

# Powder Processing and Properties Characterization of Polyamide 11-Graphene Nanocomposites for Selective Laser Sintering

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## Abstract

Nano-graphene platelets (NGPs) were added to polyamide 11 (PA11) powder in 1%, 3%, and 5% weight loading in an attempt to create electrostatic dissipative polymer nanocomposites (PNC) using SLS, a rapid manufacturing process. Powder-powder mixing techniques were explored as a potential replacement for twin-screw extrusion for dispersing nano-graphene platelets (NGPs) within a PA11 matrix. The Resodyn<sup>TM</sup> Resonant Acoustic Mixer as well as the Thinky<sup>TM</sup> mixer were studied as powder-powder mixing techniques. After mixing, the powder samples were pressed into thin-films for characterization on TGA, SEM, four-probe conductivity, and Raman spectroscopy. TGA results indicate a slight decrease in thermal stability with the addition of NGPs. This suggests an inadequate dispersion of NGP within the polymer matrix. SEM images support this hypothesis with evidence of artifacts, a sign of electron charging, as well as clusters of NGPs. The four-probe conductivity measurements indicate that all of the samples studied exceed the sensitivity range of the machines used, which is estimated to be  $4.5 \times 10^{10} \Omega/\square$ . This indicates that all of the samples are at least in the upper region of the range for electrostatic dissipation, if not out of it entirely. Further research will include twin-screw extrusion as well as surface functionalization of NGPs for better dispersion.

## Introduction

Nanocomposites extend the paradigm of traditional composite materials by introducing fillers in the nano-scale to ceramic, metal, or polymer matrices. Polymer nanocomposites (PNCs) is a developing field in which nanofillers are introduced to polymer matrices to produce materials with improved properties and even novel characteristics. This PNC field has generated a lot of interest due to significantly improved mechanical, thermal, electrical, and barrier properties, even at low filler contents [1,2]. Of the properties that can typically be improved, electrical conductivity is one of the most desirable. Generally, by introducing carbon-based fillers such as graphite, carbon black, carbon nanotubes, and graphene, electrical conductivity in the range of electrostatic dissipation (ESD) or higher can be achieved. The minimum weight loading of nanofiller that is needed to induce this conductivity in the insulative polymer matrix is known as the percolation threshold. In order to achieve the percolation threshold, a network of conductive filler is needed, and this depends largely on the filler properties, polymer matrix properties, and processing techniques and parameters [3,4].

Among the available processing techniques for polymer nanocomposites, it has been recently demonstrated by Das, et al. that selective laser sintering (SLS) can help to lower the percolation threshold by preserving conductive filler networks [5]. However, the process of SLS requires a large amount of powder mixture. In order to determine the working parameters for making fully dense parts of novel materials such as polymer nanocomposites, a lot of process formulation needs to take place. Therefore, a suitable mixing procedure for dispersing the nanofiller within the polymer matrix must be determined first before any work can be done on the SLS. Twin-screw extrusion has been shown to provide enough shear forces to break apart and exfoliate the nano-graphene platelets (NGP), which induces good dispersion within the polymer matrix. However, SLS is a powder process; so in order to use twin-screw extruded nanocomposites for SLS, cryogenic grinding must be performed to process the PNC into powder. This is an extra step, and it can often prove to be costly and time consuming. Therefore, for this research, we explore the use of powder mixing techniques to disperse NGP in polyamide 11 (PA11).

## **Materials**

xGnP<sup>®</sup> nano-graphene platelets (NGP) were obtained from XG Sciences, Inc., which is a company based in East Lansing, Michigan. The individual platelets range from 5 microns to 25+ microns in diameter [6]. However, the company ships the product in millimeter-size clusters due to certain concerns with the health effects of inhaling nano-sized particles. It is not an area that is well studied, so companies and individuals are taking caution. Neat PA11 powder was obtained from Arkema, a chemicals company in France. Polyamide 11 was chosen for its good material properties, popularity in industry, and ease of use for SLS.

## **Experimental**

### *Materials Preparation and Processing*

The Resodyn<sup>™</sup> acoustic mixer (RAM) was the first method used to mix the PA11 and nano-graphene. The mixer has three options: intensity (Gs), mixing time, and frequency (Hz). The frequency setting was set on “auto,” which automatically adjusts the frequency to the natural frequency of the sample. The intensity setting was adjusted from 70% maximum to 90% maximum at the same mixing times to study the effects of changing intensity on mixing. Via visual inspection, the different mixing intensities showed no difference in the sample dispersion. By inspection under the fume hood, the samples all had large clusters of nano-graphene still present. This seems to be independent of filler amount, mixing time, intensity, and frequency. This observation suggests that the RAM is unable to break down and shear the as-received nanoparticles into nano-size.

To resolve this issue, zirconia grinding media (3 mm in diameter) were inserted into the sample containers to assist in breaking down the clusters. Through trial and error, the best mixing condition was found to be 90% intensity for 9 minutes. By visual inspection, the mixture

shows good dispersion. The color of the mixture changed from white powder to a consistent grey-black in color.

The Thinky™ mixer (model ARV-310) was another method chosen to mix the nanocomposite in powder form. The machine is made by a company based in Japan. It utilizes both rotating and revolving motion to aid in the mixing. The powder container, once inside the machine, revolves around both the central axis of the machine as well as the central axis of the container itself. This was also aided by the addition of zirconia grinding media (10 mm in diameter). The mixture was rotated at 2000 rpm in 10 series, with 15 seconds per series.

The mixed samples were then pressed into thin-films using a hydraulic heat press. Roughly 11.5 mL (0.7 in<sup>3</sup>) of powder was placed in a folded sheet of aluminum foil with a coating of silicon release spray. Aluminum plates were also used to aid in the pressing. The temperature was set to 204°C, which is just above the melting temperature of PA11 listed as 183°C - 190°C by Arkema [7]. In order to make void-free films, the samples were first pressed at roughly 100 psi for 1 minute. Then the pressure was released for several seconds. Finally, the samples were re-introduced to roughly 100 psi for 5-6 minutes.

#### *Characterization of Pressed Films*

Approximately 0.26 mm thick pieces of the pressed films, weighing roughly 5 mg, were cut for use in thermogravimetric analysis (TGA), which is a method for characterizing the thermal stability of materials. The samples were heated at 10°C/min and 20°C/min from 40°C to 600°C in nitrogen gas.

