

Transmission electron microscopy of polymer-graphene nanocomposites

K. M. Kohlhaas^{*}, E. A. Stach^{**}, S. Stankovich^{*}, R. S. Ruoff^{*}

^{*}Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208

^{**}School of Materials Engineering, Purdue University, 501 Northwestern Avenue, West Lafayette, IN 47907

The properties associated with polymer-matrix composites are a function of the filler size, shape, and dispersion, and of interaction between the matrix and filler. The morphology and structural analysis of nanocomposites is often done with scanning electron microscopy (SEM) and X-ray diffraction (XRD). We have recently developed a method for dispersing single sheets of graphite (graphene) in a polymer matrix. Since our filler is not a layered material, XRD is not suitable for examining the structure of the nanocomposite. Also, SEM is unable to spatially resolve the thickness of an individual graphene sheet. While it is a useful technique for examining the dispersion on a larger length scale, SEM images cannot test whether our filler is dispersed as single, exfoliated graphene sheets or not. To determine if the filler was indeed present in the composite as single, exfoliated sheets or multi-layered platelets, we employed transmission electron microscopy (TEM).

Extensive high-resolution phase contrast imaging showed no evidence of multi-layer stacks, even though SEM of the same slices clearly indicated the presence of nanoplatelets, a result of the lack of mass or diffraction contrast between the (primarily) carbon matrix and the carbon filler. Selected area electron diffraction (SAED) of composite samples, however, yielded spot patterns showing the six-fold rotational symmetry expected for diffraction with the beam incident along [0001] (Figures 1a, b insets). The patterns allowed determination of d-spacings, which indicate that there are diffraction spots present at 4.23 and 2.45 Å.

To further understand the nature of these diffraction spots, we performed extensive electron diffraction simulations. We found that neither graphite nor AA-stacked graphene yielded diffraction spots with d-spacings of 4.23 Å and 2.45 Å. This is explained by the occurrence of destructive interference caused by the presence of planes in both of the structures that are situated halfway between those planes separated by each of these two distances. Electron scatter from an atom is (first Born approximation) proportional to the Fourier transform of the scattering potential [1]. To simulate the expected electron diffraction pattern from a single graphene sheet, “atoms” were placed into an simulated “image” based on Planar Space Group p3, with $a = 0.2471$ nm, $c = 6.391$ Å and with atoms at $x = 1/3, y = 2/3$ and $x = 2/3, y = 1/3$. A Fast Fourier transform was then performed on the “image” to create the diffraction pattern. Similar simulations were performed using an image of the projected electron potential (calculated by MacTempas). In each case, diffraction spots consistent with d-spacings of 0.42 nm, 0.24 nm, 0.21 nm, 0.16 nm, and 0.14 nm were observed.

Thus, TEM shows that the filler material in our polymer matrix composites is dispersed to the level of single graphene sheets. [2]

References

[1] B. Fultz and J.M. Howe, *Transmission Electron Microscopy and Diffractometry of Materials*, Springer-Verlag, Berlin Heidelberg, 2001.

[2] This research was supported by the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat) under award No. NCC-1-02037

