NANO-PARTICLE ENHANCED POLYMER MATERIALS FOR SPACE FLIGHT APPLICATIONS

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ABSTRACT

Recent advances in materials technology both in polymer chemistry and nano-materials warrant development of enhanced structures for space flight applications. This work aims to develop spacecraft structures based on polymer matrix composites (PMCs) that utilize these advancements. Multi-wall carbon nano-tubes (MWCNTs) are expected to increase mechanical performance, lower coefficient of thermal expansion (CTE), increase electrical conductivity (mitigate electrostatic charge), increase thermal conductivity, and reduce moisture absorption of the resultant space structures. In this work, blends of MWCNTs with PETI-330 were prepared and characterized. The nano-reinforced resins were then resin transfer molded (RTM) into composite panels using M55J carbon fabric and compared to baseline panels fabricated from a cyanate ester (RS-3) or a polyimide (PETI-330) resin containing no MWCNTs. In addition, methods of pre-loading the fabric with the MWCNTs were also investigated. The effects of the MWCNTs on the resin processing properties and on the composite end-use properties were also determined.

1. INTRODUCTION

Composites cross cut many of NASA mission directorates including: Aeronautics Research Mission Directorate (ARMD), Exploration Systems Mission Directorate (ESMD), Science Mission Directorates (SMD) and Space Operations Mission Directorate (SOMD). Composites with improved properties have applications to airframes, propulsion and spacecraft. The objective of this work is to advance materials technology by implementing nano-particulate enhanced polymer materials for NASA missions.

Advances in materials technology both in polymer resins [1-13] and nano-materials fabrication & characterization [14-29] warrant development of enhanced structural materials and structures for space flight applications. By leveraging experience and past successes in the area of nano-materials by researchers at NASA Goddard Space Flight Center (GSFC), NASA Langley Research Center (LaRC), NASA Glenn Research Center (GRC), M&P Technologies, Clark Atlanta University (CAU), and the Georgina Institute of Technology we aim to develop

enhanced structural materials and spacecraft structure-components that utilize these advancements [14-17]. Multi-wall carbon nanotubes (MWCNTs) of micron lengths and nanometer diameters, often referred as nano-fibers, are expected to increase mechanical performance, lower CTE, increase electrical- & thermal-conductivity (mitigate electrostatic charge and disperse concentrated heat loads), and reduce moisture absorption of the space structures produced by exploiting the inherent properties of MWCNTs [17-29].

Therefore, the objective of this effort is to assess the benefits of using MWCNTs in PMCs for aerospace and space applications. Due to the space applications being targeted on this program, the RTM process was selected for manufacturing the PMCs. Several methods for combining the MWCNTs nano-reinforcement, the resin and the fabric materials to achieve high quality PMCs were investigated and the "best method(s)" to give good dispersion of the MWCNT particles in the polymer matrix using the RTM process were determined. These mixing methods were then used to prepare MWCNT loaded resin that was subsequently used to RTM high quality PMC laminates. The laminates were characterized to determine the benefits and feasibility of using MWCNTs in RTM PMCs.

A method to fabricate high quality PMCs with homogeneous dispersion of the MWCNTs in the polymer matrix was developed and demonstrated. This work culminated in demonstrating the feasibility of fabricating PMCs with MWCNTs pre-loaded in the resin, pre-loaded on the fabric, and a combination of both. Although this work was still in progress at the time of paper submission, the results thus far are presented below.

2. EXPERIMENTATION

2.1 Development of MWCNT and Resin Blends

The MWCNT additives, M55J fabric, RS-3 resin, and PETI-330 resin were procured from Swan Chemicals, Hexcel, YLA and UBE America, Inc., respectively. Once the materials were received different mixing methods were investigated using both RS-3 and PETI-330 resins containing varying loadings of MWCNTs. The components were dry mixed and ball-milled prior to melt mixing or melt mixed without ball-milling. Some of the samples were subsequently mixed by sonicating in a solvent and then drying. Lastly, some of the components were dry mixed and then mixed using an improved melt mixing approach [29]. All of the melt mixing was performed in a HAKKE Rheomixer™. During mixing, the torque was monitored as a function of MWCNT concentration, rpm and time. Based on our initial study we determined that for higher concentrations of MWCNTs (> 1%) the viscosity was too high for Resin Transfer Molding (RTM) processing. Therefore, we investigated lower concentration blends.

The RS-3 resin was supplied in frozen form. The resin was chipped out of the container and placed in a beaker. Due to the low resin viscosity at room temperature the resin was melt mixed with MWCNTs using a mechanical stirrer instead of the HAAKE Rheomixer. The resin was initially dried in an oven at 110°C under vacuum. Initially the resin heated to 110°C prior to mixing. However, upon addition of the MWCNTs and subsequent mixing, these blends gelled in the beaker. This may be due to the MWCNTs catalyzing the cyanate ester curing reaction since the resin is reported to be stable at 110°C. For these reasons the investigation focused on making

blends of MWCNTs with PETI-330 resin, a powder that melts at a higher temperature and is more amenable to melt mixing.

2.2 Rheology

Dynamic rheological data was collected using circular parallel aluminum plates (diameter = 25 mm) on a TA Instruments AR-G2 rheometer. Samples were prepared by pressing disks of powdered resin or resin/MWCNT mixtures into approximately 1.0 mm thick disks under 13,000 psi for 2 min. Isothermal data was collected at 288°C to determine the effect that the MWCNTs have on processability or viscosity and pot life. Temperature ramp experiments were carried out at 3°C/min from 50 to 400°C. All experiments were conducted at 100 rad/sec (max shear rate) since high shear rates would be expected during injection during RTM processing.

2.3 Fabrication of PMCs

Baseline panels were fabricated using the RTM process and the vendor recommended process and cure cycle for their respective resins, RS-3 or PETI-330. The 0.5 wt % MWCNT in PETI-330 blend was prepared by first dry mixing and then subsequently ball-mill mixing the PETI-330 powder resin with the MWCNTs for 48 h. The resultant blend was then used to RTM fabricate a composite panel using M55J fabric. This process was then repeated using the same blend except that an additional 2 days ball-milling was performed prior to panel fabrication. Both panels were quasi-isotropic, 8 plies and had the specific lay-up [45/0/-45/90]s. Both of these PMCs were determined to have inadequate dispersion of the MWCNTs by scanning electron microscopy (SEM). Therefore, subsequent panels utilized PETI-330/MWCNT blends that had been prepared using an improved melt mixing method developed in parallel studies [29].

Three additional PMCs were fabricated using a low concentration of MWCNTs in PETI-330 and by pre-loading the resin, pre-loading the fabric, and a combination panel made from pre-loading both the resin and the fabric. The specifics of pre-loading the fabric with the MWCNTs will be presented in a subsequent communication.

2.4 SEM Analysis

Analysis of MWCNT dispersion was performed using the InLens detector on a LEO 1530 SEM and a Hitachi S-800 SEM. Each sample was fractured for representative cross sections. Samples were sputter coated with gold to facilitate imaging. Several images from multiple specimens from each sample were imaged for accurate conclusions on MWCNT morphology.

2.5 Composite Characterization

The quality of the PMCs was determined by ultrasonic, dimensional, photomicrographic, acid digestion, and Dynamic Mechanical Thermal Analysis (DMTA). Thermal Mechanical Analysis (TMA) was used to determine (T_g) and CTE, using a Seiko model TMA210, on rectangular samples (approx. 6-10 mm in length and width) from 25°C to 400°C, at a heating rate of 10°C/min. Dynamic Mechanical Thermal Analysis (DMTA) was performed on rectangular samples approximately 1½" x ½" to determine T_g, and storage and loss moduli (E' and E", respectively) as a function of temperature using a TA Instruments AR-G2 Rheometer. Under a constant angular frequency of 1 Hz and 0.025 percent strain of 0.025. The temperature was increased from 30°C to 415°C at a ramp rate of 5°C/min. Surface and volume resistivity were measured

using a Prostat model PRS-801 Resistance System. Resistivity was measured at nine points on both front and back of the composite panels. Moisture absorption was determined using ASTM D5229/D5229M.

3. RESULTS

Under this program a process for incorporating homogenously dispersed MWCNTs in the matrix of RTM PMCs was developed and demonstrated. Various mixing methods were investigated including: dry mixing, ball-milling, melt mixing, sonicating in solvent, and combinations thereof. The MWCNTs studied on this program proved to be difficult to disperse and methods used on past programs [14-17] did not lead to homogenously dispersed MWCNTs. The effect the MWCNTs have on processability was determined by conducting an extensive rheology study over a wide range of MWCNT loadings (0.05 – 30 wt%). From this study the optimum MWCNT concentration for the various mixing methods was determined.

