1 Introduction
Freestanding mats of densely entangled carbon nanotubes, so-called “buckypapers” were studied in a various applications including artificial muscles [1], sensors and actuator [2, 3]. More recently, it has been shown that graphite oxide can be exfoliated in water to yield hydrophilic, oxygenated graphene oxide nanosheets that can be macroscopically assembled into a paper-like structure through vacuum filtration [4]. Some of previous buckypaper research was focused on the effect of CNT morphology on the pore size [5] or its barrier properties [6]. However, there are very few reports on the fabrication of carbon nanotube and graphite or graphene hybrid freestanding sheets and the effect of morphology of CNT or graphite on their mechanical and electrical characteristics.

In this work, freestanding hybrid sheets that are comprised of multiwalled carbon nanotubes (MWNTs) and exfoliated graphite nanoplatelets (xGnPs) with different types of MWNTs and xGnPs were fabricated by vacuum filtration and their unique mechanical and electrical properties were studied.

2 Experimental
2.1 Materials
Exfoliated graphite nanoplatelets with an average size of 5 μm (xGnP M-5) and 15 μm (xGnP M-15) were purchased from XG Sciences (East Lansing, MI). Typical TEM images and SEM images of both surface and cross section of xGnP particles are shown in Fig. 1- (a) and (b).

Fig.1. – Typical SEM and TEM micrographs of the surface and the cross sectional view of xGnPs (a ; M-5, b ; M-15 respectively,) and (c) Raman spectra.
High aspect ratio of the platelet is evidenced by the large lateral dimension of the particle versus the thickness, which is less than 20 nm and 10 nm for xGnP-M-5 and 15, respectively. The Raman spectrum of both xGnP M-5 and M-15 particles are shown in Fig. 1c. The small D band and a sharp G band confirm the sp² type bonding of the carbon atoms in the basal plane. It is thus believed that the intercalation process and subsequent pulverization processes did not oxidize the surface of the xGnP which might degrade the electrical and mechanical properties of an individual platelet. The lengths of CVD grown MWNTs (100nm and 250nm) are indicated in their product names, CM-100 and CM-250, both of which were purchased from Hanwha Nanotech.

2.2 Preparation of MWNT-xGnP Hybrid Sheets

Surfactants of sodium lauryl sulfate (SLS) and Triton X-100 were purchased from Aldrich and Daegung Chemicals, respectively, and solutions were prepared with a concentration of 0.05 wt.% in methyl alcohol. 120mg of MWNTs or xGnP-MWNT mixture with proportions of xGnP versus MWNTs 5:5 with various MWNT and xGnP types were dispersed in 2L of SLS / Triton X-100 solution. After 1 hr of stirring and 3 hrs of sonication in bath type sonicator, the solutions were further treated for 2 hrs using a horn-type sonicator. A nylon membrane (0.45 μm pore size, Millipore) was used for paper making by vacuum filtration. Two liters of the suspension was filtered to make one 78 mm diameter paper. The paper was then washed using methanol and acetone to remove residual surfactants and then placed in an oven and dried at 60°C overnight before being peeled off the membrane.

3 Results and Discussions

3.1 Surface Area and Morphology

It is noted in Fig. 3a that the hybrid sheet is robust under flexural stress, and Fig. 3b and c show basal plane morphology of the CM-250/M-5 hybrid sheet before and after stretching. In Fig. 3c, crack morphology suggests that the surface adhesion between MWNT and xGnP is very strong because of their van der Waals interaction and π-π interaction of sp² carbons.

The surface areas of xGnP measured by BET using N₂ adsorption at 77 K are shown in Table 1. The reported specific surface area (A_BET) of MWNT buckypaper is around 200m²/g [7] and our measurement showed a similar value. From the BET measurement, it is clear that the buckypaper has much higher surface area as compared to hybrid sheets because of its morphology and scale. The measured A_BET’s of xGnP M-5 and M-15 were around 90 m²/g and 70 m²/g, respectively. The A_BET’s of hybrid sheets were in good agreement with the calculated values.

