5 hrs. Thus, the properties quoted after 760°C heat treatment actually refer to a specimen which has been cured at 80°C for 1 hr followed by 5 hrs at 250°C, plus 5 hrs at 430°C, plus 5 hrs at 540°C, plus 8 hrs at 650°C, and finally 5 hrs at 760°C. Heat treatments were carried out in a refractory furnace, in air, with heating rates of approximately 10°C/min.

2.3 Static Flexure Procedure and Calculations

3-point static flexure testing was based on ASTM C1341 [17]. The test fixture had a 45.4 mm support span, producing a support span-to-specimen thickness ratio of approximately 18:1. Flexure testing was conducted in a screw-type load frame at 0.005 mm/sec with a 445 N tension load cell, and force as a function of time was recorded for each test. The flexural modulus (E) and toughness (U_T) were calculated from the recorded data according to equations (1) and (2) [17,18]:

\[
E = \frac{1}{4} \frac{L^3 M}{b d^3} \quad (1)
\]

\[
U_T = \int_0^f \sigma d\varepsilon \quad (2)
\]
DMA AS A METHOD OF MEASURING TOUGHNESS IN INORGANIC POLYMER MATRIX COMPOSITES

where:

- \( b \) = test specimen width (mm)
- \( d \) = test specimen thickness (mm)
- \( L \) = support span length (mm)
- \( m \) = slope of tangent to the initial straight-line portion of the force-deflection curve (\( \frac{N}{mm} \))
- \( P_U \) = maximum force (N)
- \( \sigma \) = stress in outer fibers (MPa)
- \( \epsilon \) = strain in outer fibers (\( \frac{mm}{mm} \))
- \( \epsilon_f \) = strain at failure force (\( \frac{mm}{mm} \))

The mass and rectangular dimensions of each specimen were recorded prior to each flexure test. Flexural modulus was measured for each specimen in the as-cured condition and after each subsequent heat treatment. Toughness was measured for select specimens in the as-cured condition and after the 540°C and 760°C heat treatments. Specimens were loaded to 44 N to measure flexural modulus, or loaded to failure to measure toughness. The specimens were determined to have failed if they could no longer support more than 80% of the maximum load [17]. The recorded data were averages of three specimens and modulus was normalized to 50% fiber volume fraction. Flexural toughness, as measured by this technique, is the area under the stress-strain curve and is directly related to the energy stored in the specimen at failure.

2.4 DMA Test Procedure

DMA testing was carried using a 01dB-Metavib Viscoanalyseur, model VA2000, in the ACCIS Laboratory at the University of Bristol, UK, as shown in figure 5. The associated DMA analysis software used was Dynatest, version 6.73. Specimens were tested in a 3-point bend configuration, with a test span of 48 mm, under ambient conditions, after each increment of heat treatment. A static mid-span displacement of nominally 0.05 mm was applied to ensure that the specimen remained in contact with the 3-point bend fixturing. This was equal to between 5 – 10 N depending on the beam dimensions and stiffness. Sinusoidal loading, for the results described in this paper, was applied at 1 Hz. A dynamic strain amplitude of 0.02% was programmed for application and the resulting applied dynamic strain was recorded as 0.0192%.

This resulted in a dynamic force ranging from approximately 5 – 10 N. The lowest resultant forces were for the carbon-coated beams and the highest for the cleaned beams, as the forces are directly related to the beam stiffness. Beams were tested twice each after each heat treatment, first with the ‘T’-bar molded surface up and then inverted, to remove any possible effects of fiber migration during specimen preparation. The reported results are an average of the two loadings, even though little variation was noted during testing. Load and response waveforms were visually monitored, in real time, to ensure stability of the specimen on the fixture, and thus, reliability of the testing. Upon completion of a dynamic loading sequence, the system generated a report of the storage modulus, \( E' \), the loss modulus, \( E'' \), and the loss tangent, \( \tan \delta \). For a brittle material the storage modulus, \( E' \), is effectively equivalent to the elastic modulus. The loss tangent is the ratio of the loss modulus divided by the storage modulus, and gives an indication of the internal material damping. However, the loss modulus, \( E'' \), can be directly related, at a fundamental level, to the energy loss, or dissipation within the specimen in the elastic range. The dynamic work/energy relationship, for work/unit volume/cycle of steady-state sinusoidal oscillation, can be written [19]:

\[
W = \frac{1}{2} \pi \omega \epsilon_0^2 E''(\omega)
\]

where:

\( \epsilon_0 \) = maximum strain in the applied waveform
Thus, $E''$ is proportional to the energy dissipated per cycle and can be related to the specimen toughness in a way consistent with the toughness measured in static bending by ASTM C1341.