High quality PMCs incorporating the MWCNTs reinforced PETI-330 and M55H fabric were fabricated infusing MWCNT loaded PETI-330 via RTM. In addition to incorporating the MWCNTs in the resin, MWCNTs were also dispersed on the M55J fabric prior to composite fabrication. This work culminated in fabricating and testing high quality PMCs using reinforced PETI-330, and ultimately a "combined" MWCNT pre-loaded fabric and pre-loaded resin were used to fabricate a PMC in an attempt to maximize the MWCNT loading. The results of this work are presented below.

3.1 Effect of MWCNTs on Rheology

An extensive rheology study was conducted to determine the effect the MWCNTs and the specific mixing methods had on the PETI-330 resin melt viscosity. Figure 1 shows an overlay of the rheology curves for PETI-330 and MWCNT melt mixed blends for 0, 0.5, 1, 2, 5, 10 and 20 wt % MWCNT loadings. From the graphs, it is observed that loadings higher than 1 percent increase the minimum viscosity well above 100 Poise, which is too high for the resin transfer molding process. Therefore, we decided to examine lower loadings (less than 1%) in more detail. We also determined, by SEM, that all of the initial melt mixed blends did not have adequately dispersed MWCNTs. Instead, these blends had agglomerates of entangled MWCNTs ranging from ~400 nm – 10 μm in diameter. Therefore, several other blending methods were investigated including ball milling, sonicating in solvents with and without the parent resin, and a high torque melt mixing method.

Figure 2 gives the isothermal rheology traces for a 0.5 wt % percent MWCNT/PETI blends that were mixed in a ball-mill for 2 and 4 days. In previous work we were able to achieve well dispersed nano-composites with various nano-particulates using ball-milling [14-17]. Since the MWCNTs used in this study are much longer than those used in our previous work they were more prone to entanglement, and we had less success with ball-milling on this program. Two days of additional ball-milling resulted in an increased melt viscosity which indicates the sample was better dispersed. Based on the SEM analysis (discussed below) of the blends and PMCs, it was determined that none of the dry mixed, melt mixed, ball-milled, or sonicated blends resulted in sufficient dispersion of the MWCNTs. However, improved melt mixing gave excellent dispersion. Therefore, we decided to focus on improved melt mixing for these MWCNT/PETI-

330 mixtures and investigated 0, 0.5, 1 and 3 wt % MWCNTs in order to determine the optimum or maximum loading that would still allow for RTM processing of the blends. Figure 3 gives overlays of the rheology curves for 0, 0.5, 1 and 3 wt % MWCNT/PETI-330 blends. From this data it appears that 0.5 wt % MWCNTs represents the maximum loading in order to still process the blend using RTM.

Once improved melt mixing gave MWCNT/PETI-330 blends that looked promising isothermal rheology data was recorded at 288°C to determine if the blends had sufficient melt stability needed for RTM processing. Therefore, isothermal rheology was conducted using 4, 1 and 0.5 wt % MWCNT/PETI-330 blends that had been prepared by improved melt mixing. From these results, we estimated that 0.35 wt % MWCNT was the maximum concentration of MWCNTs to still allow RTM processing. However, upon preparing the 0.35 wt % blend, the isothermal viscosity proved to be too high (94 poise). Therefore, we remodeled the isothermal viscosity using a linear relationship with only the lower concentrations (i.e. 1, 0.5 and 0.35 wt %) and setting the y-intercept to 1 poise (viscosity of neat PETI-330). Based on this model it was predicted that 0.125 wt % MWCNT loading was the maximum allowable and that it would result in approximately 20 poise at 288°C. Once prepared, a 0.125 wt % blend of MWCNT/PETI-330 gave a minimum viscosity of 17 poise at 288°C, which is a good fit to our linear model. The isothermal rheology traces for all of the "new" high torque blends are given in Figure 4.
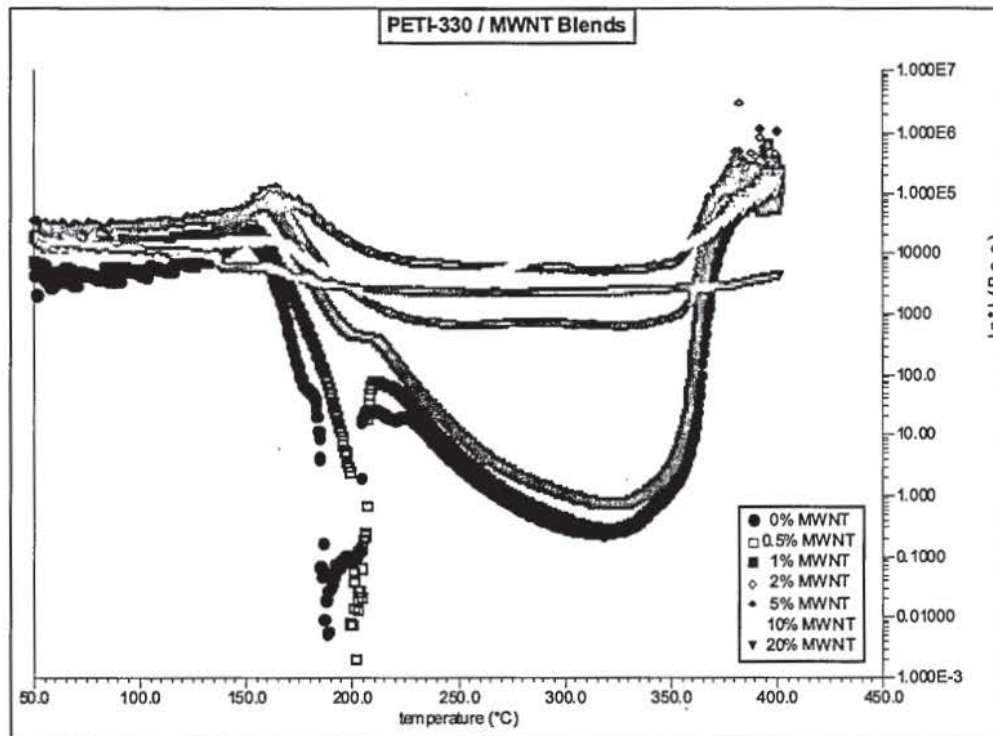

Figure 1. Dynamic rheological traces of initially melt-mixed PETI/MWCNT blends.
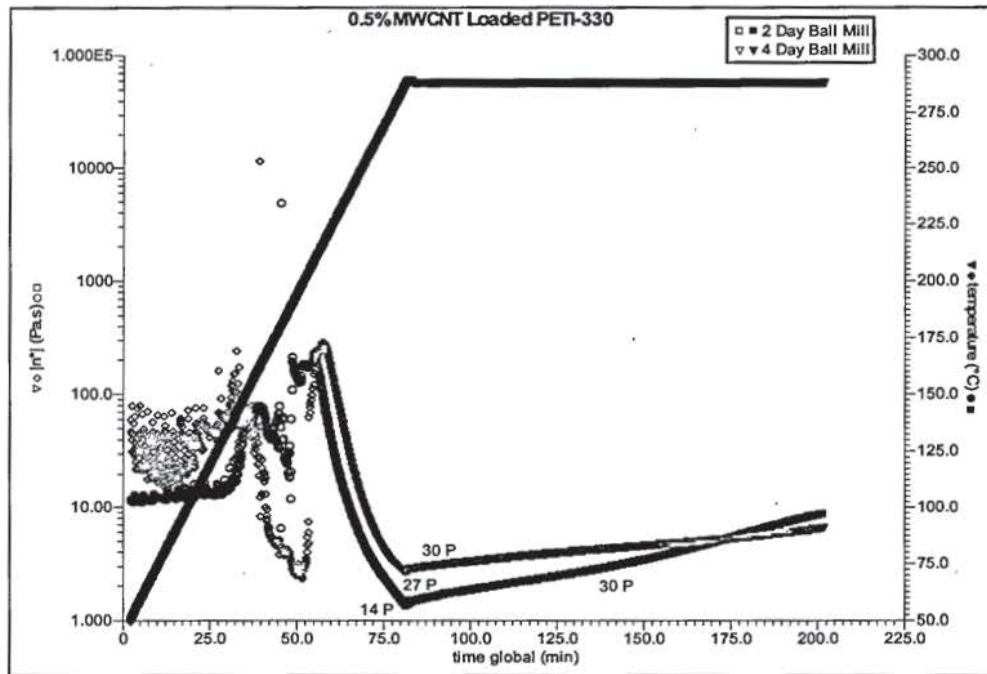
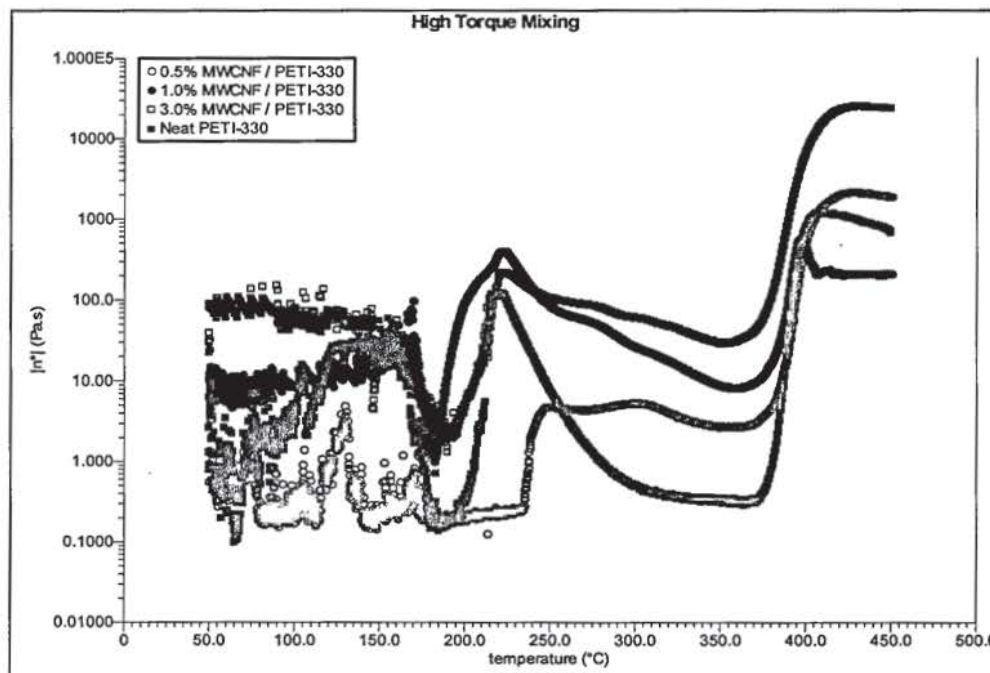Figure 2. Complex Viscosity for 0.5% MWCNT PETI-330 ball-milled blends.

