Determining the level and location of functional groups on few-layer graphene and their effect on the mechanical properties of nanocomposites

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ABSTRACT  
Graphene is a highly desirable material for a variety of applications, in the case of nanocomposites, it can be functionalized and added as a nanofiller to alter the ultimate product properties, such as tensile strength. However, often the material properties of the functionalized graphene and the location of any chemical species, attached via different functionalization processes, are not known. Thus, it is not necessarily understood why improvements in product performance are achieved, which hinders the rate of product development. Here, a commercially-available powder containing few-layer graphene (FLG) flakes is characterized before and after plasma or chemical functionalization with either nitrogen or oxygen species. A range of measurement techniques, including tip-enhanced Raman spectroscopy (TERS), time of flight secondary ion mass spectrometry (ToF-SIMS) and NanoSIMS, were used to examine the physical and chemical changes in the FLG material at both the micro- and nanoscale. This is the first reported TERS imaging of commercially-available FLG flakes of sub-micron lateral size, revealing the location of the defects (edge versus basal plane) and variations in the level of functionalization. Graphene-polymer composites were then produced and the dispersion of the graphitic material in the matrix was visualized using ToF-SIMS. Finally, mechanical testing of the composites demonstrated that the final product performance could be enhanced, but differed depending on the properties of the original graphitic material.

KEYWORDS (5-7)

graphene, commercial, functionalization, composites, characterization, defects, tip-enhanced Raman spectroscopy.

Graphene is a nanomaterial with disruptive potential in many technological areas, such as coatings1,2, flexible electronics3–5 and nanocomposites,6–10 due to its high tensile strength,11 optical transparency12,13 and electrical14,15 and thermal conductivity.16 Some applications of graphene need further research and development to demonstrate their commercial viability, while other applications such as nanocomposites are already in production.17,18 Graphene flakes in a powder form can be produced via many different top-down methods, such as liquid phase exfoliation,19–22 roll milling,23,24 ball milling,25,26 electrochemical exfoliation27,28 and chemical exfoliation.29,30 The resulting material can then be used as-produced or can undergo another processing step to add chemical groups in order to tune the material properties.31–33

However, it is crucial to understand the detailed chemical and physical properties of the graphene flakes if they are to be used in real-world applications, so as to determine how the final product performance is affected by the original material properties. Thus, it is important to determine whether the functionalization process is successful and where the functional groups are located on the graphitic flakes. This will aid industry to optimize the production of the desired material, with the appropriate level of functionalization for the required application. For mechanical improvement of nanocomposites, the level of functionalization is expected to alter the level of agglomeration of graphitic material in a matrix, where a high level of agglomeration could limit the mechanical properties.34 While functionalization is expected to improve the dispersion and interfacial shear strength, too much functionalization on the basal plane could reduce the high tensile strength of graphene and thus the composite.35–37

In this study, a range of techniques were used to extensively characterize a commercially-available graphitic powder containing few-layer graphene flakes (FLG) at the macroscale, microscale and nanoscale. This powder has been functionalized by plasma or chemical processes, with the aim to add either oxide (O) or amine (NH3) functional groups via each process, resulting in four different industrially-relevant functionalized samples, as outlined in the methods section. It is expected that the plasma and chemical processes will provide different levels of functionalization, while the oxide and amine functional groups will provide different chemical properties for dispersion in a polymer. In turn, these will result in different mechanical properties of the final composite. It is shown that the lateral size range of the flakes is consistent before and after these four methods of functionalization, based on images produced using scanning electron microscopy (SEM), suggesting any changes in mechanical properties are not due to the size of the flakes. The bulk material was characterized using confocal Raman spectroscopy to determine the overall level of disorder, that is, the presence of defects in the graphitic lattice, by calculating the intensity ratio of the Raman D- and G-peaks (*I*D/*I*G) and the full width at half maximum of the D-peak (FWHM[D]).38–41 The elemental composition of the materials was then determined using X-ray photoelectron spectroscopy (XPS) to confirm the presence of the expected elements before and after functionalization.

Tip-enhanced Raman spectroscopy (TERS) measurements were performed on individual flakes from the samples with different functionalization processes to investigate changes and variations in the location of defects at the nanoscale.42,43 While the ability of TERS to map point defects within mechanically-exfoliated single layers of graphene has been demonstrated before,42 no study has been carried out on commercially-available graphene typically used in industry. In this particular case, the FLG powders are used for mechanical reinforcement, therefore, the powders were also dispersed in polymers for mechanical testing to examine changes in material performance under stress and strain. Time of flight secondary ion mass spectrometry (ToF-SIMS) measurements were able to show changes in the distribution of the graphitic powder in the composite materials at the microscale.44

RESULTS AND DISCUSSION

Representative SEM images of the unfunctionalized samples are shown in Figure 1a and 1b, at two different magnifications (×10,000 and ×50,000). SEM images of the functionalized material in Figure S1 qualitatively show that there is consistency in the lateral size of the flakes across all the samples. Within any one sample, a range of lateral sizes are apparent, ranging from below 1 μm up to approximately 3 μm in size.



**Figure 1.** SEM images of the unfunctionalized material at (a) × 10,000 magnification and (b) × 50,000 magnification. (c) Average Raman spectra of the unfunctionalized (unfunc), chemically functionalized amine (chem-N) and oxide (chem-O), and plasma functionalized amine (plasma-N) and oxide (plasma-O) samples, with the D-, D’-, G- and 2D-peaks labelled, (d) FWHM[D] and *I*D/*I*G for each of the 5 samples shown in (c).