In order to further study the state of exfoliation and dispersion of NGPs within the PA11, scanning electron microscopy (SEM) was conducted. First, a stress concentration was introduced to the film samples. Second, the samples were ripped along their cross sections. Finally, images of the samples were taken at their fractured cross sections in order to study the relatively undisturbed microstructure of the nanocomposite. No conductive coating was used for the SEM images.

In addition to TGA and SEM characterization, standard four-probe conductivity was measured to determine the sheet resistivity of the samples. Four probes were placed in-line, with the outer probes connected to the current source provided by Keithley (model 6221 DC and AC current source) and ground. The inner probes were connected to Keithley (model 6514 system electrometer). This allows for a highly accurate assessment of the sheet resistivity of the samples. The estimated maximum sensitivity for this test is  $4.5 \times 10^{10} \Omega/\square$ .

Finally, Raman spectroscopy was conducted to further study the state of exfoliation and dispersion of the nano-graphene platelets. Both point readings and scans were performed using the Raman laser. However, the laser burned through the polymer during the scans, which required a long time to conduct due to large background noise. Therefore, only the initial data acquired during the scans are accurate. This will be discussed in detail under results and discussion.

## Results and Discussion

### *Thermogravimetric Analysis*

Upon inspection of the TGA data as shown in Figures 1-4, there is no discernable trend with the addition of NGPs on the thermal stability of the overall nanocomposite with the Thinky mixing method. The 3wt% RAM samples experienced errors during the TGA run, and their results are not presented here. However, the overall trend of the thermal stability can be adequately illustrated by the 1wt% and 5wt% sample curves. The TGA results of the RAM samples seem to show that the thermal stability is actually decreasing. However, it is highly unlikely that NGPs do not improve the thermal stability of PA11, as NGPs have been demonstrated to achieve significant thermal stability improvements in polymer matrices in the past [8-10]. Therefore, it is probable that the NGPs in this case are not well exfoliated or well dispersed within the polymer matrix. Also, the zirconia grinding media introduced during processing may have pulverized the NGP clusters and reduced their aspect ratio, which would decrease their effectiveness.