Figure 3. Dynamic rheological traces of PETI/MWCNT improved melt mixing blends showing effect of MWCNT concentration on viscosity.
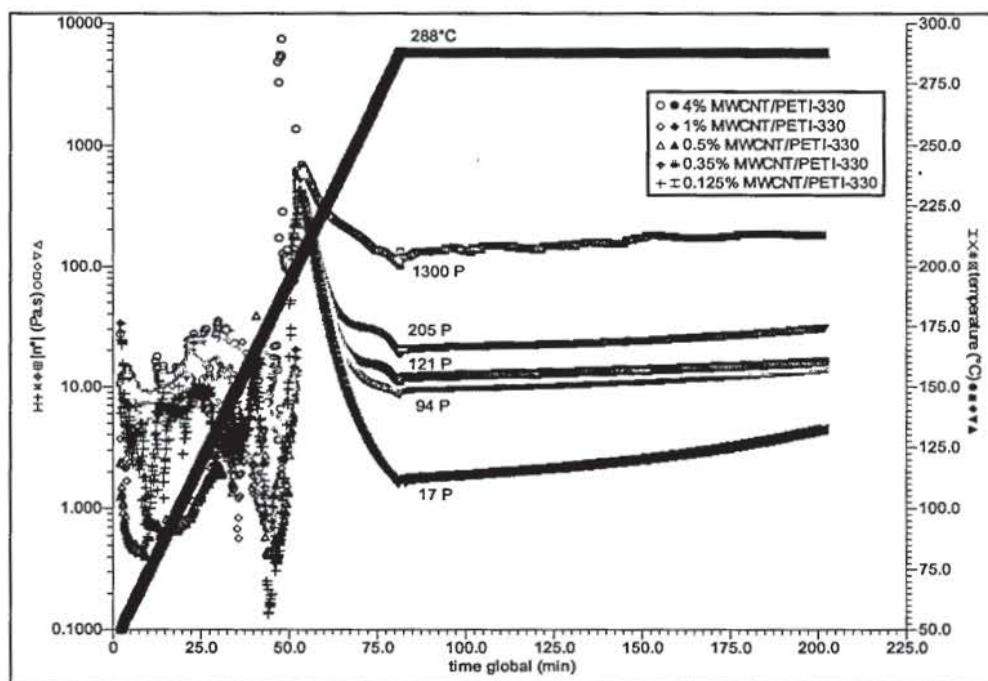
Figure 4. Isothermal rheological traces of PETI/MWCNT improved melt mixing blends showing effect of MWCNT concentration on viscosity at 288°C.

3.2 SEM Analysis of Blends

SEM and TEM images of neat MWCNTs as obtained from the vendor are given in Figures 5A and 5B, respectively, for reference. From these images, the entangled nature of the neat MWCNTs can be seen and hints at the difficulty one may have in dispersing these materials. For this reason, the mixing methodologies used in this work were investigated along with SEM analysis to determine if adequate dispersion and un-entanglement had occurred during mixing. Early mixing trials were unsuccessful at adequately dispersing the MWCNTs. Figure 6 shows SEM images from samples that were dry-mixed, ball-milled and then cured and imaged. Figure 7 shows SEM images from a 0.5 wt % MWCNT sample that was ball-milled and then subsequently melt mixed. Figure 8 shows SEM images from samples that were dry-mixed, ball-milled and then sonicated in a solvent. Figure 9 gives an SEM image of a sample that was only melt mixed. All of the images show inadequate dispersion of the MWCNTs. From this study improved melt mixing was the only mixing method that was found to adequately disperse the MWCNTs.

Figure 10 shows SEM images of a 4 wt % MWCNT/PETI blend that was mixed using improved melt mixing and exhibits excellent dispersion of the MWCNTs. Figure 11 shows a SEM image of an early trial with melt mixing and shows there to be some agglomerates present. Although the blend has homogeneous dispersion, the agglomerates might be filtered out during RTM processing. Therefore, this blending was repeated with modified settings in an attempt to obtain better dispersion. Figure 12 shows the SEM images from this trial and shows that the improved melt mixing method was successful in obtaining great dispersion of the MWCNTs in this blend.
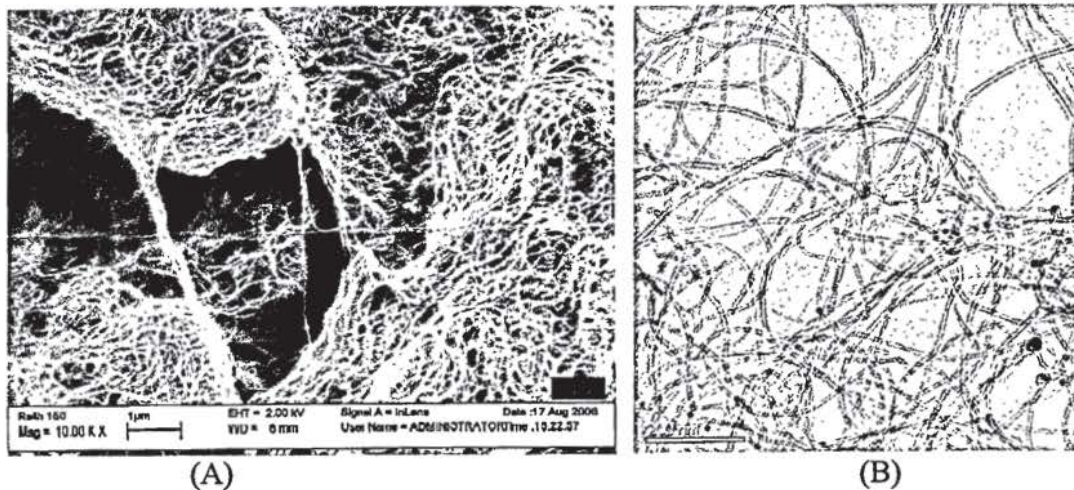
Figure 5. (A) SEM and (B) TEM Images of the neat MWCNTs obtained from the vendor.
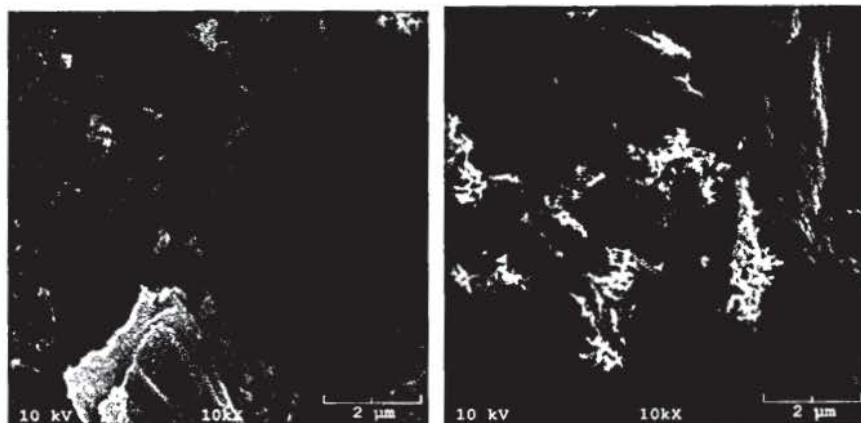