Confocal Raman spectroscopy can be used to determine the overall level of disorder within graphene.45–47 In graphitic samples, FWHM[D] increases with an increasing level of disorder in the material i.e. with a greater defect density.38,48 Similarly, the *I*D/*I*G ratio indicates the level of disorder, including point defects and edge defects.49,50 In this case, the higher the value of *I*D/*I*G, the more defective the sample as SEM confirms no change in the lateral size. The graph in Figure 1c displays the average Raman spectra for the bulk powders containing FLG. Small changes are visible in the Raman spectra between different types of functionalization (Figure 1d). The spectra vary across each sample (error bars show standard deviation), however the average values indicate a higher *I*D/*I*G and a higher FWHM[D] for the two different plasma-functionalized samples, suggesting a higher level of disorder for these two materials. Figure 1d indicates a similar FWHM[D] and *I*D/*I*G for the unfunctionalized (labelled as ‘unfunc’) and chemically functionalized flakes. Additional results from the Raman spectroscopy analysis can be found in Table S1.

XPS is a technique that can be used to identify the elemental composition of a sample as well as gain information about the bonding environment of the elements. In this case, the variation in functionalization is expected to be due to the addition of nitrogen and oxygen. 3-aminopropyltriethoxysilane (APTES, C9H23NO3Si) was used in the amine chemical functionalization process (labelled as ‘chem-N’) and therefore the addition of three oxygen atoms per nitrogen atom was anticipated. A nitric acid and sulfuric acid treatment was used for the oxide chemical functionalization (‘chem-O’) sample. Allylamine (C3H7N) was used in the nitrogen plasma functionalization process (‘plasma-N’) and acrylic acid (C3H4O2) was used for the oxide plasma functionalization (‘plasma-O’) process. By comparing the nitrogen and oxygen levels in the different materials, an estimate of the success of the functionalization process can be made and compared to the change in the level of disorder observed in the Raman spectra.



**Figure 2.** XPS of the functionalized and unfunctionalized materials, showing (a) the carbon 1s peak normalized to the maximum intensity, (b) oxygen 1s peak and (c) nitrogen 1s peak from each sample. In (a-c) the plasma-O and plasma-N spectra are offset as a visual aid. The concentrations (atomic %) of carbon, oxygen and nitrogen in each sample (d-f), are calculated from the XPS survey spectra.

The carbon 1s spectra from XPS of pressed pellets of the various powders in Figure 2a shows a slight increase in the intensity around 285.5 eV for the functionalized samples compared to the unfunctionalized (black line) sample. This is suspected to be due to an increase in C–­OH ­­­bonds leading to an associated C 1s peak.51 The spectra are normalized to the maximum intensity to aid comparison of the spectra in this region. The oxygen 1s spectra in Figure 2b (in this case showing the raw intensity to allow comparison of the concentration of oxygen present) shows an increase in the level of oxygen for the functionalized samples compared to the unfunctionalized material, with the highest level of oxygen found for plasma-N. The plasma-N and chem-N samples show a clear nitrogen peak in Figure 2c, while there are only trace amounts of nitrogen detected for the other samples, as expected. The plasma-O and plasma-N spectra in Figure 2a, 2b and 2c are offset as a visual aid.

The concentration of carbon, oxygen and nitrogen within each sample can be calculated from the XPS survey spectra (Figure S2). The results of these calculations are shown in Figure 2d-f. As expected, the carbon concentration shows that the unfunctionalized material has the highest concentration of carbon, at ~98.4%.The oxygen concentration in Figure 2e suggests that the plasma functionalized samples result in the highest concentration of oxygen, with ~4.8 at% for plasma-N compared to ~3.3 at% for chem-N and ~3.7 at% for plasma-O compared to ~2.6 at% for chem-O. The nitrogen functionalized samples have a higher concentration of oxygen than the oxide functionalized samples. This is most likely due to the process for functionalizing the flakes with nitrogen. The chemical process involved APTES, which contains oxygen and silicon, however no silicon was detected in the XPS spectra. This could be because the silicon signal is too low to be detected by XPS (< 0.1 at%).52 Due to the increased sensitivity of the ToF-SIMS technique, a silicon signal was detected in the ToF-SIMS spectra from the chem-N sample, at a level significantly greater than for the other materials (Figure S3). Meanwhile, for the plasma-N sample, the plasma-functionalization process is expected to introduce oxygen species due to free radical sites reacting with atmospheric oxygen and water.53 As expected, the nitrogen functionalized samples have the highest nitrogen concentrations, with around 1 at% of nitrogen, while the other samples have below 0.25 at% of nitrogen (Figure 2f), consistent with the presence of trace amounts of nitrogen at the surface of the sample due to atmospheric exposure of the samples prior to measurement, and which is at the detection limit for nitrogen in a carbon matrix (0.3 at%).52 The comparisons between the chemical and plasma functionalization samples in Figure 2 support the confocal Raman spectroscopy data in Figure 1d.

ToF-SIMS images of the unfunctionalized material (Figure 3a), plasma-O (Figure 3b), plasma-N (Figure 3c) and chem-N (Figure 3d) after pressing into pellets, show the CN- ion signal with the same intensity scale. This confirms the presence of CN- in the nitrogen functionalized samples, with very little detected in the plasma-O and chem-O (Figure S4) samples as expected, consistent with the XPS data in Figure 2f. Additionally, the plasma-N sample in Figure 3c has a higher CN- signal than the chem-N sample in Figure 3d, also consistent with the XPS data in Figure 2f and the higher level of disorder observed in the plasma functionalized samples from the confocal Raman spectroscopy results in Figure 1d.

