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IMAGING CARBON NANOTUBES IN HIGH PERFORMANCE POLYMER COMPOSITES VIA MAGNETIC FORCE MICROSCOPY

PETER T. LILLEHEI[*], CHEOL PARK[†,**], JASON H. ROUSE[†,**], AND EMILIE J. SIOCHI[*]

Abstract. Application of carbon nanotubes as reinforcement in structural composites is dependent on the efficient dispersion of the nanotubes in a high performance polymer matrix. The characterization of such dispersion is limited by the lack of available tools to visualize the quality of the matrix/carbon nanotube interaction. The work reported herein demonstrates the use of magnetic force microscopy (MFM) as a promising technique for characterizing the dispersion of nanotubes in a high performance polymer matrix.

Key words. magnetic force microscopy, carbon nanotubes, structural composites

Subject classification. Structure and Materials

1. Introduction. Since the discovery of carbon nanotubes by Iijima [1] in 1991, intense interest has been generated in utilizing their remarkable mechanical properties [2] for structural and materials applications. Incorporation of carbon nanotubes into polymeric materials has the potential to improve the mechanical properties of polymer composites significantly; thereby expanding their use in structural applications usually afforded only to more robust materials. However, the full potential for the use of carbon nanotubes as composite reinforcement is hampered by several problems. A major issue involves efficiently dispersing the nanotubes into the composite polymer matrix to achieve the load transfer required for enhanced mechanical response in high performance polymers. This has led to an effort to optimize nanotube dispersion to improve the nanotube/matrix interaction in polyimide matrices. [3,4] This effort requires a means of investigating and qualifying the dispersion for various polymer composites. Noting the fact that carbon nanotubes interact with a magnetic field,[5-7] it was theorized that Magnetic Force Microscopy (MFM) should permit the imaging of carbon nanotubes in a polymer matrix. The work reported here shows that the use of the scanning probe technique of MFM allows for the rapid examination of the dispersion of carbon nanotubes into these polymer composites.

Optical techniques are typically used for characterizing the dispersion but lack the ability to visualize single bundles of nanotubes. Electron microscopy studies are hampered by a lack of contrast between the polymer and the carbon nanotube. Advanced imaging techniques are required to visualize either the nanotubes themselves or the effect the nanotubes have on the surrounding matrix. Electron microscopy studies and detailed characterizations of the composites are presented elsewhere.[3,4] The MFM technique [8,9] presented here is able to map the topography as well as the magnetic field at a fixed height above the surface thus enabling a direct visualization of the nanotubes in the polymer.

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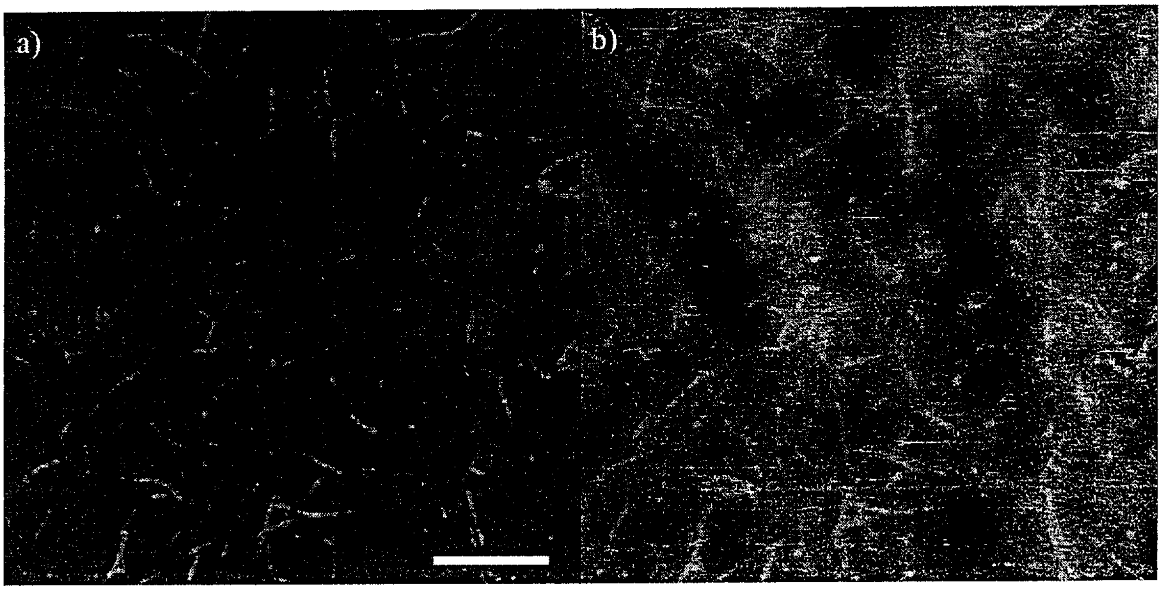

FIG. 1. *MFM image of carbon nanotubes on a silicon wafer: a) Topography, b) Phase. Phase map provides details on the magnetic field above the sample. Scale bar is 2.0 μm.*

2. Experimental. The scanning probe microscope used was a Digital Instruments Nanoscope IIIa Multimode SPM operated in MFM mode. The tip was a cobalt coated sharpened silicon nitride cantilever with an approximate radius of curvature of 60 nm (Digital Instruments model MESP). The MFM operates in a lift mode whereby a single scan line is taken to determine the topography in tapping mode, [10] followed by a repeat scan where the tip is lifted a fixed distance above the surface. This second scan records the long-range forces acting on the probe due to the magnetic field gradient above the sample. Typical lift heights were on the order of 10nm and could be adjusted to give better contrast.