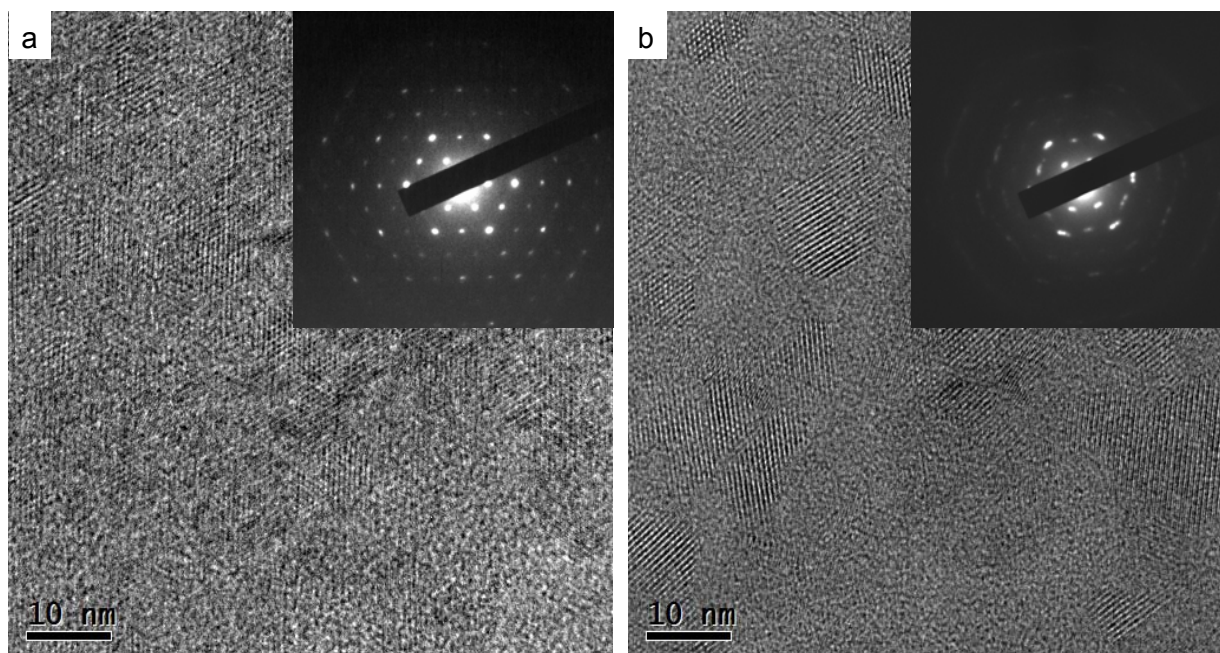


Fig. 1: TEM of (a) cast film and (b) microtomed composite samples. The SAED patterns show the rotational symmetry expected for diffraction along $[0001]$, and the d-spacings at 4.23 and 2.45 Å are consistent only with diffraction from a single graphene sheet.

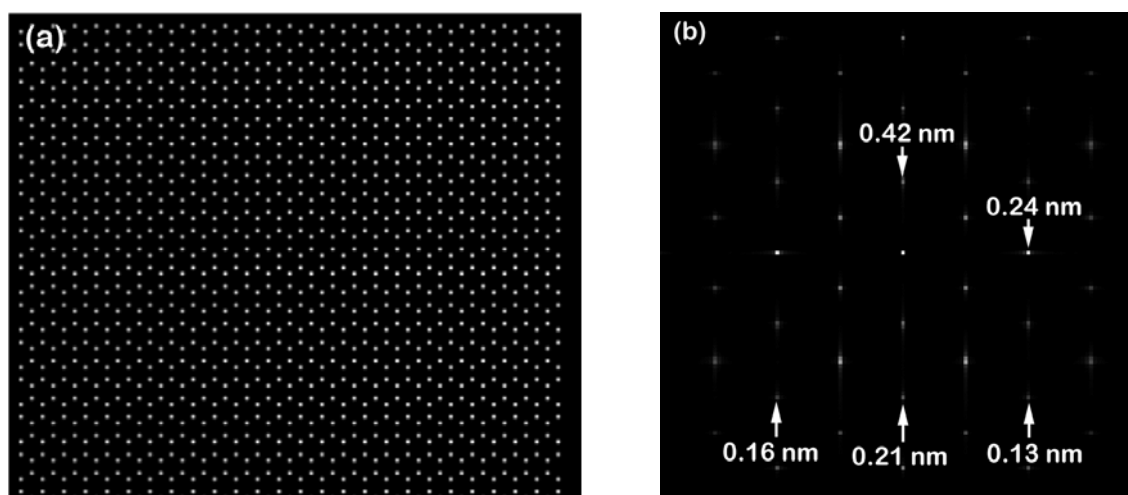


Fig. 2: (a) Simulated hexagonal lattice for a graphene sheet and (b) resultant Fourier transform, and thus the equivalent diffraction pattern.