Graphene Nanoplatelet Membranes for Aerospace Applications

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ABSTRACT

Graphene nanoplatelets (GnP), conceptually described as unrolled carbon nanotubes, exhibit attractive properties including the highest thermal conductivity known and twice the surface area of carbon nanotubes. By blending with a minimal ratio of carbon nanotubes in a papermaking-like process, a thin, robust membrane is produced which can be pre-impregnated with resin and handled similarly to carbon fiber prepreg materials. This paper-like membrane can be easily and strategically inserted in traditional composite manufacturing including autoclave and out-of-autoclave processing without the introduction of additional steps or cure cycle alterations. In addition to offering thermal and electrical property enhancements similar to or surpassing those accomplished with carbon nanotubes, the graphene nanoplatelets are significantly cheaper and easier to disperse. Space application development efforts with graphene nanoplatelet membranes have included thermal management and electromagnetic environmental effects protection of composite structures, and energy storage related applications. This paper presents the results of processing and evaluation of GnP membranes for aerospace applications.

Keywords: graphene nanoplatelets, paper-like-membrane, thermal management, energy storage, electromagnetic environment effects

1 INTRODUCTION

Allotropes of carbon, in the forms of carbon nanotubes (CNTs) and graphene nanoplatelets (GnPs)), are known to exhibit very high thermal conductivity with the experimentally determined room temperature value of around 2500-3000 W/mK for an individual multi-walled CNT and about 3500 W/mK for an individual single-walled CNT. These values exceed those of the best bulk crystalline thermal conductor, diamond, or flexible graphite foils (eGRAF Spreadershield) which has the thermal conductivity in the range of 1000–2200 W/mK. More specifically, the monolayer graphene is reported to exhibit Young's modulus (~1,100 GPa), thermal conductivity (~5,000 W /m-K1), mobility of charge carriers (200,000 cm^2/Vs), and specific surface area (calculated value, 2,630 m^2/g) [1-4]. In essence, both the CNT and graphene materials exhibit excellent combination of thermal, mechanical and electrical properties, which could be exploited for diverse aerospace applications.

These applications include aerospace elements such as structural panels, tubes, electrical cables, electronic boxes and enclosures, thermal straps, thermal interface materials, radiators, and ultracapacitors. For example, using the outer ply of thin CNT based sheet material Lockheed Martin (LM) Space Systems Company has processed a few tubular and structural polymer composite panels for a NASA mission spacecraft. The co-processed thin CNT sheet provides the ease of integration to obtain the electrostatic dissipation (ESD)/electromagnetic interference (EMI) shielding attributes in the structural elements. Building upon this successful experience, the objective of the ongoing nanotechnology effort has been to evaluate the GnP materials for space applications.

An affordable manufacturing approach was used to process, GnP based paper like membranes, which could be scaled up to manufacture rolls of sheet material. It was recognized that the GnP material had to be mixed with as low as 20% CNT material to process GnP/CNT hybrid membranes, which were robust and flexible enogh for handling purposes. After establishing the nearly optimum processing methodology for GnP based membranes, the sheet material was evaluated for EMI/ESD, thermal interface, and ultracapacitor type applications. This paper briefly documents the processing of GnP based membranes, and results of its evaluation for the thermal interface, ultracapacitor electrodes, and ESD/EMI shielding applications.

2 GRAPHENE NANOPLATELET MEMBRANES

Overall objective of this effort was to develop affordable materials and processes to evaluate graphene or GnP based materials for potential space applications. Monolayer graphene is being produced at the laboratory scale at several research facilities, and it was found not to be readily commercially available. Therefore, the project was directed to evaluate GnP material available from two key sources: Angstron Materials Inc., Dayton, OH; and XG Sciences, Lansing, MI. It was recognized that product at both sources were being manufactured to produce different grades of materials, with improvement in the yield and material properties.

2.1 Graphene Nanoplatelet Materials

General specifications (per Material Safety and Data Sheet (MSDS)) of the GnP material evaluated in this effort, are as follows.

i) Source: Angstron Materials Inc.
   Product specification: "N0006-010-PNGP"
   Bulk Density: 0.07-0.72 g/cc (MSDS)
   Avergae x and y dimension: 0.6 µm (At least 75% of nanoplatelets having thickness < 10nm) (MSDS)
ii) Source: XG Sciences
   Product specification: "XGnP Grade M:25 µm "
   Bulk Density: 0.18-0.25 g/cc (MSDS)
   Average particle size: 25 µm , 5-10 nm thickness (MSDS)