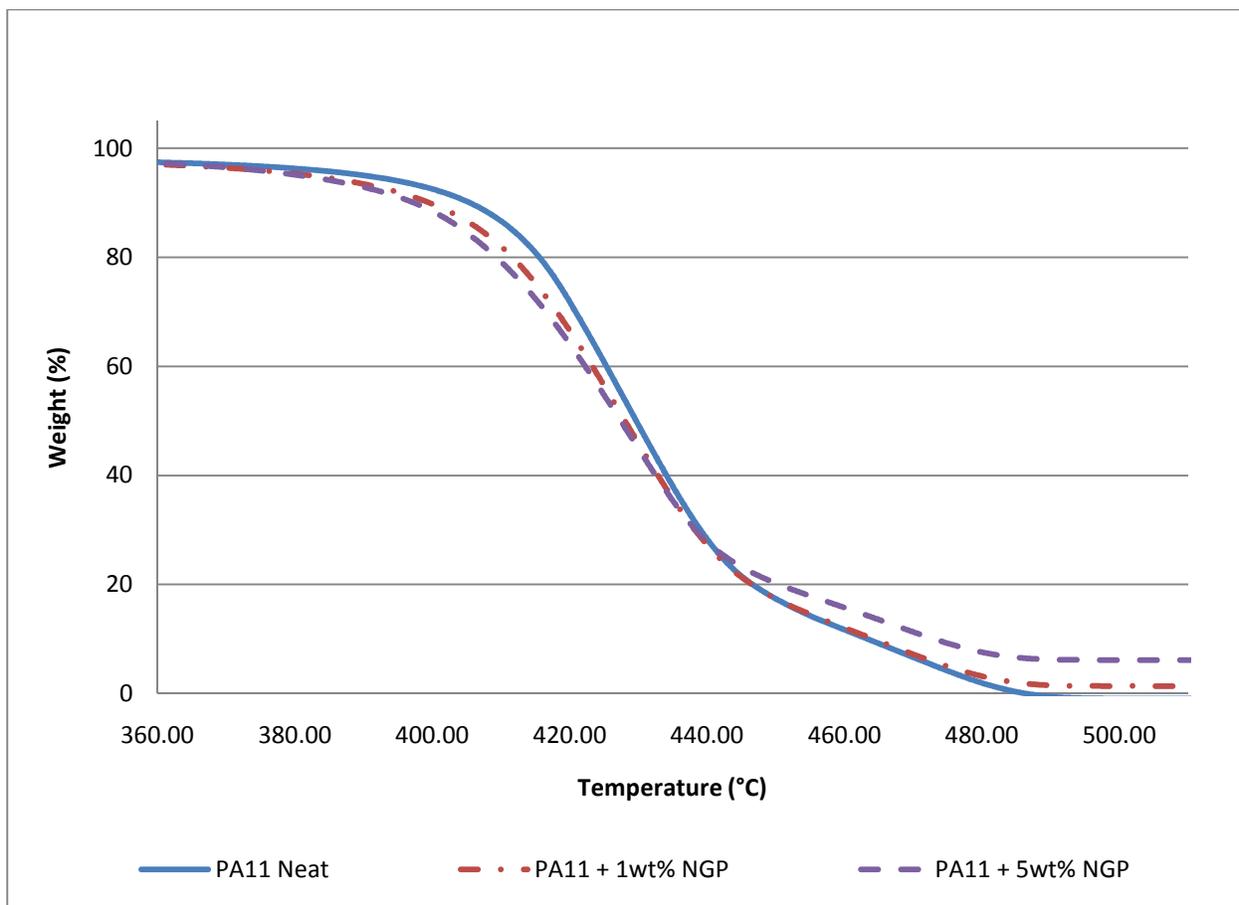


Figure 1: TGA results of RAM samples heated at 10°C/min in nitrogen

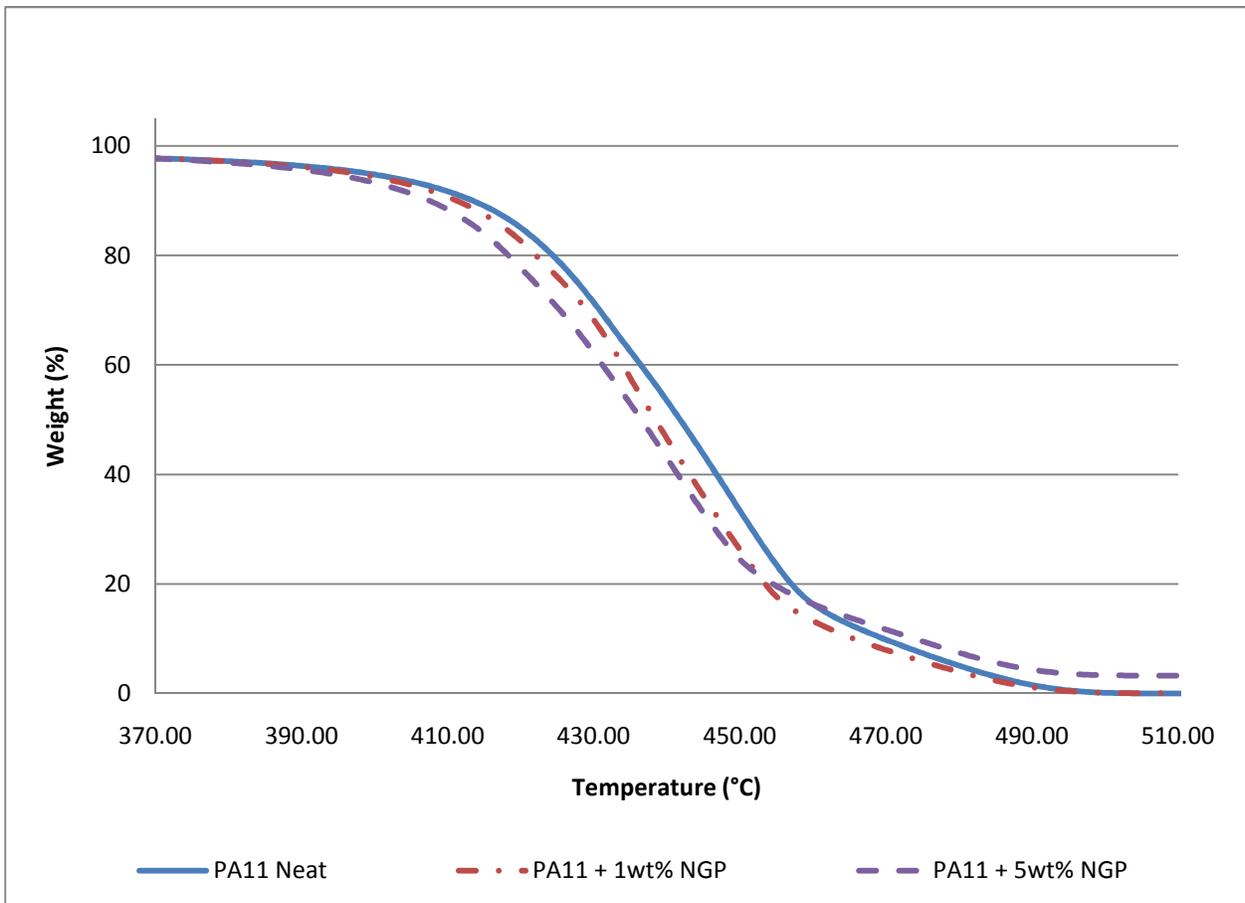


Figure 2: TGA results of RAM samples heated at 20°C/min in nitrogen

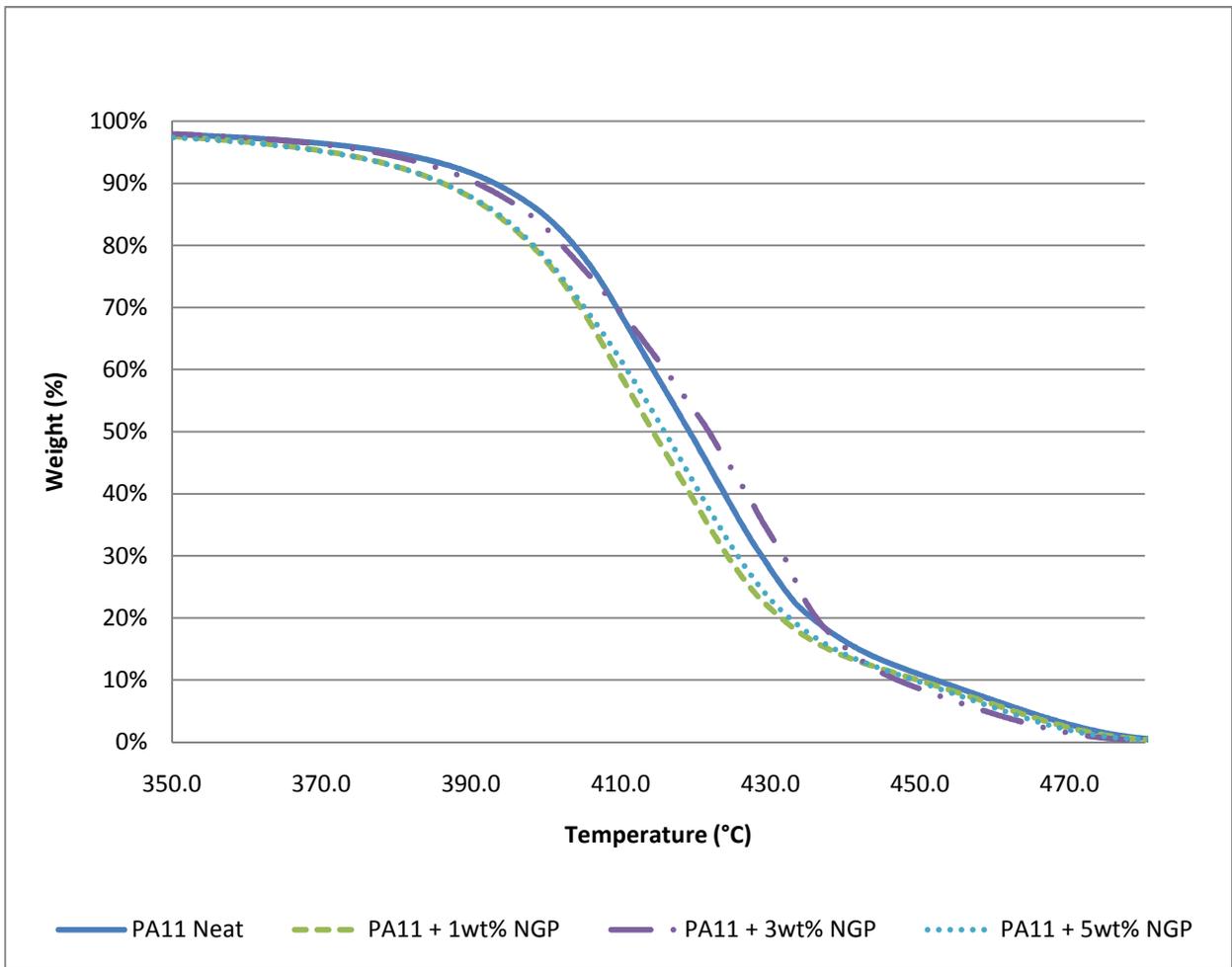


Figure 3: TGA results of Thinky samples heated at 10°C/min in nitrogen

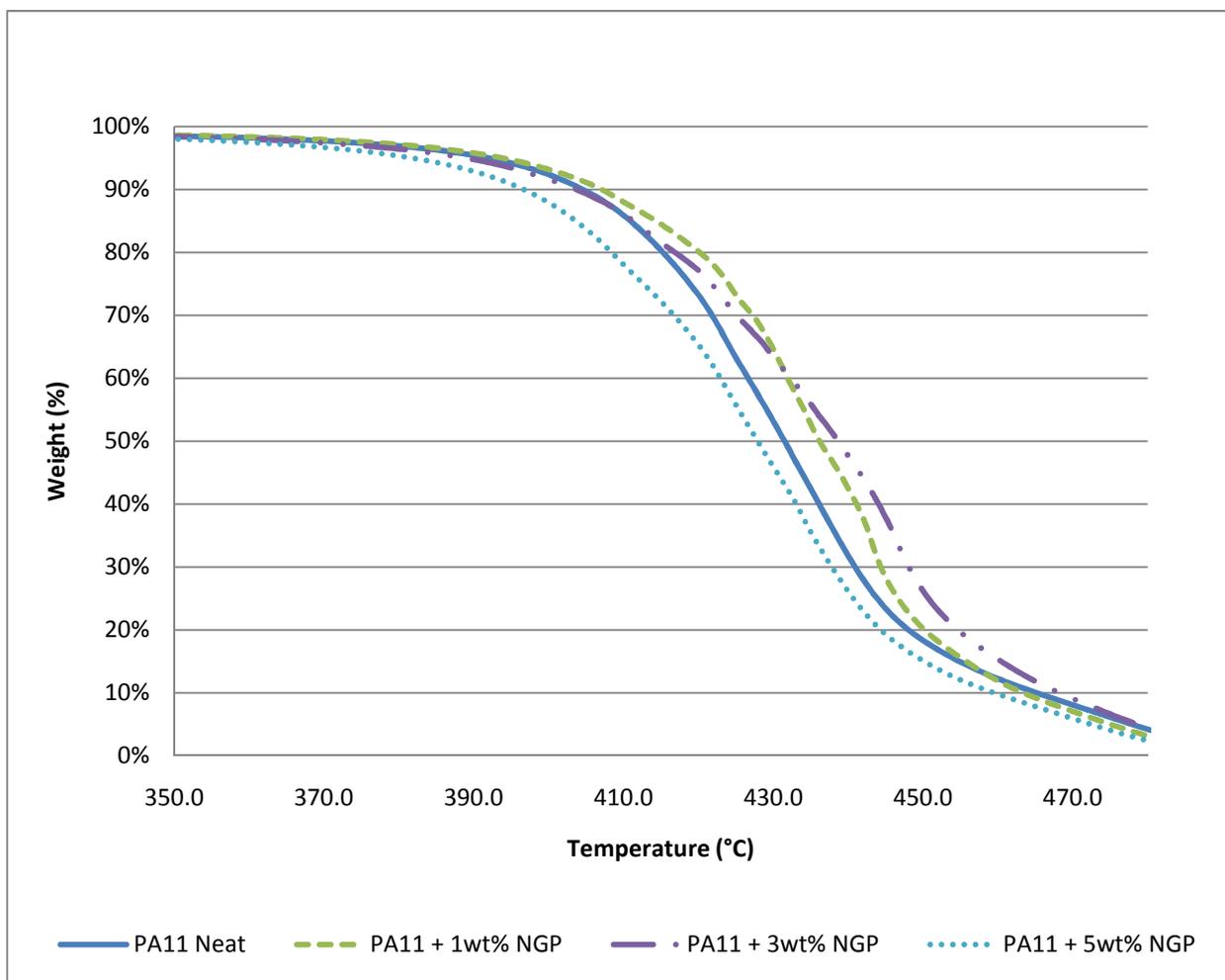


Figure 4: TGA results of Thinky samples heated at 20°C/min in nitrogen

### Scanning Electron Microscopy

In order to facilitate the morphological analysis, an SEM image of the NGP used in this research is shown in Figure 5, which depicts the NGP obtained from XG Sciences with a plate-like, flake-like morphology. This is as expected for nano-graphene, as it is essentially a two dimensional plane of covalently bonded carbon atoms arranged in a hexagonal pattern. Notice also that the image has a relatively constant contrast throughout. As SEM images determine contrast through various factors such as topology, and relative conductivity, this indicates that the NGPs in the image have very flat surfaces, and also have relatively the same conductivity values. This image will serve as a guide for analyzing the other SEM images and finding similar morphologies.