In order to confirm that the increased CN- signal was due to the flakes themselves and not from other sources within the sample, NanoSIMS imaging, which has a lateral resolution of typically <50 nm, was performed on individual flakes, rather than a pressed pellet. The NanoSIMS images show the CN/C2 ratio from an unfunctionalized flake (Figure 3e) and plasma-N flake (Figure 3f). These reveal a much greater CN- signal for the functionalized flake, indicating that the CN- ion signal measured using ToF-SIMS is due to the presence of functional groups on the flakes themselves. The spatial correlation between the signals in the NanoSIMS images (shown in Figure 3e and 3f) and the graphitic material is confirmed by the topography of the same features measured using tapping-mode AFM, shown in Figure S5.



**Figure 3.** ToF-SIMS images of the CN- ion signal in (a) the unfunctionalized, (b) plasma-O, (c) plasma-N and (d) chem-N materials in pellet form. NanoSIMS CN/C2 ratio images of (e) an unfunctionalized flake and (f) a plasma-N flake.

A high-resolution Raman spectroscopy image can be obtained using TERS, providing more detailed information about the location of functional groups, observed as defects. TERS combines the high spatial resolution of AFM and high chemical sensitivity of surface-enhanced Raman spectroscopy (SERS) to provide molecular information at the nanoscale.54–57 When metal nanoparticles are placed in the electromagnetic (EM) field of a laser, their conduction band electrons start oscillating with the frequency of the incident laser, which is referred to as a localized surface plasmon (LSP).58,59 Resonant excitation of LSPs with a matched wavelength results in localized surface plasmon resonance (LSPR) enhancing the intensity of EM field at the nanoparticle surface by several orders of magnitude.60,61 In TERS, the phenomenon of LSPR is utilized to produce a highly intense and confined EM field (also called near‑field) at the apex of a metallic scanning probe microscopy (SPM) probe placed in the focal spot of the excitation laser of a Raman microscope,57,62 which simultaneously improves the sensitivity of Raman microscopy and pushes its spatial resolution far beyond the Abbe diffraction limit and to the nanoscale.55,63 The spatial resolution in TERS imaging is limited by the size of the near-field.57,64 TERS has been shown to be a powerful technique for nanoscale chemical characterization of graphene.42,43,65–69

TERS imaging of an unfunctionalized flake is presented in Figure 4, where a higher D-peak intensity is observed at the edges of the flake (Figure 4a). This increase in the D-peak intensity is expected, due to the breakdown of the sp2-hybridised carbon lattice at the edge of the flake. The variation of the D-peak intensity around the edge of the flake is most likely due to the difference in the edge structure, such as armchair or zigzag, which show different D-peak intensities.43,70,71 The TERS spectra at positions 1 and 2 from Figure 4a are displayed in Figure 4c, where the center of the flake at position 2 has a lower *I*D/*I*G ratio compared to the edge (*I*D/*I*G ~1) at position 1. The *I*D/*I*G ratio of the basal plane (bp) compared to *I*D/*I*G at the edge (ed) of the flake (*I*D/*I*G(bp) / *I*D/*I*G(ed)) is 0.48. This was calculated using the average *I*D/*I*G ratio of an area of the basal plane and of the edge of the flake.



**Figure 4.** Nanoscale chemical imaging of an unfunctionalized flake using TERS, showing the changes in the (a) D-peak and (b) G-peak intensity. Step size: 16 nm. Spectrum integration time: 1 s. (c) TERS spectra measured at positions 1 and 2 marked in (a) showing a lower D-peak intensity at the center of the flake (position 2). (d) Contact-mode AFM topography image of the flake. (e) Height variation of the flake across the dashed line marked in (d).

TERS imaging of the G-peak intensity in Figure 4b, shows only slight variations across the flake. This suggests that the D-peak intensity image (Figure 4a) should look similar to the *I*D/*I*G ratio image for this flake, which is confirmed in Figure S6. The G- and D-peak intensity images correlate well with the shape of the flake in the AFM topography image in Figure 4d, indicating the improved lateral resolution of the TERS system compared to the resolution possible with confocal Raman spectroscopy. The same TERS instrument has previously shown a lateral resolution of ~20 nm,42,43,66 which is similar to the results observed in this work, as shown in Figure S7, where a comparison of the near-field and far-field signals is also included. It should be noted that contributions to the Raman peaks from the far-field (confocal Raman spectroscopy) are also expected to be observed in the TERS images.64,72 From the AFM image, the height of this unfunctionalized flake is determined to be ~18 nm, as shown in Figure 4e. TERS measurements of two additional unfunctionalized flakes of different thicknesses are presented in Figures S7 and S8.

The *I*D/*I*G ratio of a separate, unfunctionalized flake is shown in Figure 5a, for comparison with the functionalized flakes in Figures 5b-d. The D- and G-peak TERS images and the AFM topography image of the flake in Figure 5a, are shown in Figure S7. This second unfunctionalized flake has similar attributes to the one in Figure 4. The *I*D/*I*G ratio is generally higher at the edges, with position 1 showing a considerably higher D peak than position 2 at the center of the flake (Figure 5e) with a *I*D/*I*G(bp) / *I*D/*I*G(ed) of 0.24. The average *I*D/*I*G(bp) / *I*D/*I*G(ed) ratio for the unfunctionalized material measured across three flakes is 0.4 ± 0.2 (Figure S9).