2.1 Processing of GnP Sheets

Using the proven paper-like continuous membrane manufacturing process developed at Buckeye Composites, OH for CNTs, initial trial experiments were conducted to manufacture GnP sheets with 100% GnP, and different mixtures of GnP and multiwall nanotubes (MWNTs). Based on these experiments it was found that the sheets with maximum 80 weight% GnP/20 weight % MWNT could be easily manufactured to provide desired ease of handling and multifunctional property attributes. The GnP/MWNT sheet produced from both the GnP sources, easily passed the 3/16" bend radius test, thus verifying the flexibility and handlability of the as-processed GnP sheets. Typical thickness for 80% GnP membrane at 60gsm areal weight ranged from 182 to 234 microns. Several sheets ranging from 80%, 75%, 60%, and 25% GnP with remaining MWNTs were successfully fabricated for different evaluation tests discussed in the following sections. Figure 1 shows a roll of the GnP based sheet being produced during the manufacturing process, and Figure 2 shows the microstructure revealing GnPs intertwined by the MWNTs.

Affordable manufacturing of CNT and GnP based membrane is driven by two key components: i) raw material cost, and ii) the filter paper availability and cost. Using reasonable cost raw materials, and by scaling to continuous buckypaper manufacturing processes, Buckeye Composites has significantly increased the throughput. The continuous GnP based sheet production requires filter papers with certain properties, and in some cases different filter papers must be employed for different buckypaper formulations.

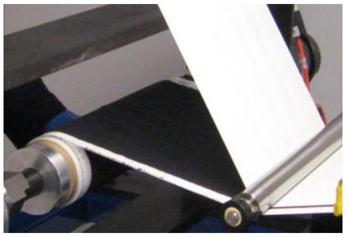

Figure 1: Paper-like manufacturing process to produce GnP sheets.

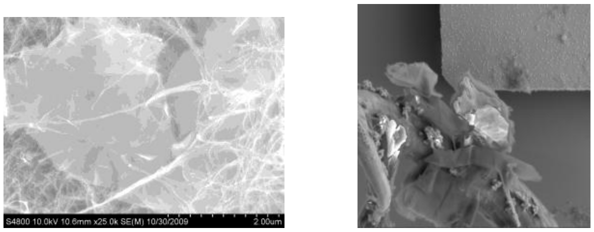

Figure 2: Microstructure of GnP Membrane showing the GnPs tangled with MWNTs

3 EXPERIMENTATION

3.1 Key Application-Specific Tests:

The as-processed GnP/MWNT sheets were evaluated for the following tests:

1. Electrical (Surface Resistivity) measurements, of as-processed and resin-infltrated GnP sheet. A Keithley Instruments Four point probe wasused to measure the surface resitivity of as processed sheets and co-cured GnP/MWNT sheet on a composite laminate.

2. Thermal conductivity measurements were performed both at the GnP, and sheet levels. In addition thermal conductivity of cyanate ester infiltrated 4-ply 80%GnP/20%MWNT laminate was measured by Fourier thermal conductivity test method. Also, the thermal conductivity of RTV infiltrated GnP sheet was measured as a thermal interface material.

3. Specific surface area (m^2/g) of each of the sheet materials was measured by the Brunauer-Emmett-Teller (BET) method. Subsequently, GnP based sheets were prepared as electrodes for the ultracapacitors. A few coin cell shaped ultracapacitors were prepared and the specific capacitance measurements were performed using inorganic acid and ionic liquid elctrolytes.

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4 RESULTS

Specific results of each of the test results are presented in this section. These tests include surface electrical resistivity, thermal conductivity, and specific capacitance measurements.

4.1 Surface Electrical Resistivity

Table 1 lists the typical electrical properties of as-processed sheets. Like several of the CNT materials, GnP based sheets exhibited surface electrical resistivity of 1-2 Ohm/square. Subsequently when these sheets were co-cured as the outerplay of a composite laminate, the surface resistivity increased to about 10-15 Ohm/sq. These measurements confirmed that GnP sheets can be used for several of the EMI/ESD related applications on aerospace structural elements.

Table 1: Typical Surface Electrical Resistivity Measured values for the GnP membranes

Property	**GNP Membrane 80GNP/20MWNT (KB-070710,080610)**	**GNP Membrane 25GNP/75MWNT (KM-100909)**
Areal Density (gsm)	60.3	44.6
Density (g/cm^3)	0.44- 0.45	0.43
Electrical Resistivity (Ohm/Square)	1.07-1.37	1.88
Bulk Electrical Resistivity (Ohm-cm)	0.0144	0.0195
Electrical Conductivity (S/cm)	53- 69.5	51.2

Figure 3 shows the 80%GnP/20% MWNT sheets produced from the GnP received from both the sources. The measured surface electrical resistivity values were nearly identical: 80wt% XGnP 60 gsm membrane was ~ 1.07 ohm/sq, compared to N006 GNP membrane at ~ 1.48 ohm/sq.