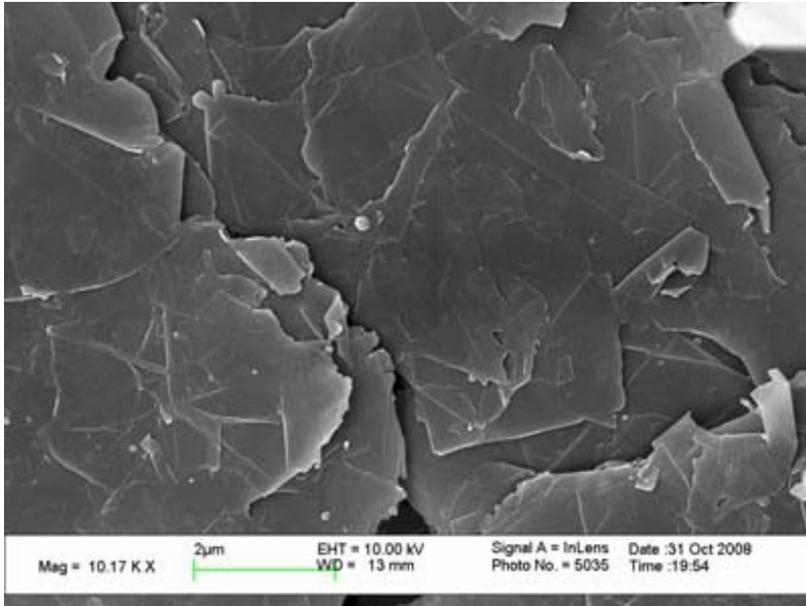


Figure 5: SEM image of NGPs obtained from XG Sciences

Figure 6 shows the cross-section of the 3wt% Thinky sample. Notice the artifacts of bright lines across the image. This is the result of a phenomenon known as charging. Scanning electron microscopy requires samples to be conductive for good images. Samples “charge” when they are not quite conductive enough to dissipate the excess electrons from the electron beam. Charging, and the manifestation of artifacts in the images, is another indication that the samples are not well mixed. Again, it is unlikely that the NGPs do not improve the conductivity of PA11, as conductive polymer nanocomposites with a low percolation threshold have been demonstrated by XG Sciences using their NGP and nylon 66 [11,12].

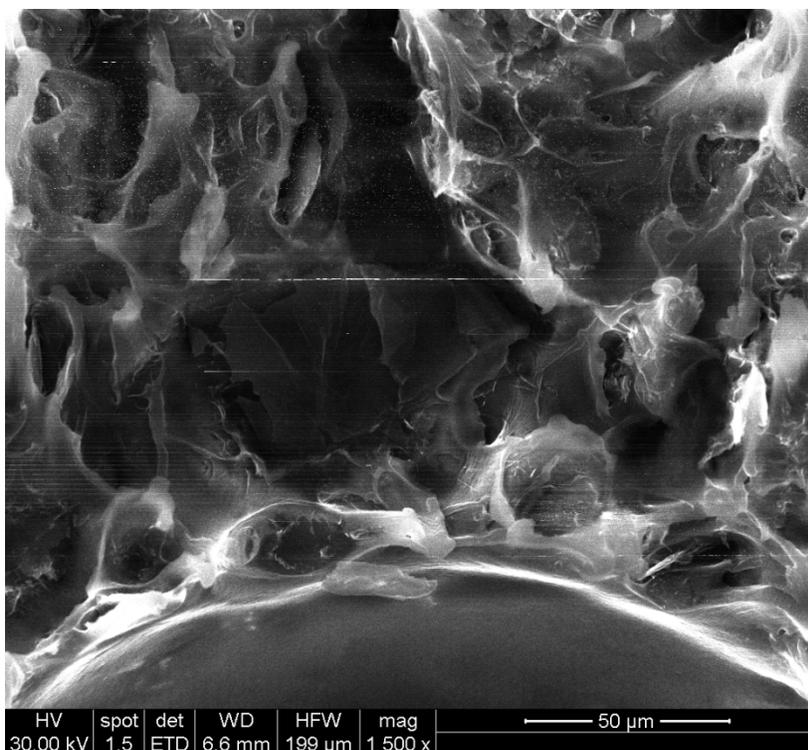


Figure 6: PA11 + 3wt% NGP mixed via Thinky

As mentioned earlier, SEM determines image contrast via topology and relative conductivity, among other factors. Therefore, we can deduce that the brighter, lighter areas in the images represent areas dominated by PA11, and the darker, more conductive areas represent areas consisting mainly of NGP. If we zoom in on the darker area depicted in Figure 6, we can observe, in Figure 7, a very similar morphology to that depicted in Figure 5 for neat NGP. Applying this idea to the other samples, we notice the same phenomena. The 5wt% Thinky sample illustrates this well, as the charging effect was less severe. Figures 8-10 depict this idea for the 5wt% sample. Figure 8 shows the overall cross-section. There are very noticeable dark areas within this mesh of bright polymer areas. If we zoom in on one of these darker areas, we can see, in Figure 9, the same plate-like morphology of NGP. Similarly, if we zoom in on one of these brighter areas, Figure 10, we can see the strand-like morphology of molten polymer. These images provide a very good indication that the exfoliation and dispersion of these NGPs is inadequate to enhance the electrical conductivity and thermal stability properties.

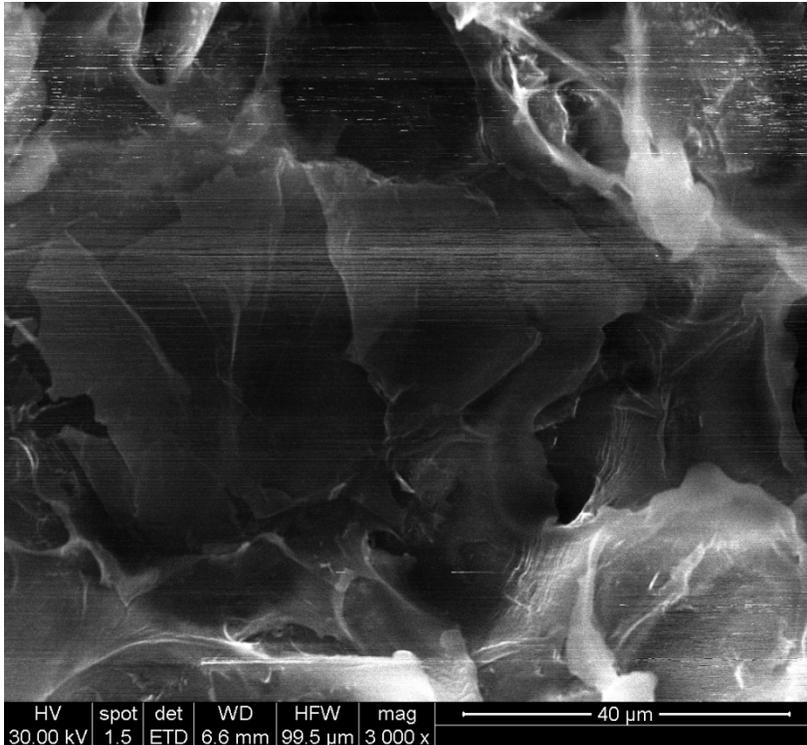


Figure 7: PA11 + 3wt% NGP mixed via Thinky (higher magnification)