**Figure 5.** Selected TERS images showing the variation in *I*D/*I*G in the flakes with (a) no functionalization, (b) plasma-O functionalization, (c) plasma-N functionalization and (d) chem-N functionalization. These TERS images were generated by applying a threshold such that pixels with weak Raman signals ((a) *I*G < 20, (b) and (d) *I*G < 5 and (c) <27.5) were set to zero in order to remove artefacts. TERS spectra measured at the points marked in (a)-(d) are shown in (e)-(h), respectively.

Figure 5b shows the *I*D/*I*G ratio TERS image of a plasma-O functionalized flake. In this image, a much higher *I*D/*I*G ratio is observed at the edges compared to the basal plane, which is further confirmed in the TERS spectra from locations 1-3 shown in Figure 5f. However, this did appear to vary between individual flakes as shown in Figures S10 and S11, where a high *I*D/*I*G ratio is also observed from the basal plane of the flake in Figure S11f. Overall, the functionalized material in Figure 5b showed an increased *I*D/*I*G compared to the unfunctionalized sample in Figure 5a, with a *I*D/*I*G(bp) / *I*D/*I*G(ed) ratio of 0.05 due to the particularly high *I*D/*I*G at the edge. The average *I*D/*I*G(bp) / *I*D/*I*G(ed) ratio for the plasma-O material across three flakes is 0.5 ± 0.4 (Figure S9), where the uncertainty is the standard deviation. The high uncertainly value of 0.4 represents large variations of *I*D/*I*G over different flakes, indicating that the location of functionalization varies from flake to flake for the plasma-O material.

The TERS image of a plasma-N functionalized flake is shown in Figure 5c. Here, the *I*D/*I*G ratio is relatively constant across the whole flake (Figure 5g) and a *I*D/*I*G(bp) / *I*D/*I*G(ed) of 0.84. When comparing the two flakes from the plasma functionalized samples, the changes in *I*D/*I*G show that the nitrogen functionalized flake has a higher level of defects in the basal plane than the oxide functionalized flake. The average *I*D/*I*G(bp) / *I*D/*I*G(ed) for the plasma-N material across multiple flakes is 0.8 ± 0.1. This low uncertainty indicates similar variations of *I*D/*I*G across the measured flakes, as shown in Figures S11 and S12.

The confocal Raman spectroscopy and XPS measurements suggest that the chemically functionalized material has a lower level of functionalization than the plasma functionalized material. In particular, the chem-O sample appears to have similar *I*D/*I*G ratio and carbon content values as the unfunctionalized sample, as shown in Figures 1d and 2d. Furthermore, the XPS results suggest that the chem-N sample has more functional groups present than the chem-O sample. Therefore, the chem-N sample was chosen for comparison with the two plasma-functionalized samples using TERS.

Unlike the plasma-N sample, a lower *I*D/*I*G ratio is observed across the basal plane of the chem-N flake (Figures 5d and 5h) and a higher *I*D/*I*G ratio at the edges, similar to the unfunctionalized flakes in Figures 4 and 5a. The *I*D/*I*G(bp) / *I*D/*I*G(ed) for the chem-N flake in Figure 5d is 0.24, which indicates a lower level of defects across the basal plane of the chem-N sample compared to the plasma-N sample, suggesting a lower level of functionalization across the basal plane, with repeat measurements (Figure S13) from this sample exhibiting consistent TERS results. APTES may attach to existing hydroxyl groups present at the edge of the flakes, which would therefore not lead to an increased D-peak signal in the basal plane.73

The results from the confocal Raman spectroscopy, XPS and TERS measurements indicate that the plasma-functionalized samples have the highest level of functionalization, with NanoSIMS confirming that these functional groups are co-located with the graphitic flakes themselves. From the TERS results in Figure 5 and S11 showing the variation of the *I*D/*I*G ratio, associated with the presence of functional groups, it is likely that the plasma functionalization process produces material with functional groups that are present on the basal plane of the graphitic material. The plasma-N material is shown to have functional groups present on the basal plane for all the flakes measured, whereas the functional groups present on the basal plane of the plasma-O material varies between flakes. These TERS results correspond to the chemical characterization results obtained.

Therefore, these plasma functionalized powders were chosen along with the unfunctionalized material for dispersion in polymers to form mechanically-reinforced nanocomposites. Polyurethane and epoxy resin polymers were selected for optimal interaction with the oxide and nitrogen functional groups, respectively, that were expected to be present on the flakes,74–76 to improve the dispersion of the graphitic material throughout the polymer. ToF-SIMS depth profile imaging was used to compare the dispersion of the functionalized materials within the polymers. Each image in Figure 6 is a 2D representation of a 3D image (see Methods). Due to the large area imaged with respect to the flake sizes observed from the SEM images, any concentrated signal is expected to be from agglomeration rather than a single flake. Through monitoring characteristic ion peak signals from both the graphitic powders and the polymers, the level of agglomeration and regularity throughout the composite could be probed (Figure 6). The polyurethane only (Figure 6a and 6b) and the epoxy resin only (Figure 6c and 6d) images give a reference for comparing the addition of the graphitic powders, with a relatively uniform distribution of the CH- and C2H- ion signals observed over the imaged area, which are indicative of the respective polymers. It should be pointed out that the SiO2- signal in these samples is due to the presence of a de-foaming additive introduced during the formation of the polyurethane, hence it is present in all 3 polyurethane samples (Figure 6a, 6b, 6e, 6f, 6i and 6j).