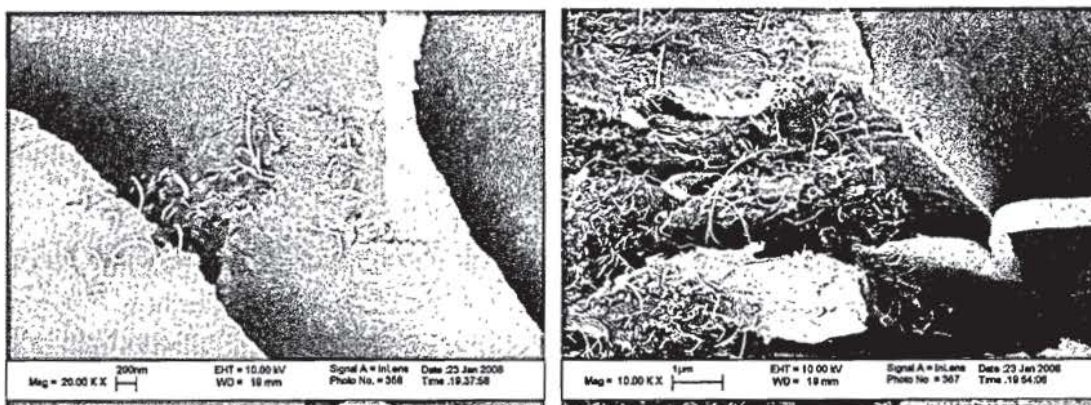Figure 6. SEM pictures showing inadequate dispersion in ball-milled cured samples.

Figure 7. SEM pictures showing inadequate dispersion in 0.5 wt% MWCNT ball-milled un-cured samples.
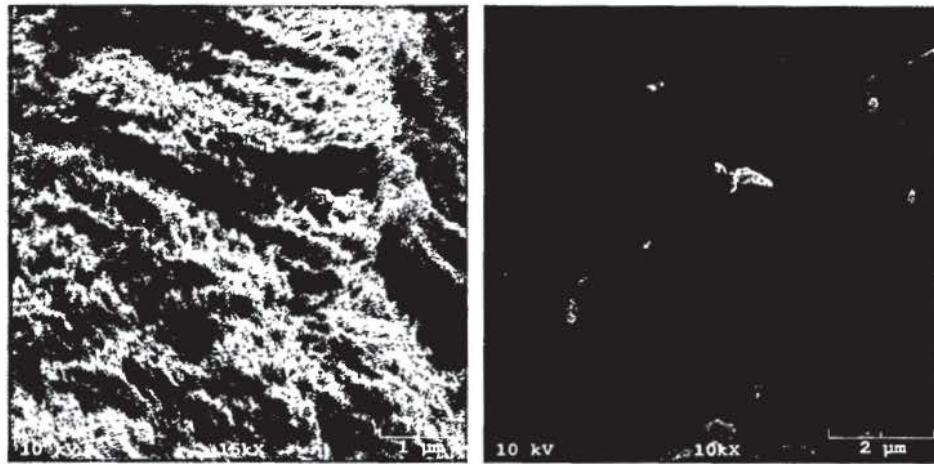
Figure 8. SEM pictures of samples that were ball-milled and sonicated in a solvent.
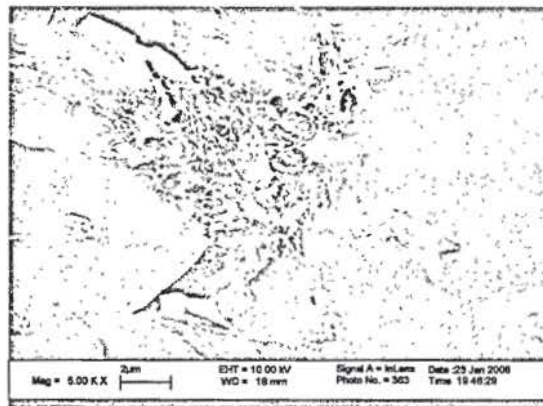

Figure 9. SEM picture of melt mixed sample showing inadequate dispersion.
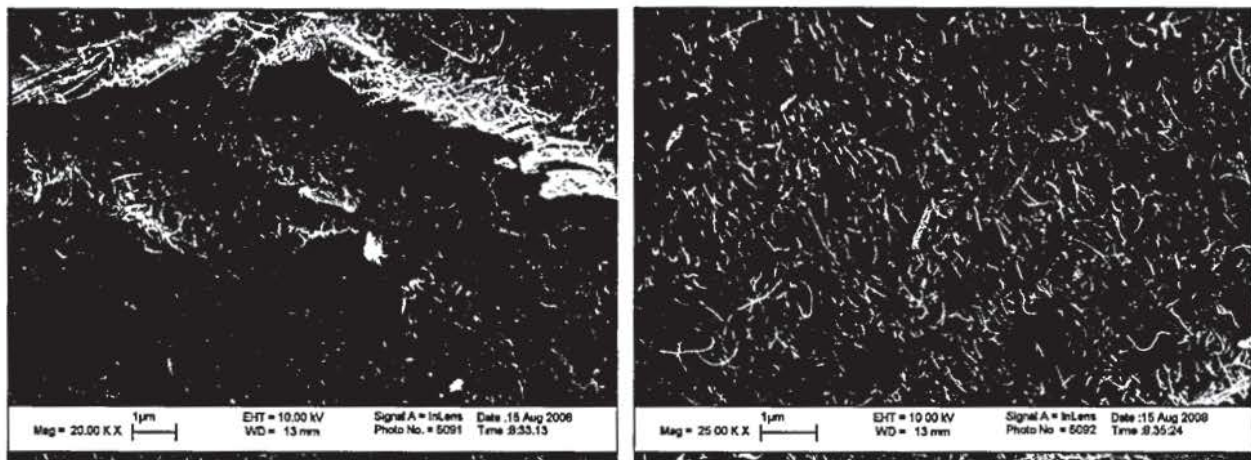

Figure 10. SEM pictures of High Torque 4 wt% MWCNT/PETI blend showing homogeneous dispersion.
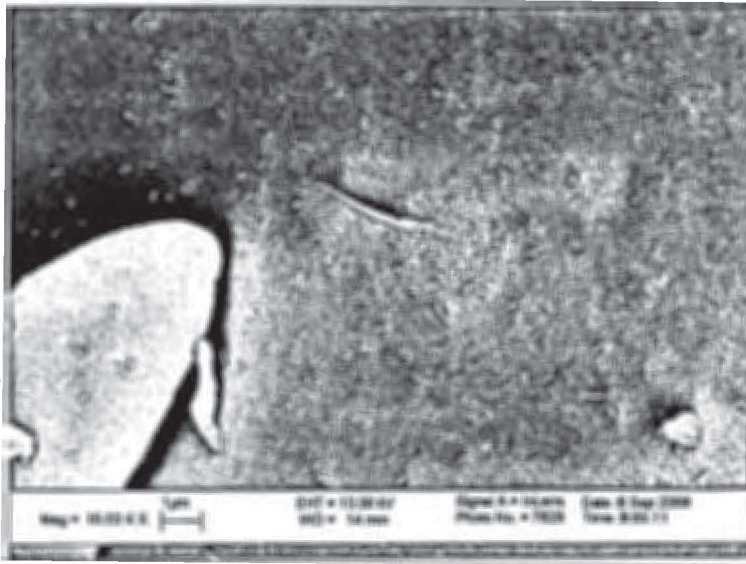
Figure 11. SEM picture of High Torque 0.125 wt% MWCNT/PETI blend showing good distribution but showing that some agglomerates are present.
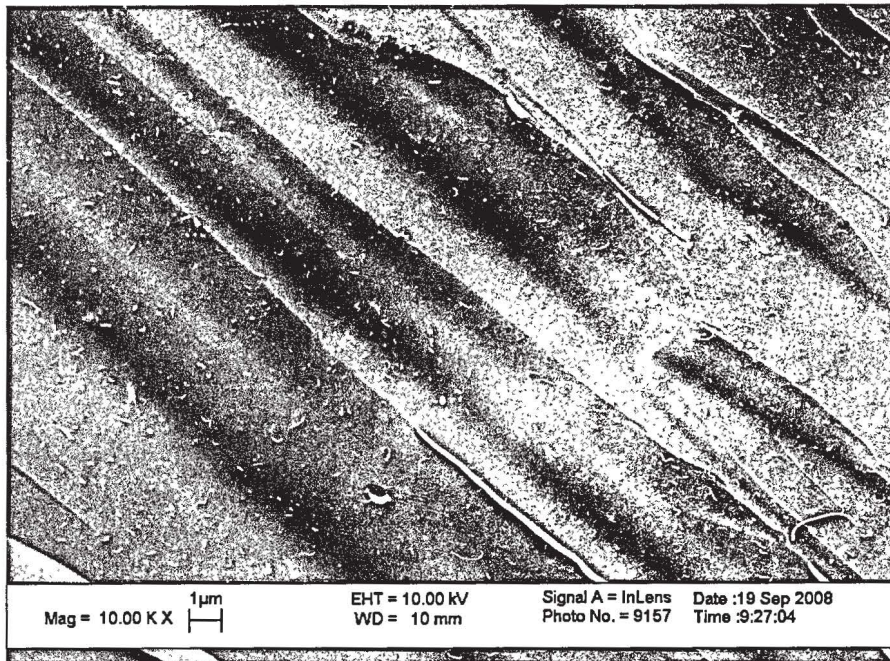