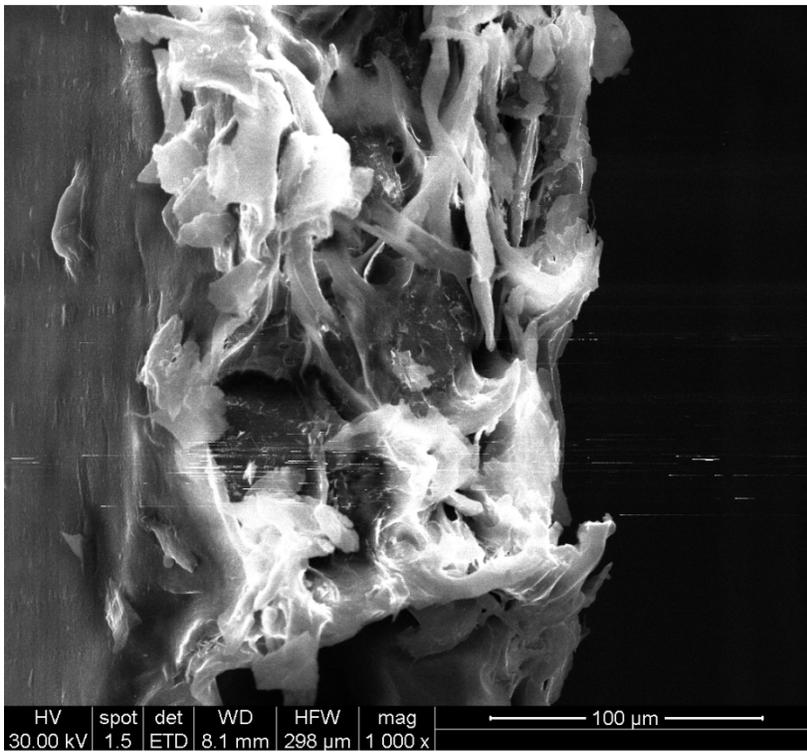


Figure 8: PA11 + 5wt% NGP mixed via Thinky

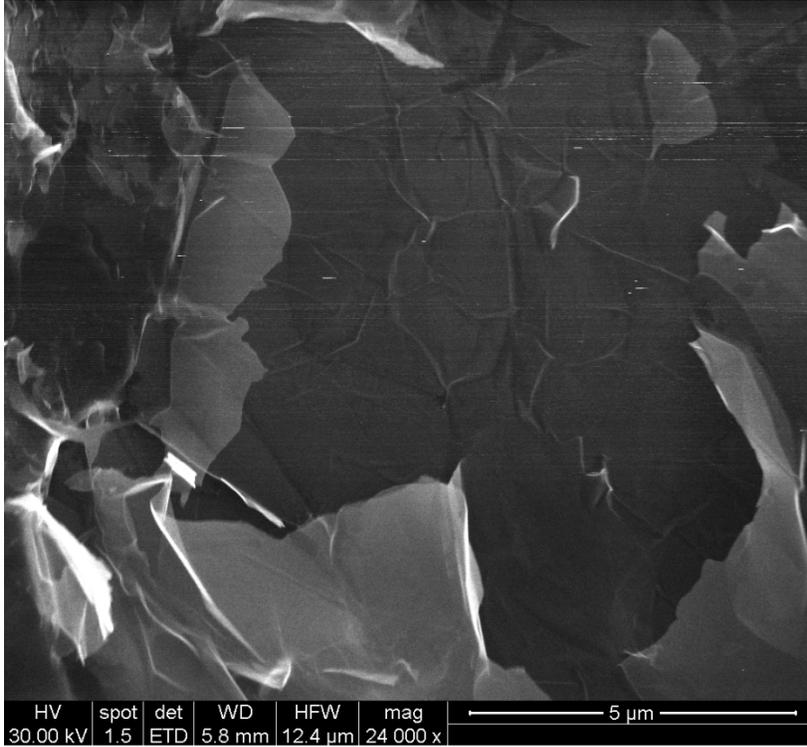


Figure 9: PA11 + 5wt% NGP mixed via Thinky (higher magnification - NGP rich area)

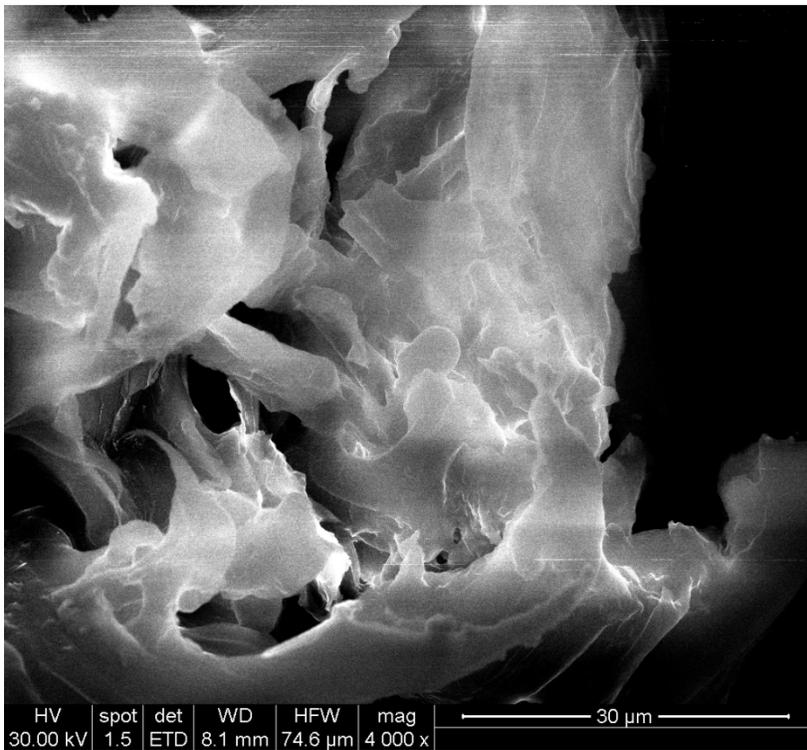


Figure 10: PA11 + 5wt% NGP (higher magnification - resin rich area)

### *Electrical Conductivity*

In addition to TGA and SEM characterization, standard four-probe conductivity was conducted to determine the sheet resistivity of the samples. Four probes were placed in-line, with the outer probes connected to the current source provided by Keithley (model 6221 DC and AC current source) and ground. The inner probes were connected to Keithley (model 6514 system electrometer). This allows for a highly accurate assessment of the sheet resistivity of the samples. The estimated maximum sensitivity for this test is  $4.5 \times 10^{10} \Omega/\square$ . Unfortunately, all of the nanocomposite samples exceeded this machine sensitivity range. Therefore, their estimated sheet resistances are greater than  $4.5 \times 10^{10} \Omega/\square$ , which is in the upper region of the range defined for electrostatic dissipative polymers,  $10^5$  to  $10^{12} \Omega/\square$  [13,14]. The insulative properties of the polymer dominate these samples, again indicating inadequate exfoliation and dispersion of the NGP.