When adding the unfunctionalized material separately to both the polyurethane (Figure 6e and 6f) and epoxy resin (Figure 6g and 6h), the C2- ions in red, characteristic of regions with high graphitic content, show the areas of agglomeration in Figure 6e and 6g. The same areas of agglomeration can also be observed in Figure 6k with the addition of the plasma-N functionalized material in the resin. These areas of agglomeration are much less pronounced in Figure 6i with the addition of the plasma-O functionalized material in polyurethane, suggesting the oxide functionalization process is aiding dispersion in polyurethane, which is not the case for the plasma-N functionalized material in the epoxy resin. This may be due to the material processing requiring further optimization.



**Figure 6.** ToF-SIMS images of the polyurethane, showing (a) C2-, CH- and SiO2- ions, (b) CF3SO3- and SiO2- ions. ToF-SIMS images of the epoxy resin, showing (c) C2-, CH- and SiO2- ions, (d) CF3SO3- and SiO2- ions. ToF-SIMS images of the unfunctionalized material, showing (e) C2-, CH- and SiO2- ions in polyurethane, (f) CF3SO3- and SiO2- ions in polyurethane, (g) C2-, CH- and SiO2- ions in epoxy resin and (h) CF3SO3- and SiO2- ions in epoxy resin. ToF-SIMS images of the plasma–O functionalized material in polyurethane, showing (i) C2-, CH- and SiO2- ions and (j) CF3SO3- and SiO2- ions. ToF-SIMS images of the plasma–N functionalized material in epoxy resin, showing (k) C2-, CH- and SiO2- ions and (l) CF3SO3- and SiO2- ions. Note that the SiO2 species are present due to a defoaming agent in the polyurethane.

In order to confirm the distribution of the powder within the polymer matrix, it is useful to identify a characteristic signature of the powder which is not present in the polymer material. From Figure 6, when there is agglomeration which forms regions with clear graphitic signals, it is possible to isolate the C2- signature from that of the polymer material. However, comparing Figure 6i and 6k to the corresponding images from the bare polymers there is clearly also a C2- ion peak signal coming from the polymers. The uniformity in the C2- signal outside the areas of agglomeration suggests that the powder is well distributed within the polymer, but this is not possible to confirm from this information alone. By studying the ToF-SIMS spectra for the functionalized and unfunctionalized powders in more detail, shown in Figure S14, it was possible to isolate an ion peak with a mass of 148.95 m/z, assigned to CF3SO3- indicative of the ionic liquid used in the exfoliation process, which is not present in the polymers.

From Figure 6b and 6d, there is no CF3SO3- signal detected in the polymer materials, however it is observed uniformly throughout the regions probed for the mixed compounds, as further indicated by the depth profile plot in Figure S15. This CF3SO3- signal can therefore be used as an indicator for the graphitic material itself and reveals a more even distribution of the powders within the nanocomposites matrices, apart from the areas which show agglomeration. Note that the CF3SO3- peak intensity in Figure 6h and 6l is actually reduced in the areas that correspond to the agglomeration (red areas in Figure 6g and 6k respectively), due to the decrease in sputtering yield for the graphitic material in those areas.

Due to the improved dispersion of the powder samples within polyurethane, these samples were chosen for mechanical tests to compare the properties of the original polyurethane with the nanocomposites after adding the unfunctionalized and plasma-O powders. Representative stress-strain plots for each of the sample types are shown in Figure 7a. Compared to polyurethane alone, both composite samples showed improved mechanical properties, achieving higher ultimate tensile stresses (UTS, Figure 7c) and elongation at break (EL, Figure 7d). Interestingly, the initial elastic modulus was unaffected (Figure 7b). The unfunctionalized material gave a slightly larger improvement than the functionalized material, however both are preferred to the polyurethane alone.



**Figure 7.** Mechanical testing of polyurethane, polyurethane with the addition of the unfunctionalized material and polyurethane with the addition of the functionalized, plasma-O material. (a) The stress-strain curve for representative specimens taken from the samples tested. Mean results for the initial elastic modulus (b), ultimate tensile stress (c) and elongation at break (d) determined from 5 individual tests.

Although the substantial improvement in UTS (85% and 75%) and EL (54% and 40%) for the commercially-available graphitic powders (unfunctionalized and plasma-O respectively) shows the potential of powders containing FLG to mechanically reinforce polyurethane, it is perhaps surprising that although the ToF-SIMS results show that the dispersion of the material is improved after the functionalization process (Figure 6), the UTS values are similar and the EL in fact shows a slight decrease for the functionalized material. These mechanical testing results are likely to be due to the introduction of defects into the basal plane of some of the flakes, such that while there is an observable improvement in the dispersion of the functionalized material, this improvement could be offset by a decrease in the mechanical robustness of the nanofiller due to the defects observed. The mechanical tests for the unfunctionalized and plasma-N functionalized material in the epoxy resin are shown in Figure S16, revealing no significant improvement in performance. Further studies are needed to determine the optimized functionalization process to facilitate improved dispersion as well as maintain the mechanical properties associated with the unfunctionalized material.