Figure 12. SEM picture of High Torque 0.125 wt% MWCNT/PETI blend trial number 2 showing great dispersion and no agglomerates.

3.3 Characterization of PMCs

3.3.1 Quality Analysis

The composite panels were ultrasonically inspected to determine their quality and to identify any areas of porosity that might be present. By this analysis all of the panels fabricated in this study were of high quality. A representative C-scan is given in Figure 13. The thickness was determined on all panels. Table 1 lists the PMC panels initially fabricated under this program where ball milling was used for blending the MWCNT into the resin. It also gives the panel's thickness along with the calculated fiber volumes, based on fiber areal weight (FAW) and fiber density, and with their fiber volumes based on acid digestion. Acid digestion was performed to determine the resin content, fiber volume and porosity content for the initial panels only. Table 2 lists similar data for all of the panels fabricated after we determined that ball milling was not adequate for obtaining well dispersed MWCNTs in the PMCs. The MWCNT PMCs in this table were fabricated from either high torque melt mixed blends and/or from pre-loading the M55J preform with MWCNTs prior to RTM.

Photomicrographs were obtained from the panel's representative best, worst and/or typical areas as determined from the C-scans (ultrasonic inspection). The photomicrographs showed all of the composites to be of high quality with very little to no observable porosity. The photomicrograph of the 0.5 wt % MWCNT-PETI PMC fabricated from loaded resin prepared by ball-milling for 2 days exhibited some micro-cracking. Micro-cracking was very low or not observed in all other photomicrographs including the PMC prepared from resin/MWCNT that had been ball-milled for 4 days. This suggests that the MWCNTs were not well dispersed after only 2 days of ball-milling, and showed up as black specs in the photomicrographs (refer to Figure 14B). Additional ball-milling for a total of 4 days resulted in better dispersion which eliminated the micro-cracking. Figure 14 gives photomicrographs of the baseline and nano-loaded PMCs. The PMC prepared from resin/MWCNTs that had been ball-milled for 4 days still exhibited nano-agglomerates which are seen in the photomicrograph as black specs (refer to Figure 14C). SEM analysis and DMTA (plots given in Figure 15) of specimens from the panels fabricated from the MWCNTs/PETI-330 resin ball-milled for 4 days indicted that the MWCNTs were filtered out during RTM processing. As can be seen from Figure 15 the storage modulus of the sample from the inlet side of the PMC is 20 % higher than a sample taken from the outlet side of the PMC. This also suggests that the MWCNTs increase the storage modulus of the resultant PMC. It was later determined that improved melt mixing was the method to achieve the best dispersion of the nano-particles investigated and the ball-milling approach was discontinued.

3.3.2 SEM Analysis of PMCs

SEM analysis of specimens cut from the PMCs was performed to determine the dispersion and homogeneity of the MWCNTs in the PMC. In addition, select samples were taken from the cured resin contained in the gutters of the tool and from uncured resin contained in the resin trap on the tool outlet side after PMCs had been fabricated. This allowed us to determine if the MWCNTs were filtering out during the resin infusion process.

Figure 13. C-scan of melt mixed 0.5 wt % MWCNT/PETI-330/M55J PMC.

Table 1. Summary Data for Baseline PMCs and Ball-Mill Mixed MWCNT loaded PMCs.

Panel ID	Materials	Thickness (inch)	Fiber Volume 1	Fiber Volume 2	Notes
GSFC-01-1	PETI-330/M55J	0.05716	62%	66%	Short Shot
GSFC-01-2	PETI-330/M55J	0.08120	44%	48%	High Quality
GSFC-01-3	PETI-330/M55J	0.06238	57%	63%	Short Shot
GSFC-01-4	PETI-330/M55J	0.08865	40%		High Quality
GSFC-01-5	PETI-330/M55J	0.06941	52%	48%	High Quality
GSFC-01-6	PETI-330/M55J/ 0.5% MWCNT	0.06910	52%	50%	High Quality – 2 day ball milling
GSFC-01-7	PETI-330/M55J/ 0.5% MWCNT	0.06772	53%	55%	High Quality – 4 day ball milling

* Calculated using PMC thickness and the fiber aerial weight (215 g/m^2) and density (1.9 g/cc) of the M55J fabric.
** Determined from Acid Digestion.

Table 2. Summary Data for Baseline and High Torque Melt Mixed MWCNT PMCs.

Panel ID	Materials	Thickness (inch)	Fiber Volume*	Description
GSFC-02-1	MWCNT loaded PETI-330/M55J	0.06667	53%	Pre-loaded Resin PMC
GSFC-02-2	RS-3/M55J	0.12796	56%	Baseline PMC
GSFC-02-3	PETI-330/M55J	0.12676	56%	Baseline PMC
GSFC-02-4	RS-3/M55J	0.19055	56%	Fracture Toughness Baseline
GSFC-02-5	PETI-330/M55J	0.18741	57%	Fracture Toughness Baseline
GSFC-02-6	MWCNT loaded M55J/PETI-330	0.06896	52%	Pre-loaded Fabric PMC
GSFC-02-7	MWCNT loaded PETI-330 & M55J	0.06830	52%	Combination Preloaded PMC

* Calculated using PMC thickness and the fiber aerial weight (215 g/m^2) and density (1.9 g/cc) of the M55J fabric.

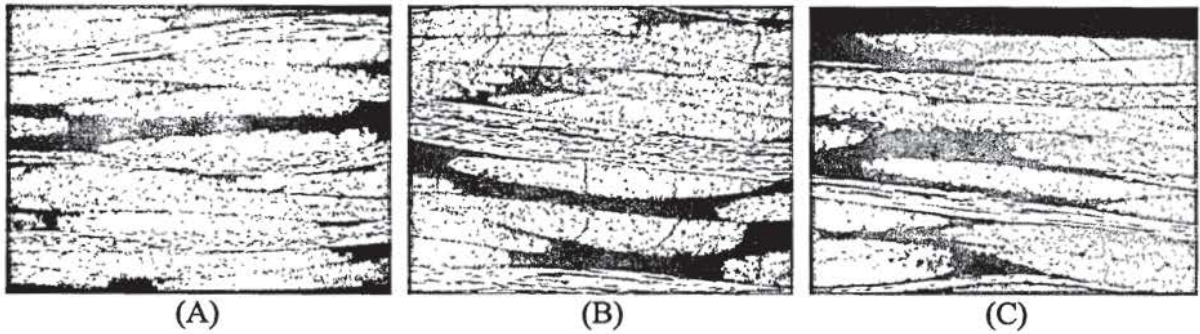(A)   (B)   (C)