![Fig. 2](image.png)

**Table 1. Specific surface area of buckypapers and hybrid sheets**

<table>
<thead>
<tr>
<th>Sample</th>
<th>A_BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM-250</td>
<td>195.0</td>
</tr>
<tr>
<td>CM-250/M-5</td>
<td>152.2</td>
</tr>
<tr>
<td>CM-250/M-15</td>
<td>139.4</td>
</tr>
<tr>
<td>CM-100</td>
<td>197.2</td>
</tr>
<tr>
<td>CM-100/M-5</td>
<td>148.8</td>
</tr>
<tr>
<td>CM-100/M-15</td>
<td>133.6</td>
</tr>
</tbody>
</table>

3.2 Mechanical Properties

Mechanical properties of buckypapers and hybrid sheets are shown in Fig. 3. Young’s modulus of buckypaper CM-250 was increased by 21% from 513 to 609 MPa with the addition of xGnP M-5, while its tensile strength and elongation were decreased from 21.3 MPa and 6.3% to 14.3 MPa and 3.5%, respectively. Despite the fact that the aspect ratio of xGnP M-15 is much higher than M-5, their efficiency of Young’s modulus enhancement is lower than CM-250/M-5 hybrid sheet (only 2.5%). This trend is also shown in the CM-100/xGnP hybrid sheets.
The Young’s moduli of the porous sheets studied can be considered to be indicative of the packing densities of the carbon nanomaterials sheets. And their strengths and elongations are governed by the interaction of carbon nanoparticles or domains. We can easily imagine from SEM images and BET results that the MWNT bundles exhibit not just strong van der Waals interaction and \( \pi-\pi \) interaction but also mechanical entanglement. This results in the higher strength and elongation of buckypapers as compared to hybrid sheets. Although it is clear that xGnPs are disturb interaction between MWNTs, sonication induced damaged small particle of xGnPs are inserted to free volume of buckypaper, hence increase the occupied volume and modulus.

![Fig. 3. Mechanical properties of xGnP-MWNT hybrid sheet with various type of MWNT and xGnP under tensile stress.](image)

![Fig. 4. Storage moduli of MWNT-xGnP hybrid sheets with frequency.](image)

### 3.3 Dynamic Mechanical Study

When the mechanical properties of a material is based on secondary bonding, such as van der Waals, \( \pi-\pi \) interaction and hydrogen bonding, high frequency vibration is sometimes critical for its elastic properties. Dynamic mechanical analysis (DMA) of buckypaper and hybrid sheet with frequency sweep test is shown in Fig. 4. The strain amplitude was determined in the
range of elastic deformation from the tensile test (20μm for all samples). Both buckypapers showed decrease in elastic factor in high frequency regions. However, addition of xGnP prevents this negative effect to increase elastic performance up to 100Hz of strain frequency. Also their average moduli show the same trend as tensile test. This effect can be very useful when hybrid sheet are applied in a high vibrational environment.

3.4 Volume and Surface Conductivities
In Fig. 5, the same trend of volume and surface resistivities of buckypapers and hybrid sheets were observed. It is easy to explain the difference in the conductivity of buckypapers based on their different lengths, it is easier to form CNT conductive network for CM-250 than CM-100. Also, xGnP exhibits inherently different morphology and lower conductivity than MWNT. This results in increase in volume resistivity of both CM-250 and CM-100 hybrid sheets.

The different resistivity with xGnP type can be explained by its aspect ratio. From Fig. 1- (a) and (b), it is clear that M-15 has higher aspect ratio compared to M-5. This means M-15 is easier to contribute to make conductive network than M-5.

4 Conclusions
xGnPs and MWNTs stabilized by SLS and Triton X-100 were successfully prepared to paper-like structure by vacuum assisted filtration, and their mechanical and electrical properties were studied. Young’s modulus was increased with addition of xGnPs while their ultimate strength and maximum elongation were decreased due to the additive effect of xGnP. With xGnP type, M-5 shows much higher reinforcing effect to modulus as compared to M-15 in both CM-250 and CM-100 hybrid sheets due to their particle size. DMA study revealed that elastic performance of hybrid sheet is maintained in high frequency deformation region, and it can be useful for highly vibrational environment applications. Complex interactive mechanism of MWNT length and aspect ratio of xGnPs affects the conductivities of buckypapers and hybrid sheets, which show the same trend in both volume and surface resistivities.

References