CONCLUSION

This study successfully characterizes the material properties of powders containing FLG that have undergone different functionalization processes, from the macroscopic powder down to the nanoscale, investigating individual flakes. Overall, it was found that the plasma functionalization process produced graphitic flakes with the highest level of functionalization. Using TERS to reveal the location of functional groups on commercially-produced graphitic flakes for the first time, the plasma-N samples were shown to have nitrogen functional groups bonded to the basal plane of the flakes, whereas the location of functional groups for the plasma-O sample appeared to vary, with some flakes having functional groups present predominantly at the edges. The chemically functionalized material showed little change in the confocal Raman spectroscopy and the TERS measurements compared to the unfunctionalized material, but as chemical changes were observed in XPS, ToF-SIMS and NanoSIMS, this would suggest that there was functionalization limited to the edges of the flakes, where a large *I*D/*I*G peak intensity ratio was observed using TERS.

The ToF-SIMS depth-profiling results of nanocomposites subsequently produced, showed that the plasma-O material in polyurethane agglomerated the least within the polymer matrices in this study. However, the functionalization process did not improve the mechanical properties of the nanocomposites any farther than when the unfunctionalized material was present in this study, which gave the improvements of 85% in the UTS and 54% of the EL, likely due to the basal plane defects in the plasma-O material.

METHODS

**Production of powders -** The few-layer graphene (FLG) powder used in this study was NaneneTM provided by 2-DTech Ltd., part of Versarien plc., UK. NaneneTM is produced using a mechanochemical process based on patented procedures.77

**Plasma functionalization process -** A vacuum-plasma process has been developed to treat the NaneneTM in pure gaseous atmospheres with only small and controlled levels of impurity air species. Discharges were struck in pure acrylic acid and allylamine to attempt to incorporate primarily OH and NH3 functional groups into the graphene flakes respectively. The plasma was sustained by mid-frequency (40 kHz) voltage excitation applied to a planer electrode placed above an electrically grounded crucible containing the graphitic powder. The powder was continually mechanically shaken at 40 Hz by a linear actuator to provide effective plasma coverage to all the material and aid in de-agglomeration of the flakes. The plasma was maintained at a nominal power of 150 W and a pressure of 0.05 mbar, with powder treatment times of 20 minutes in each case.

**Chemical functionalization process -** Amine functionalization on NaneneTM was carried out by using a 3-aminopropyltriethoxysilane (APTES) reaction. In a typical reaction, 3 g of powder was dispersed in 900 ml of ethanol:water (2:1) mixture through ultrasonication (in water bath) for ~ 1 hr. The mixture was then heated on hot plate to 65 °C. Approximately 6 ml of APTES (Acros Organic, 430941000) was added dropwise to the mixture and stirred for 18 hrs. The reacted powder was washed and vacuum filtered (47 mm Anodisc filter disc with 200 nm pore size) with ethanol at least 5 times, followed by drying in oven for at least 12 hrs at 60 °C. The resulting functionalized powder obtained was referred as chem-N.

Oxygen functionalization on NaneneTM was carried out by acid treatment. In a typical reaction, 2 g of powder was added to ~400 ml of nitric acid:sulfuric acid (1:3) mixture under magnetic stirring for ~2.5 hr. The temperature was maintained < 40 °C using water bath. The mixture was transferred to separating funnel and 2L of DI water was added slowly to avoid any exotherm. The precipitated powder was carefully removed and washed and vacuum filtered (47 mm Anodisc filter disc with 200 nm pore size) with copious warm water (40 °C) until the pH is neutral. The resultant powder is dried in oven for at least 12 hrs at 60 °C and referred as chem-O.

**Pelletization of powders** - Pellets of graphitic powders were made for XPS and ToF-SIMS measurements by mechanically pressing the powders in a KBr Quick Press pellet kit (Alfa Aesar, UK), producing circular pellets 7 mm in diameter and roughly 2 mm thick. These pellets were then mounted on 10 mm × 10 mm silicon wafers using conductive carbon tape, which could then be mounted directly on the XPS or ToF-SIMS sample stages.

**SEM measurements** - powders were dispersed in DI water and deposited onto Si wafers with a native oxide layer. The measurements were taken with a Zeiss (Oberkochen, Germany) Supra Microscope (In lens, 30 μm aperture, 5 kV accelerating voltage).

**Confocal Raman spectroscopy** - Confocal Raman spectroscopy was carried out using an inVia spectrometer (Renishaw, UK) on powder that had been filtered to produce a film. The powders containing FLG were dispersed in isopropanol (IPA) and vacuum filtered through filter paper with a pore size of 20 nm. A 532 nm laser was used with a 100×, 0.9 NA objective lens, with a power at the sample of 0.12 mW. An average of 2 acquisitions of 10 s each was used to acquire Raman spectra at each measurement location. For each sample, spectra were recorded from 8 locations over a 2 cm × 2 cm area. The spectra were normalized to the maximum of the G-peak and averaged for Figure 1c. Peaks were fitted to Lorentzian line shapes using OriginPro 2017 software, with the D’-peak constrained between 1618 cm-1 and 1622 cm-1. For each sample, the peak parameters were then averaged and the standard deviation was calculated to determine the associated uncertainty.