Figure 14. Photomicrographs of (A) the Baseline PMC and 0.5 wt % MWCNT-PETI-330 PMCs
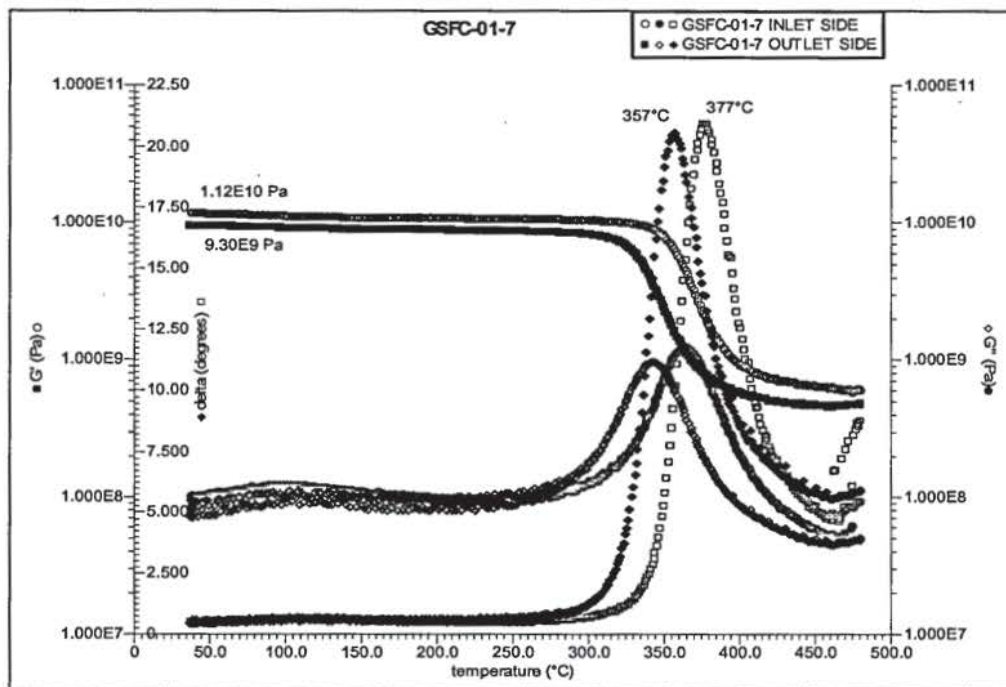made from (B) two and (C) four day ball-milled blend.

Figure 15. DMTA traces for GSFC-01-7 (4 day ball mill) showing overlay of PMC samples
taken from the inlet and outlet sides of the RTM tool.

3.3.2.1 MWCNTs PMCs made from Ball Milled MWCNT/PETI-330 Blends

We performed SEM analysis on the baseline and optimally MWCNT loaded PMCs. Two
optimally loaded PMCs were fabricated from a 0.5 wt % MWCNT loaded PETI-330 that had
been ball milled 2 and 4 days. The nano-loaded PMCs were sectioned into 9 square samples and
labeled such that they could be mapped back to the RTM tool's inlet and outlet location.
MWCNTs were found in both nano-loaded PMCs on the inlet side (refer to Figure 16). Very
few MWCNTs were found in the middle (refer to Figure 17A) or the outlet side (refer to Figure
17B) of the PMC made from MWCNTS/resin that had been ball mill mixed for 2 days. This
suggests that the M55J fabric filtered out the larger MWCNT agglomerates during the infusion

process. Increasing the time of ball milling from 2 to 4 days resulted in samples showing MWCNTs throughout the PMC but still showed signs of filtering. The resin coming out of the outlet during RTM molding was black, indicating that some MWCNTs made it all the way through the preform while the larger agglomerates filtered out. These two panels prove the feasibility of fabricating nano-loaded PMCs using the RTM process.
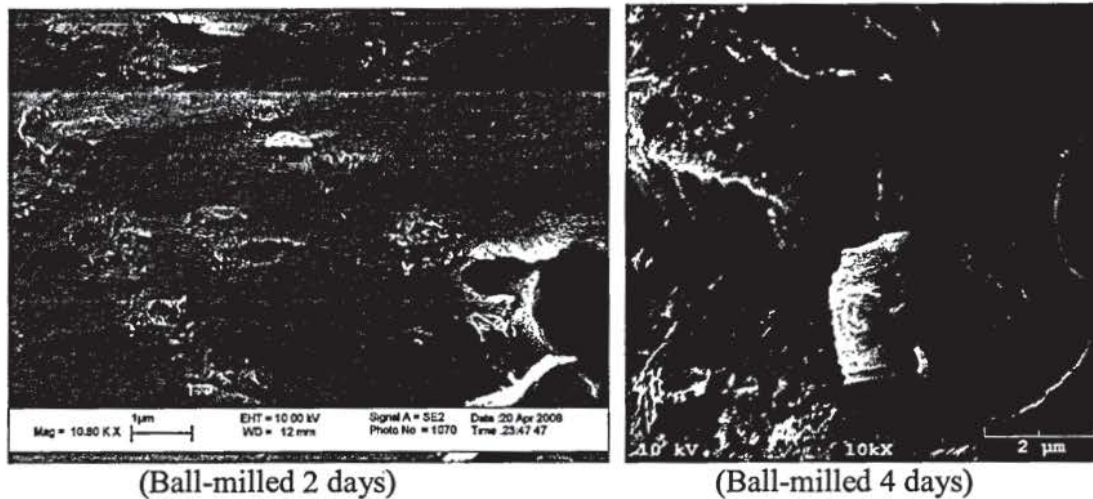

(Ball-milled 2 days)   (Ball-milled 4 days)

Figure 16. SEM pictures from Injection Side of panel showing MWCNT agglomerates in the ball-milled PMCs. GSFC-01-6 on left and GSFC-01-7 on right.

(A)   (B)

Figure 17. SEM pictures of the PMC showing no MWCNTs in the sample taken from the (A) middle and (B) outlet side of the RTM Tool (GSFC-01-6).

3.3.2.2 MWCNT/PETI-330 PMCs made from Optimally Loaded PETI-330 and/or from Pre-Loading the Fabric with the MWCNTs

SEM images of specimens from the MWCNTs/PETI-330 blends clearly indicated that the MWCNTs were wet-out and homogenously dispersed throughout the sample. The MWCNTs

were also found to be present in resin samples taken from the resin trap at the outlet of the RTM processed panels, which proved that the particles made it all the way through the preform during injection. An SEM image from the resin from the trap from the RTM of panel GSFC-02-1 is given in Figure 18. Figure 19 gives an SEM image of the PMC from the inlet side, and Figure 20 from the outlet side. From this SEM analysis MWCNTs were found to be present at the fiber/matrix interface and in the resin between the fibers. The MWCNTs were found everywhere in the PMC samples which verifies the feasibility of RTM'ing the optimum blend.

The SEM analysis of the pre-loaded fabric PMC (GSFC-02-6) is presented below in Figures 21 and 22. The SEM in Figure 21 was obtained from a sample on the inlet side of the PMC and Figure 22 is the SEM image of a sample taken from the outlet side. The figures show that the MWCNTs bridge the fibers of the fabric. SEM analysis of neat resin obtained from the RTM gutters and from the resin trap showed no sign of MWCNTs. This shows that the MWCNT particles used to pre-load the fabric did not migrate from the fabric during infusion. There was no observable difference in the dispersion of the MWCNTs from the inlet to the outlet side of the PMC. The loading of the MWCNTs was estimated to be approximately 1 wt % of the fabric weight (~0.7 wt % of the overall panel). This work represents the first time a pre-loaded MWCNT M55J/PETI-330 PMC has been fabricated and illustrates a way to "bridge" the carbon fibers using MWCNTs.
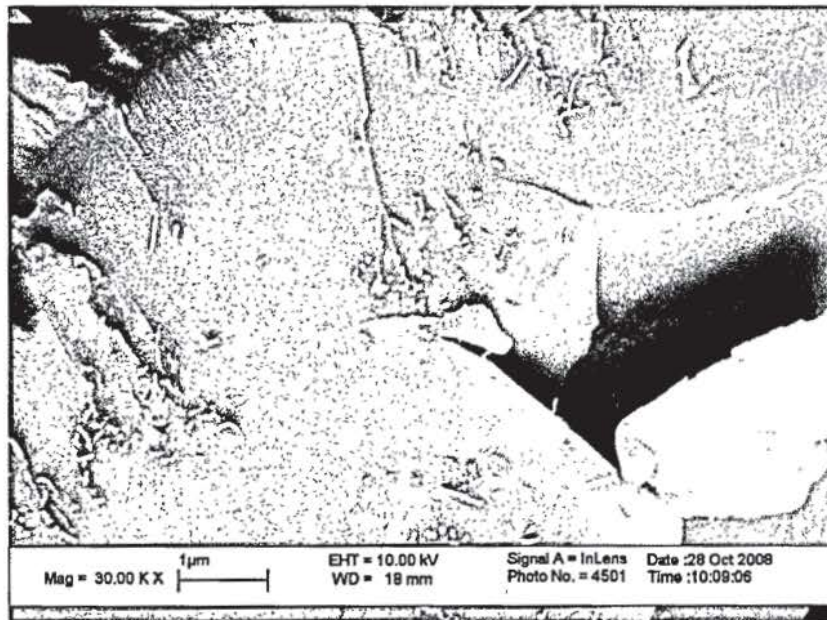