3 Results and Discussion

It was expected that neither the carbon layer at the fiber-matrix interface of the specimens, nor the carbon nanofibers in the matrix would be stable in air at the elevated heat treatment temperatures. Figure 6 shows the effect of heat treatment temperature on the observed appearance of the DMA specimens. The most obvious change in color is noted in the specimens with the carbon nanofiber additions, where the specimens transform from almost black to nearly white as the nanofibers react in air with increasing temperature. However, closer inspection shows that the specimens with a carbon coating at the fiber-matrix interface are also taking on a lighter shade of gray. Thus, it is clear from figure 6 that the carbon content is decreasing with thermal exposure.

![Color change in Nextel 610 reinforced DMA specimens due to heat treatment. Each group, from left to right; cleaned, carbon-coated, TiO$_2$ added, C-nanofiber added.](image)

3.1 Flexural Modulus

The flexural modulus for each of the four specimen variations, with respect to heat treatment, is shown in figure 7. Specimens with cleaned fibers consistently exhibit the highest modulus across the temperature range. The cleaned fiber specimens possess the higher initial modulus, which remains largely unchanged for the tests at 250°C, 540°C and 760°C. The moduli of the TiO$_2$ nanoparticle filled specimens show no significant trend, with a slightly higher value at 540°C. The modulus of the carbon coated fiber composite with no nanofillers and carbon-coated fiber composite filled with carbon nanofibers increases with temperature, from 250°C to 760°C, with the modulus of the carbon coated fiber specimens approaching that of the cleaned fiber specimens at the highest temperature.

![Fig.7. Flexural Modulus vs. Specimen Type](image)

Variations in modulus are predicted with changing interfacial bond strength. A strong interface is expected to result in good load transfer and a resulting modulus approaching a value that might be predicted by Rule of Mixtures calculations. Reduced interfacial strength is then expected to result in a reduction in the measured modulus. Based on the chemical similarity between the MEYEB matrix and Nextel fibers, the cleaned fiber specimens are predicted to have the strongest interface and thus the highest modulus. Trends indicate that the carbon coated fiber specimens experience modulus improvements corresponding to the thermal degradation of the carbon coatings with extended time at temperature. This is a result of a stronger interface developing as the carbon coating disappears and the fiber and matrix form high strength bonds, more characteristic of the cleaned fiber specimens. The modulus of the carbon nanofiber modified specimens increases with temperature, consistent with the increase in modulus of the unmodified carbon coated fiber specimens. However, it is unclear why the nanomaterial additions appear to have a detrimental effect on the magnitude of the modulus when compared at each temperature to the carbon coated fiber specimens, as it would be expected that the nanomaterial additions would have only a limited effect on the measured modulus.
3.2 Flexural Toughness

The flexural toughness results for the four specimen variations with respect to heat treatment are shown in figure 8. The cleaned fiber specimens exhibit the lowest toughness of all four types of specimens. The toughness remains relatively constant with temperature. The carbon coated fiber specimens maintain toughness through 540°C, but experience a substantial reduction at 760°C. The toughness of the nanomaterial specimens also decrease with temperature, but it must be remembered that these specimens are carbon coated Nextel fiber specimens with nanomaterial additions and thus, the carbon depletion at temperature affects the interface strength in each of these specimens.

The measured trends in toughness correspond to stronger interfaces as the carbon interface coating reacts in air at elevated temperature. It appears that the specimen toughness is more closely a function of interface than of nanomaterial addition, due to the significant reduction in toughness of the TiO₂ nanoparticle and carbon nanofiber specimens with temperature; the carbon coated fiber, and nanomaterial specimens show approximately the same toughness at 760°C.

It is important to observe that for the specimens post-cured at only 250°C, the carbon nanofiber filled specimens clearly demonstrate toughness above the other cases, and specifically, well above the carbon coated fiber specimens. This improvement over the carbon coated fiber specimens suggests that, in addition to the effectiveness of the reduced fiber-matrix interfacial strength, the carbon nanofibers are generating an additional toughening mechanism in the matrix. The TiO₂ nanoparticles are not as effective as the carbon nanofibers in generating an improvement over the carbon coated fiber case. Of course, as the heat treatment temperature increases, the carbon nanofibers are expected to be rapidly degraded by oxidation and the toughness of the carbon coated fiber specimens and the carbon nanofiber filled specimens are approximately equal at 540°C and 760°C, suggesting the remaining mechanism is only the fiber-matrix interface.