**XPS measurements** - XPS measurements were performed on the pressed pellets using an Axis-Ultra system (Kratos Analytical, UK) operating at a pass energy of 20 eV for high resolution, narrow scan-window spectra (100 meV step size, 500 ms dwell time), and 160 eV for wide scans (1000 meV step size, 200 ms dwell time), using a monochromated Al Kα X-ray source, with a photon energy of 1486.7 eV. The incident X-rays were at a 60° angle to the analyzer. Spectra were taken from three individual areas of each sample with samples measured as prepared with no pre-sputtering. No charge neutralization was needed due to the conductive nature of the pellets. Spectral peak fitting was carried out using CasaXPS with Shirley type backgrounds for the high resolution spectra, and the elemental composition was calculated from the wide scans using the NPL transmission functions and average matrix relative sensitivity factors after removal of a Tougaard or linear background.78

**TERS measurements** - the powders containing FLG were dispersed in an optimal solvent providing the least agglomeration, after which some were centrifuged. A mixture of 50% IPA and 50% water was used to disperse the samples, except for two of the plasma–O flakes imaged, which used N-methyl-2-pyrrolidone (NMP). The liquid dispersions were drop cast onto glass coverslips (0.17 mm thick) at a temperature just above the boiling point of each solution. TERS measurements were performed using a home-built system in transmission-mode, with contact-mode AFM feedback with a set-point of 80%. TERS probes were prepared by via thermal evaporation of Ag onto commercial Si AFM cantilevers (HQ:CSC17/No Al, MikroMasch Europe, Germany) at a pressure of 10-6 mbar and deposition rate of 0.05 nm/s. Prior to Ag deposition, the surface of Si AFM cantilevers was oxidized to produce a ~300 nm thick SiO2 coating using a tube furnace (Lenton Furnaces, cat. no. 4838, UK) and cleaned for 1 hour using a UV-ozone cleaner (UVOCS, cat. no. TIOXIO/OES/E, USA). The resulting diameter of the TERS probe-apex was ~50 nm,72 with different TERS probes used for the measurements of each flake. The AFM measurements were carried out using either contact-mode or tapping-mode configuration (Nanosensors PPP-NCHR probe, NanoWorld AG Switzerland) with a set point of 85% and scan rate of 0.1 Hz.

Raman spectroscopy signals were recorded in transmission-mode on a bespoke, combined AFM (Horiba Scientific, USA)/Raman (Horiba Scientific, France) system, allowing AFM measurements on the same sample area. An oil immersion, 1.49 NA, 100× objective lens (Nikon, Japan) was used for these measurements. A frequency doubled Nd:YAG laser (Coherent, USA) with a wavelength of 532 nm was used, with a liquid crystal radial polarizer (Arcoptix, Switzerland) placed in the optical path to convert the linearly polarized laser beam to a radially polarized beam. The probe-apex was aligned with the laser beam path and located by scanning the objective lens in the horizontal plane. For TERS measurements, the laser power at the sample was carefully selected between 50 μW and 150 μW to minimize probe and sample heating. Each spectrum was collected for 1 second (Figure 3, 4b, 4c, 4d), or 3 seconds (Figure 4a) for TERS imaging. The D- and G-peaks were fitted with a Lorentzian curve after subtracting a linear background intensity, using a MATLAB® program. The *I*D/*I*G ratio for each pixel in the TERS maps was calculated in MATLAB®, where a threshold has been applied so that pixels with weak Raman signals (*I*G < 2.5 up to *I*G < 27.5, depending on the flake and the near-field enhancement of the TERS probe) are set to zero to remove artefacts. The false color images were generated using SPIP (from Image Metrology A/S) without any further processing. Although the spatial resolution of the TERS system is ~20 nm, it should be noted that for some images the spatial resolution value would be larger due to the distance between the image pixel positions.

**ToF-SIMS measurements** - ToF-SIMS measurements of the powder pellets and composite samples were performed with a TOF SIMS IV time-of-flight secondary ion mass spectrometer (ION-TOF GmbH, Germany), equipped with an argon gas cluster ion beam gun and a liquid metal ion gun (LMIG) orientated at 45° to the sample surface. The LMIG utilized a Bi3+ ion source, operating at an ion current of 0.1 pA with a beam diameter of ~2 µm, raster-scanned randomly in the defined region of interest to be imaged on the sample. For pressed pellets of the powders, images were typically acquired over an area of either 150 µm × 150 µm or 500 μm × 500 μm with a cycle time of 100 µs, and a pixel density of 256 × 256 pixels. No charge compensation was needed due to the conductive nature of the pellets. The same pellets were used for both XPS and ToF-SIMS, to ensure consistency of results, with XPS carried out first to prevent any ion beam induced defects from the ToF-SIMS experiments from influencing the results. 3D depth profiles were performed on the composite materials in a non-interlaced mode, with sputtering cycles using 20 keV Ar5000 gas clusters, at an ion current of 0.4 nA and cycle time of 200 μs, over an area of 400 μm × 400 μm, interleaved with secondary ion images generated by the LMIG over an area of 150 μm × 150 μm in the center of the sputtered region. The smaller analysis region effectively gates the signal, reducing sputter crater edge effects on the quality of the spectra. At least 40 individual images were acquired during each depth profile, which are then compressed into a single image to create a 2D representation of the 3D region (see Figure 6). These depth profiles are used to determine the level of distribution of the graphitic material within the polymers and whether any re-agglomeration is taking place. Where more than one ion peak is presented in an image, these images typically consist of a red + green + blue overlay, whereby each color represents a different ion peak in the spectra, with color mixing used to indicate regions of correlation between the ion peaks (i.e. red + green = yellow). An electron flood gun was also used to compensate for charging effects during the measurements of the nanocomposites where necessary, at an operating voltage of 20 eV. For the ToF-SIMS measurement of the composite samples, 10 mm × 10 mm samples were typically cut from larger area pieces.