Figure 18. SEM picture from neat resin contained in the resin trap from the High Torque Mixed MWCNT "Optimum" PMC RTM run (GSFC-02-1) showing MWCNTs present.
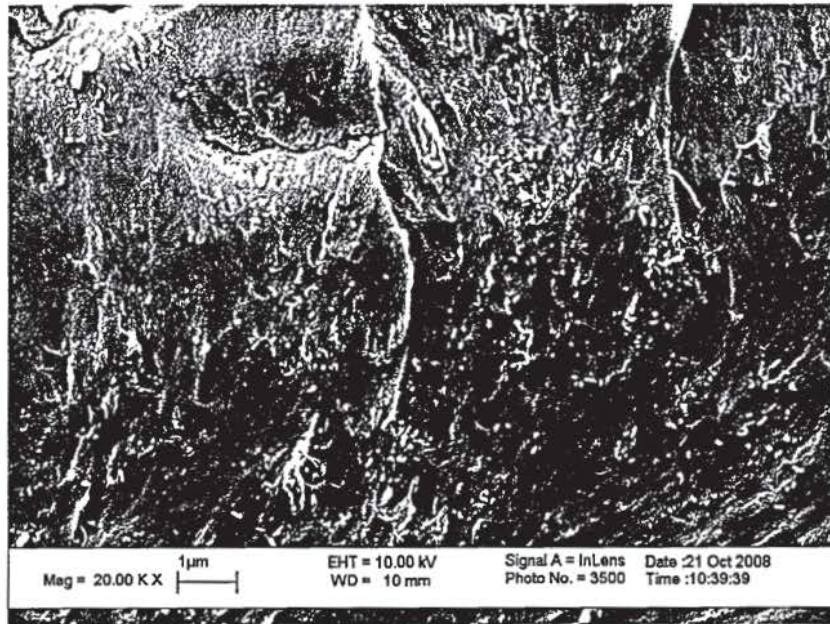
Figure 19. SEM pictures taken from PMC at the inlet side (GSFC-02-1) showing well dispersed MWCNTs present in matrix.
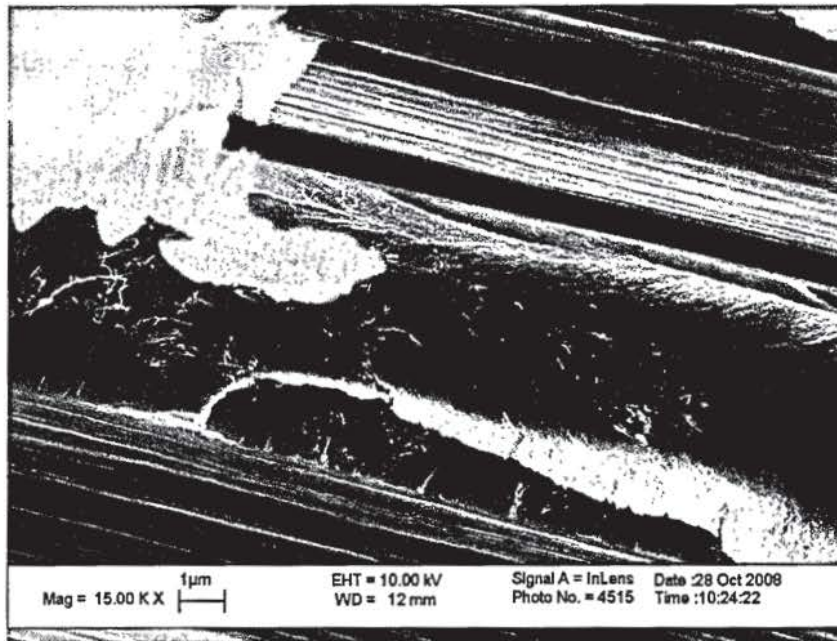

Figure 20. SEM pictures taken from PMC at the outlet side (GSFC-02-1) showing well dispersed MWCNTs and that they were not filtered out during injection.

Figure 21. SEM image showing MWCNTs between fibers on Inlet Side of pre-loaded fabric PMC.
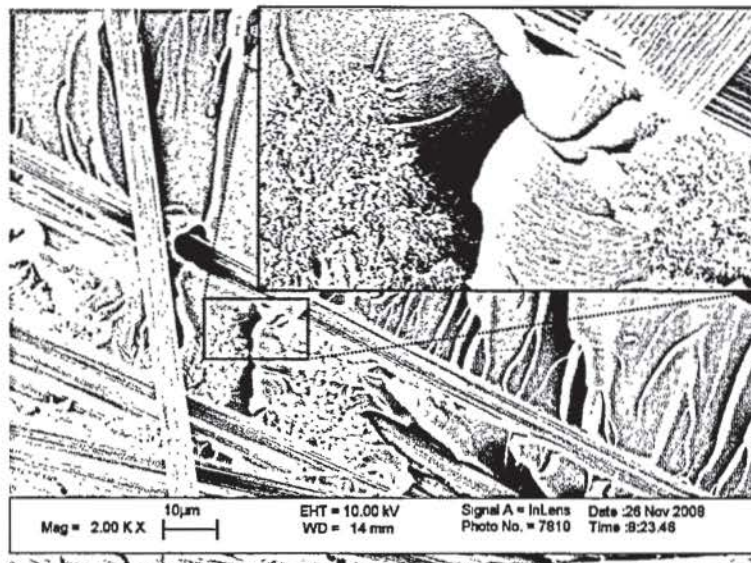
Figure 22. SEM image with inlay showing MWCNTs between fibers on Outlet Side of MWCNT pre-loaded fabric PMC.

The last panel fabricated combined pre-loading of the MWCNTs in both the resin and fabric in order to maximize the MWCNT loading level in the PMC. The SEM images from this "combined" panel are given in Figures 23A and 23B, and show well dispersed MWCNTs in the matrix (see Figure 23A). These particles are believed to be from the pre-loaded resin since the SEM image is very similar to what was observed in the pre-loaded resin only panel (GSFC-02-1). There was also evidence of MWCNT agglomerates between the fibers (see Figure 23B).

These MWCNTs agglomerates were also seen in the pre-loaded fabric panel while not observed in the pre-loaded resin panel. Hence the MWCNT agglomerates are believed to be from the pre-loaded fabric. Therefore, a method for bridging fibers with MWCNT agglomerates and a method for obtaining a well dispersed MWCNT-polymer matrix was successfully demonstrated.
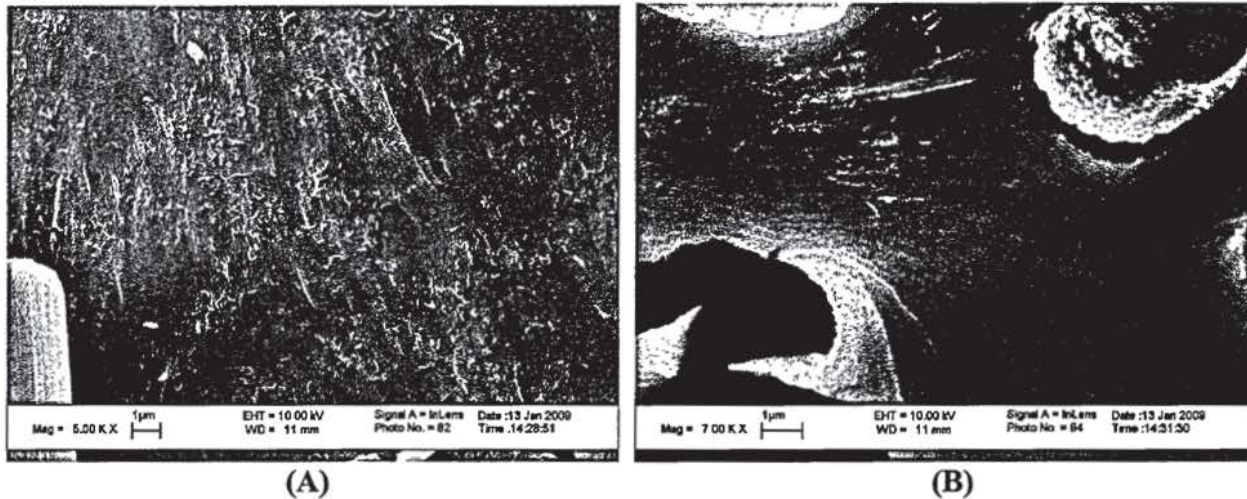

(A)   (B)

Figure 23. SEM Images from "combined" MWCNT loaded PMC showing (A) well dispersed areas and (B) MWCNT agglomerates between fibers.