3.3 DMA Results

DMA results are summarized in figures 9 and 10. The charts, showing the response of the storage modulus (E’) in figure 9 and the loss modulus (E”) in figure 10, allow comparison of the effects of heat treatment on the four specimen types.

3.3.1 Storage Modulus

As noted for the flexural modulus, figure 8, the DMA measured storage modulus, after each heat treatment, is greatest for the cleaned fiber composites. In comparison, the differences in modulus between the various specimen types are much smaller than was noted in static bend testing. After the preliminary cure and post cure at 250°C, the measured E’ value and the Flexural Modulus of the cleaned fiber specimens was reasonably consistent at approximately 155 GPa. However, while the trends for the 250°C post cure values are similar in that there is a marked drop for all three other cases using the carbon interface on the fibers, the static bend Modulus data seem suspect, showing a large drop for those specimens with the carbon interphase. The degree of reduction in stress transfer between the fiber and matrix that would be required seems extreme, and is likely an indication of difficulties in specimen manufacture and fiber wetout. (Specimens for DMA and for static bending were produced with the identical materials, but at different times.) Yet, for all three conditions with the carbon coated fibers, the general trend, with increased temperature, is an increase in the value of the storage modulus; however, this increase is not as significant as seen for the carbon coated and carbon coated plus carbon nanofiber filled static bend tests. It is worth noting that for all specimen types, the storage modulus at least
approaches 160 GPa at 540°C, while the modulus recovery measured in static bending is more subtle. Still, the increase in $E'$ with temperature for the specimens with carbon coated Nextel 610 fibers is consistent with an increased interfacial bond strength as the carbon is lost, and the bond strength between the similar fiber and matrix increases. For the specimens with no fiber-matrix interphase (cleaned) the measured modulus is consistent with predictions based on the constituent material properties. While it is possible that the reduction in Storage Modulus noted at 760°C is related to changing matrix properties, no neat matrix tests were included in this study.

3.3.2 Loss Modulus

Loss Modulus data suggests increased internal energy loss with the addition of the carbon interphase as shown for the carbon coated and TiO$_2$-filled specimens versus the cleaned specimens in figure 10.

For the cleaned specimens, the trends in static bend test determined toughness with thermal treatment are consistent with the trends in $E''$. Unfortunately, for the remaining specimen conditions, the correlation is not as clear. For all except the carbon nanofiber filled specimens, the $E''$ values do show a general improvement when compared to the cleaned fiber specimens, but this gain is not as marked as the improvement in toughness shown in figure 8. Further, the static bend test toughness shows the highest values for specimens after only the 250°C postcure, while the Loss Modulus results seem to point to the highest values after the 540°C heat treatment. This is especially true for the nanofilled specimens and may be an indication that the 1 Hz dynamic test frequency is insufficient to evaluate the effectiveness of the nanofillers. Comparing the measured toughness for the various conditions suggests that both the carbon coating and nanofillers are effective at the lower temperatures, while the loss modulus, ($E''$) does not seem sensitive to the nanofiller additions. Thus, it seems that further testing, possibly at higher frequencies, will be required to better understand the ability to correlate toughness to DMA characterization for these materials and the associated nanofillers.

4 Conclusions

The weakened interface associated with the carbon coating on the continuous reinforcing fibers results in a reduced modulus and improved toughness, measured both in static flexure and with DMA. However, the details of the effects of the nanomaterial additions, and the trends with temperature, differ somewhat between the two test approaches. While using the internal energy dissipation ($E''$) as a measure of specimen toughness seems reasonable, the results show better correlation for interface modifications than for nanomaterial additions. However, the quality control of the specimens tested in the two methods is also in question, and thus, the specimen preparation consistency needs to be addressed, as does the effect of temperature on the neat matrix properties. Future work is required to understand whether the limited correlation in the nanomaterial filled specimens is an inherent drawback of the DMA technique, or whether additional data at higher test frequencies will result in improved sensitivity to the nanoscale additions.
DMA AS A METHOD OF MEASURING TOUGHNESS IN INORGANIC POLYMER MATRIX COMPOSITES

References