### *Raman Spectroscopy*

Figure 11 illustrates the Raman spectra result for the 5wt% RAM sample taken from the scan. The spectrum presented in red (the top spectrum) was taken at an area on the 5wt% RAM sample rich in NGP. It can be seen by the parabolic shape of the curve that there is a lot of background noise. This is most likely due to the backscattering that resulted as the sample was being burned by the laser and the topography changes, which affected the laser focus. The peak at around  $1580 \text{ cm}^{-1}$  corresponds to the G-band of graphene, and the band at around  $1350 \text{ cm}^{-1}$  corresponds to the D-band, or defect band of graphene. This is consistent with previous research [15]. The NGPs from XG Sciences also has a small intensity Raman band near  $2700 \text{ cm}^{-1}$  [6]. This is most likely the result of the residual oxygen from chemical reduction of the nanographene. This band overlaps with a portion of the Raman spectrum assumed to be the PA11. The spectrum in blue (bottom spectrum) represents an area on the 5wt% RAM sample that is resin rich. The G-band is noticeably smaller, and there are the characteristic multi-peaks of polyamide 11.

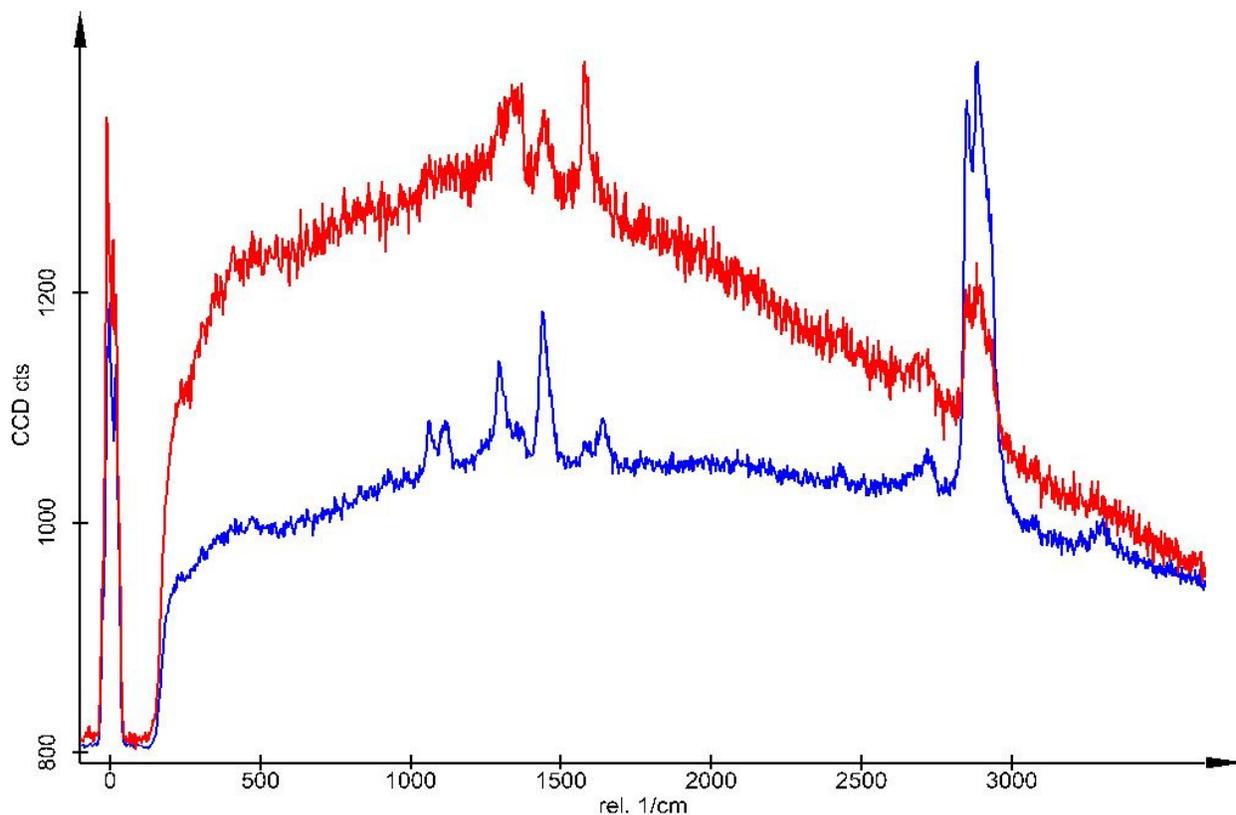


Figure 11: Raman spectra of 5wt% NGP mixed via RAM (red/top – NGP rich area, blue/bottom – resin rich area)

Figure 12 illustrates a comparison between a point spectrum taken at a much higher integration time on the 5wt% Thinky sample (blue/bottom) and the spectrum resulting from the scan of the 5wt% RAM sample on a resin rich area (red/top). Due to the longer integration time, there is much less background noise. A longer integration time was not possible for the scan because it would mean that the sample would be allowed more time to burn. The spectrum shown in blue (bottom spectrum) in Figure 12 was taken in an area determined via microscopy to be very deficient in NGP. It shows very small peaks at  $1580\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$ . By comparison, the spectra are very similar. The major difference seems to be the higher background noise and slightly higher peaks at  $1580\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$  for the RAM sample. Overall, the Raman spectra for these samples demonstrated good repeatability. Point spectra were performed without many issues, but scans proved to be difficult due to sample burning.