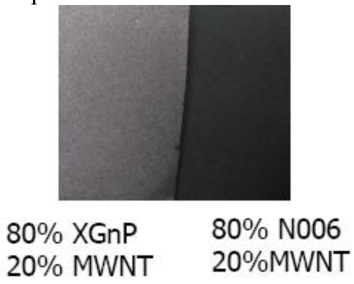
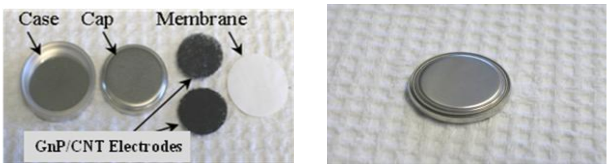


Figure 3: Typical surface appearance of 80%GnP/20% MWNT sheets

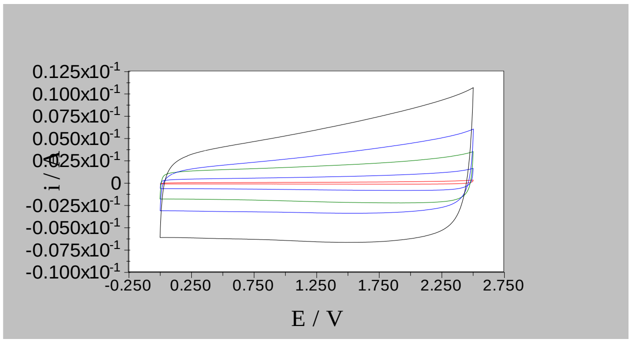
4.2 Ultracapacitor Capacitance

Typical BET surface area measurements of 80%GnP/20% MWNT, and 75%GnP/20%MWNT based membranes yielded values ranging from 75 to 125 m^2/g, which is quite consistent with some of the CNT sheet materials. But it is significantly lower than the monolayer graphene, or chemically modified graphene, which seem to provide high surface area and high specific capacitance.

The capacitance measurements yielded values ranging from 20-40 F/g at the coin cell test level [Figure 4]. Ongoing efforts are directed to prepare different blends of GnP material to obtain electrodes with improved specific surface area, and enhanced capacitance using ionic liquid electrolytes.



a) GnP/MWNT Electrode Based Ultracapacitor Coin Cell



b) Cyclic Voltammogram at RT

Figure 4: The CNT, and GnP/MWNT electrodes were used to prepare coin cell configuration, and cyclic voltammetry was used to measure capacitance of the ultracapacitor.

4.3 Thermal Conductivity

Using the innovative thermal flash method, Prof. Alexis Abrahmson at Case Western Reserve University measured the thermal conductivity of GnP (embedded in the membrane) of ~1940 w/m-K, which is quite close to the value for basal plane conductivity of 2250 W/m-K for the single crystal graphite [5].

A few thin thermal straps of 80% GnP sheets were prepared, and a test fixture was preapred to measure the thermal conductivity along the lenth. These measurements gave an estimated value of ~40 to 60 W/m-K. These measurements potentially, have an inherent error because of difficulties in establishing good contact between the membrane and heat source and thermocouples. Therefore a 4-ply laminate of cyanate ester infiltrated 80%GnP/20% MWNT was also processed. Using the Fourier thermal conductivity test method, the in-plane thermal conductivity of this laminate ranged from 10 to 12 W/m-K.

Thin sheets of 80% GnP were also infiltrated with RTV 511 silicone, as if to prepare a thermal interface material. This GnP based thermal interface material exhibited smooth and compliant surface, and measured average thermal conductivity was ~10 W/m-K, which is quite consistent or slightly better than a few of the state of the art thermal interface materials.

5 CONCLUDING REMARKS

Using commercially available graphene nanoplatelet materials, an affordable paper-like manufacturing technique was used to produce 80 weight% GnP/20 weight % MWNT membrane. The sheet material was used to determine the thermal and electrical properties of GnP based materials to evaluate its viability for the aerospace applications. Also, recognizing the attributes and potential of GnP material, these sheets were evaluated for EMI/ESD, thermal management and energy storage (ultracapacitor) applications.

Results of this study indicated that GnP based membrane is a viable candidate material for EMI/ESD and thermal interface material applications. However, for the ultracapacitor and high thermal conductivity applications, monlolayer GnP based materials with improved properties are being evaluated in the ongoing effort.

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