3.3.3 Other Characterization Results

A total of 54 surface and volume resistivity measurements were made on each panel and the averages are given in Table 3 for the MWCNT loaded PMCs made using blends mixed using the optimum method discussed above. From this data, the optimally pre-loaded resin panel (GSFC-02-1) gives the lowest resistivity. This suggests that the dispersed MWCNTs have a much larger effect on resistivity than the MWCNT agglomerates, as is expected. The GSFC-02-1 panel had the highest loading of MWCNTs in the resin. The volume resistivity of the baseline PETI PMC (GSFC-02-3) was 4460 while the MWCNT loaded panel, GSFC-01-1, was 931 Ohms*cm. Although, a direct comparison cannot be made, this represents a 79% reduction in resistivity over the baseline and infers a reduction in volume resistivity upon addition of MWCNTs as would be expected.

Table 3. Summary Resistivity Data (Averages of 54 tests).

Panel ID	Surface Resistivity (Ohms^2)	Volume Resistivity (Ohms*cm)
GSFC-02-1	8.83E+03	9.31E+02
GSFC-02-6	1.1E+04	1.7E+03
GSFC-02-7	1.3E+04	1.6E+03

Thermal Mechanical Analysis (TMA) was performed on all of the high quality PMCs fabricated in this study. A total of three specimens from each panel were tested. The T_g and CTE, measured below the T_g, was then determined from each curve. The TMA data is given in Table 4 with the averages at the end. A plot of the data is given in Figure 24 with the baseline data (different lay-ups) for comparison although a direct comparison cannot be made. From this data the combined MWCNT loaded PMC gives the lowest CTE value. This represents an approximately 24 percent reduction over the baseline PETI-330 panel (GSFC-02-3) and suggests that the MWCNTs contribute to the reduction in the CTE of the PMC. The T_g of the PETI-330 composites ranged from 275 to 282°C and the T_g of the RS-3 composites ranged from 177 to 184°C. Note that the T_g determined from TMA are always lower than that from DMTA. Moisture absorption work is still in progress but our initial results show approximately 15% decrease in moisture absorption of GSFC-02-7 (combined nano-loaded PMC discussed above) over the PETI-330 baseline (GSFC-02-3).

Table 4. Summary TMA Data.

|	TMA-run-1		TMA-run-2		TMA-run-3		TMA-AVG		
Panel ID	Tg (°C)	CTE (1/°C)	Tg (°C)	CTE (1/°C)	Tg (°C)	CTE (1/°C)	Tg (°C)	CTE (1/°C)	CTESD
GSFC-02-1	281.4	4.29E-05	280.4	3.71E-05	282.9	3.83E-05	281.5667	3.95E-05	3.07E-06
GSFC-02-6	271	3.47E-05	279.7	4.65E-05	276.3	5.07E-05	275.6667	4.40E-05	8.29E-06
GSFC-02-7	275.3	3.45E-05	291.7	5.04E-05	275.3	1.63E-05	280.7667	3.37E-05	1.70E-05
GSFC-02-2	173	4.50E-05	180.4	3.61E-05	177.3	4.20E-05	176.9	4.10E-05	4.54E-06
GSFC-02-3	273.8	4.97E-05	280	4.03E-05	271.6	4.26E-05	275.1333	4.42E-05	4.90E-06
GSFC-02-4	182	4.83E-05	183.9	5.20E-05	183.8	5.01E-05	183.2333	5.01E-05	1.87E-06
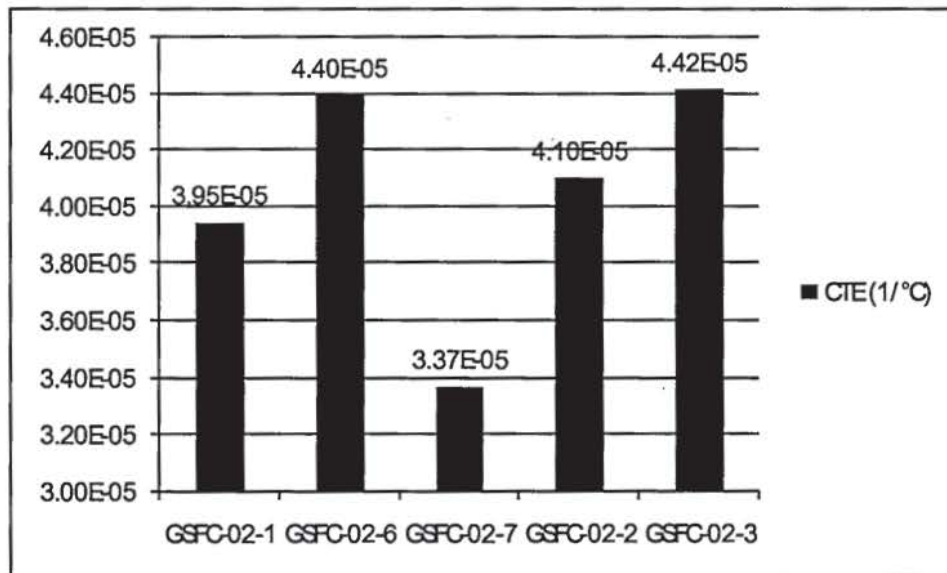
Figure 24. Comparison of CTE Averages for Nano-loaded PMC Panels (GSFC-02-1, 6 & 7) and for Baseline RS-3 (GSFC-02-2) and PETI-330 (GSFC-02-3) PMCs.

4. CONCLUSIONS

For the purpose of developing materials with enhanced properties that can be tailored, methods for fabricating PMCs with homogeneously dispersed MWCNTs in the matrix were developed and demonstrated. A cyanate ester resin (RS-3), a polyimide resin (PETI-330), M55J fabric, and long MWCNTs were selected due to past experience and applications targeted. Initial studies with RS-3 cyanate ester resin proved unsuccessful due to the resin blends prematurely cross-linking or curing during the mixing process.

After several mixing trials and methodologies were investigated, an improved melt mixing approach was determined to be the best method to obtain good dispersions of the MWCNTs in the resin. Although past work determined ball-milling to be adequate for obtaining good dispersion, the long nature of the MWCNTs investigated in this program required another approach. To date a total of five PMCs with MWCNTs in their matrix have been successfully fabricated and determined to be of high quality. All of the PMCs were fabricated using the RTM process and low cost RTM equipment developed by M&P Technologies. This demonstrates the feasibility of using RTM to fabricate MWCNT loaded PMCs. One limiting factor in RTM processing is the requirement to have a low viscosity resin for injection. This requirement limits the amount of MWCNTs that can be added to the resin prior to injection because of the large increase in viscosity that occurs upon addition of relatively small quantities of MWCNTs. Similar results were found for MWCNTs in epoxy matrix composites [18]. For this reason methods to add the MWCNTs to the composite preform prior to resin injection were developed and demonstrated. By utilizing a nano-loaded resin developed and optimized under this program and a nano-loaded fabric preform co-developed by CAU and M&P Technologies, we demonstrated fabrication of a panel with ~1 wt % MWCNT on a total weight basis. Higher loadings of the MWCNTs are believed to be possible.

The volume resistivity of the PETI PMC was shown to be reduced from 4460 to 931 Ohms*cm and represents a 79 % reduction in resistivity. Although, a direct comparison cannot be made because the baseline panel has twice the number of plies as the loaded panels, these results suggest a reduction in volume resistivity upon addition of MWCNTs as would be expected. This work also suggests the feasibility in using MWCNTs for mitigating electrostatic charge dissipation in PMCs. A CTE as low as 3.4 E-5 (1/°C) has been achieved for the MWCNT loaded PMC. This represents approximately a 25 percent reduction in CTE over the baseline PETI PMC (4.4×10^5) although a direct comparison is not implied. Our initial findings also suggest that addition of MWCNTs increase the storage modulus of the PMC but more studies are needed to determine significance. Our initial results show approximately 15% reduction in moisture absorption upon addition of less than 1% MWCNT in the PMC.

The feasibility of pre-loading resin and/or fabric with MWCNTs in the RTM of aerospace quality PMCs has been demonstrated. All composite made with MWCNTs have been of high quality. Although this is a work in progress, the data to date is very promising for allowing the fabrication of enhanced PMCs having lower CTE (better dimensional stability), increased electrical and thermal conductivity (mitigate electrostatic charge dissipation and disperse concentrated heat loads), and reduced moisture absorption of the space structures produced. The effect of the MWCNTs on the PMC mechanical properties are still under investigation and will be reported in another paper.

5. ACKNOWLEDGMENT

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