**NanoSIMS measurements** - NanoSIMS images were acquired using a Cameca NanoSIMS 50L instrument (Cameca Instruments, France). A Cs+ primary ion beam with an impact energy of 16 keV per ion was used to sputter the sample surface and secondary ions were collected. The primary beam current measured in the primary column (Fcp) was 70 nA and a 100 m primary aperture (D1-5) was used to help focus the beam to a spot size of approximately 100nm. The beam current at the sample (Fco) was 0.65 pA. Flakes for analysis were either preselected with SEM images or chosen using a combination of the optical microscope housed on the NanoSIMS and its ability to produced ion beam induced secondary electron images. Images were collected in either multicollection mode with detectors set for 12C, 12C1H, 16O, 12C2, 12C21H, 12C14N, or in combined analysis mode with magnetic field switching with detectors set for 1H at one magnetic field strength and 12C1H, 16O, 16O1H, 12C2, 12C21H, 12C14N at the second, higher field strength. Data analysis was conducted using Fiji/ImageJ with the OpenMIMS (BWH Center for NanoImaging, USA) plugin.

**Composite production** - The supply and casting of PU and epoxy nanocomposites was provided by Acoustic Polymers Limited and Bitrez Limited, respectively. The graphitic powder was dispersed into a two part PU resin, which was then cast on to a flat mould and then heat and pressure was applied to cure. Dumbbell-shaped test samples were then punched out for mechanical testing. The graphitic powder was mixed in to the epoxy resin, then the hardener was added and the resin was cast into dumbbell moulds. Loadings of the graphitic powder were 1 wt% for all composites measured.

**Mechanical testing -** All mechanical tests were conducted on an Instron 5500 screw driven test machine (Instron, UK) fitted with a 20 kN load cell calibrated to class 0.5. Testing was carried out on Type 1 dumb-bell test pieces as detailed in BS ISO 37:2017. Specimens were gripped in the test machine using pneumatic side action grips, with a supply pressure of ~ 3.5 bar, and loaded at a crosshead displacement rate of 1 mm/min. Strain was measured during testing via an Imetrum non-contact video system using a Sony XCD-SX910 camera with a 25 mm lens placed at a focal distance of ~ 1.5 m. Strain was determined by tracking the relative displacements of points marked within the uniform gauge section of the specimens, using either permanent or silver paint markers. To improve contrast between the specimen background and marker point, some specimens were first spray painted matt black before markers were applied. The elastic Modulus was determined by taking a linear fit of the stress-strain data between 0.0 and 5.0% strain.

ASSOCIATED CONTENT

**Supporting Information**.

The Supporting Information is available free of charge on the [ACS Publications website](http://pubs.acs.org/) at DOI: [10.1021/acsnano.XXXXXX](http://pubs.acs.org/doi/abs/10.1021/acsnano.9b04046). The Supporting Information (SI) includes SEM images of each sample, additional information on the confocal Raman spectra, XPS survey spectra, ToF-SIMS measurements of Si+ and imaging of the CN- ions in the chem-O functionalized sample and the AFM images for the flakes measured with NanoSIMS. The SI also includes additional TERS data including the G- and D- peak intensity images, the associated *I*D/*I*G and AFM images, with example line profiles and Raman spectra, for other flakes measured. Additional ToF-SIMS data showing the mass spectra for the polyurethane samples and the depth profiles of the CF3SO3- ion is shown. Mechanical testing for the epoxy resin samples is also contained in the SI.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. AJP, BB, AJS, JWB, APAR and CPD designed the experiments, EJL performed TERS, Raman spectroscopy and AFM measurements and analysis, BB performed ToF-SIMS and XPS measurements and analysis, KRP performed Raman spectroscopy experiments and analysis, MW performed SEM measurements and analysis, GM performed NanoSIMS measurements and analysis, APAR, CPD and SH undertook the chemical functionalization process, APAR and CPD dispersed the powders into PU and epoxy resin samples, RP performed mechanical testing and analysis, AJS performed the plasma functionalization processing, NK, JWB, VS, SRPS and SH provided guidance in the analysis of the results.

Funding Sources

EJL, KRP, MW, GM, RP, NK, BB, AJP acknowledge funding from the National Measurement System of the Department of Business, Energy & Industrial Strategy (BEIS), UK. This work was funded by the Analysis for Innovators Programme of Innovate UK as well as the Industrial Strategy Challenge Fund of the Department of Business, Energy & Industrial Strategy (BEIS), project number 103718. EJL acknowledges funding from EPSRC in the UK for funding in a DOCCAT collaboration and support from grants EP/R025304/1 & EP/L02263X/1.

ACKNOWLEDGMENT

Thank you to T. Whitmore and all at Henniker Plasma for their help and expertise in carrying out the plasma functionalization procedures. APAR, CPD and SH acknowledge Acoustic Polymers Limited and Bitrez Limited for supply and casting of PU and epoxy nanocomposites, respectively. The authors thank S. Wood and A. G. Shard at the National Physical Laboratory, UK, for discussion associated with the manuscript.

ABBREVIATIONS

TERS, tip-enhanced Raman spectroscopy; ToF-SIMS, time of flight secondary ion mass spectrometry; SEM, scanning electron microscopy; XPS, X-ray photoelectron spectroscopy; AFM, atomic force microscopy.

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