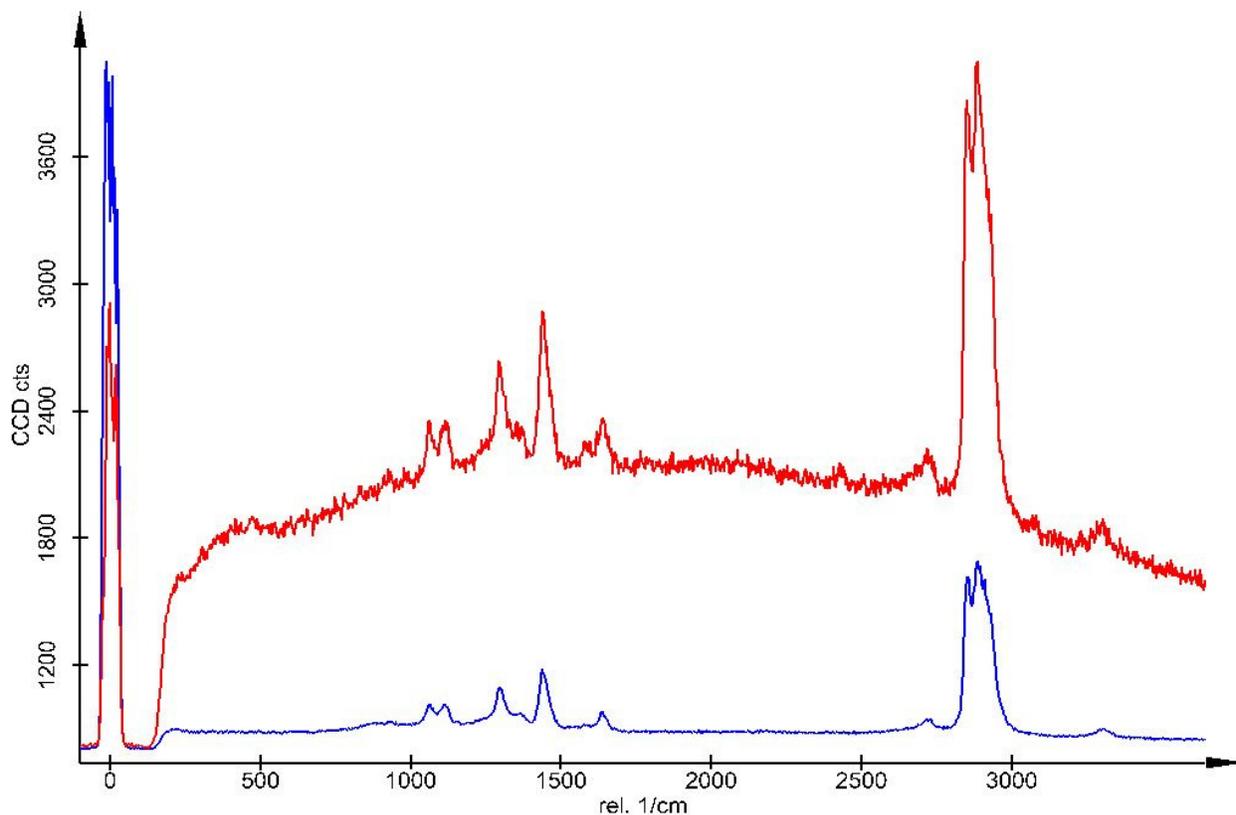


Figure 12: Comparison of Raman scan of 5wt% RAM at resin rich area (red/top) with point spectrum of 5wt% Thinky at resin rich area with longer integration time (blue/bottom)

Figure 13 depicts a Raman scan performed on the 5wt% RAM sample. It essentially takes many point readings looking for the peaks at  $1580\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$  and plots them on a relative intensity image. The brighter areas indicate the areas that have higher concentrations of graphene. However, as discussed earlier, the sample was burned by the laser during scanning. Therefore, only the area near the top of the scan was accurate. Even so, there is clearly a large cluster of NGP as indicated by the bright spot on the top-left of the scan. Moreover, it is relatively isolated, as its surroundings are largely resin rich. More scans are needed, but preliminary results seem to reinforce the idea that the exfoliation and dispersion of nanographene platelets within PA11 is not ideal.

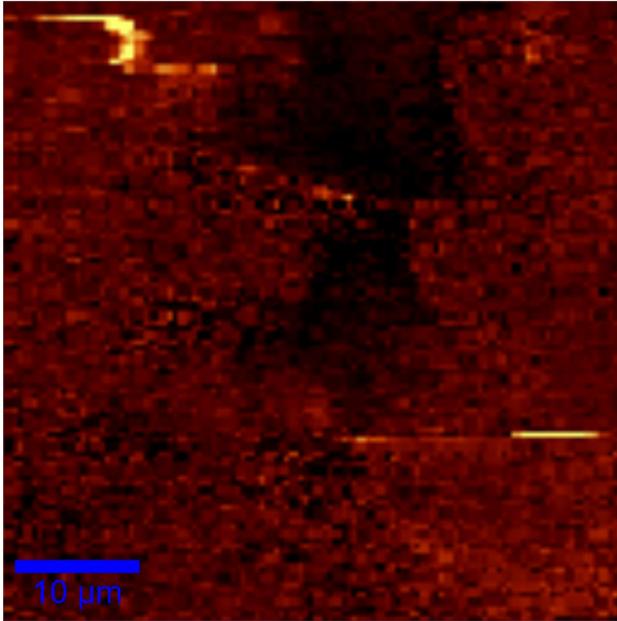


Figure 13: Relative intensity image of Raman scan for G-band (1580 cm<sup>-1</sup>) and D-band (1350 cm<sup>-1</sup>)

### Conclusion and Future Research

Polymer nanocomposites of PA11 and nano-graphene platelets were mixed using powder mixing techniques. The Resodyn<sup>TM</sup> resonant acoustic mixer and Thinky mixer were used with the addition of zirconia grinding media to aid in the breaking and exfoliation of graphene clusters. The samples were characterized via TGA, SEM, four-probe conductivity, and Raman spectroscopy. The results indicate convincingly that the state of exfoliation and dispersion of the NGP within the PA11 matrix is inadequate for improvements in thermal stability and electrical conductivity. The nano-graphene platelets require a larger amount of shear forces in order to properly exfoliate. In future research, we will focus on chemical processes for exfoliation using solvents as well as using twin-screw extrusion plus cryogenic grinding.

### Acknowledgements

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