Lateral resolution is on the order of 20nm for this lift mode procedure. Although, this may seem poor, the ability to resolve and the ability to "see" are not mutually exclusive. Carbon nanotubes are routinely imaged in both the topographic and magnetic force modes, albeit with an apparent width that is much thicker than their true width. Thus, two nanotubes positioned less than 20nm apart will appear as a single tube rather than two resolved tubes.

3. Results and Discussion. The ability to see the carbon nanotubes is clearly demonstrated in Figure 1, showing both the topography and the magnetic force images for a sample of single walled carbon nanotubes (SWNT) (HiPco, Rice University [11]) adsorbed on a polished silicon (100) wafer. The topographical image shows clearly resolved nanotubes. Although the magnetic field image shows a loss of resolution required to detect detailed SWNT features the tubes remain clearly visible. Figure 2 shows the topography and magnetic field images for a carbon nanotube paper (laser ablated SWNT, Rice University [12]). The topographic image clearly shows that the nanotubes are in the form of bundles, and the magnetic field image is able to provide additional detail about the bundling not seen in the topographic image. While the phase image has a resolution of approximately 20nm, details on tube wrapping are clearly

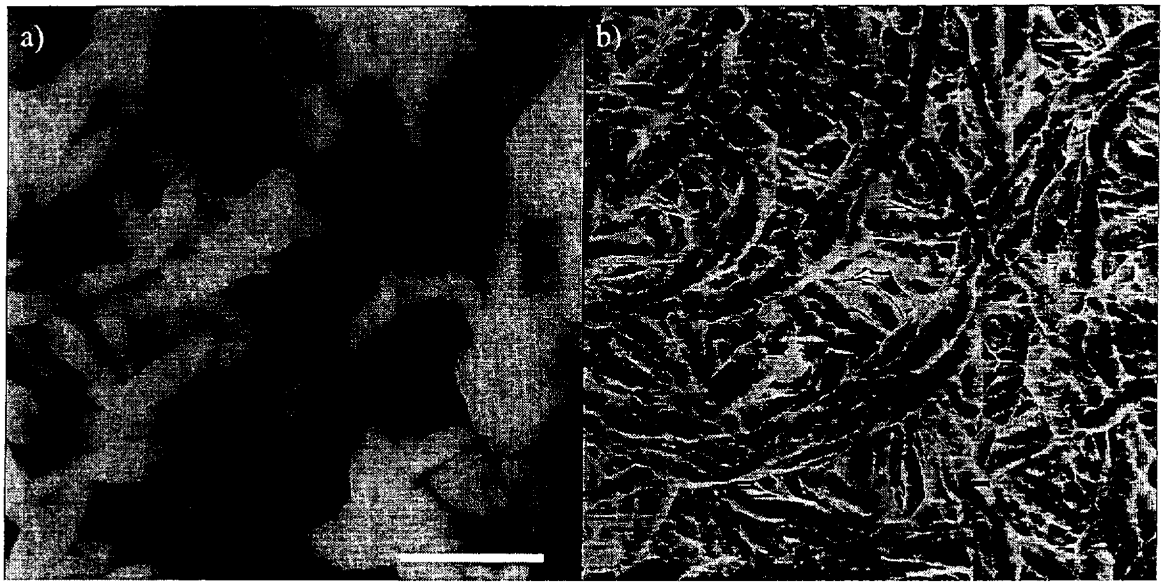

FIG. 2. *MFM image of a carbon nanotube paper: a) Topography, b) Phase. Scale bar is 500 nm image of carbon nanotubes.*

evident. This contrast is consistent with the MFM theory for imaging soft elements at low lift heights. [13,14] Strong contrast in the MFM image is found when the polar magnetization is aligned perpendicular to the surface, while longitudinal orientation provides moderate contrast at the transitions.

The ability of the magnetic probe to detect the nanotubes on the surface is clearly seen in Figures 1 and 2, but the probe should also be able to detect nanotubes that penetrate into a surface. This was the impetus for applying the MFM to examine carbon nanotube composite materials. The ability of the magnetic probe to detect the nanotubes at or just below the surface should aid in the characterization of the degree of dispersion of the nanotubes in various polymer matrices. The magnetic field gradient maps, or phase images are able to visualize the nanotubes within the polymer matrix while conventional tapping mode can only see the topography.

Figure 3 shows topographical and phase images obtained on a sample of 0.2 vol% SWNT (laser ablated, Rice Universty) in a colorless polyimide (CP2) film. The SWNT-CP2 composites were prepared by *in situ* polymerization under sonication; details of the synthesis are described elsewhere. [4] SWNT was pre-dispersed in a solvent of interest using sonication. The entire *in situ* polymerization reaction was carried out using the pre-dispersed SWNT solution with stirring, in a nitrogen-purged flask immersed in a 40 kHz ultrasonic bath until the solution viscosity increased and stabilized. Sonication was terminated after the solution viscosity stabilized and stirring was continued for additional several hours to form a SWNT-poly(amic acid) solution. The prepared SWNT-poly(amic acid) was imidized chemically and then cast to prepare free-standing films.

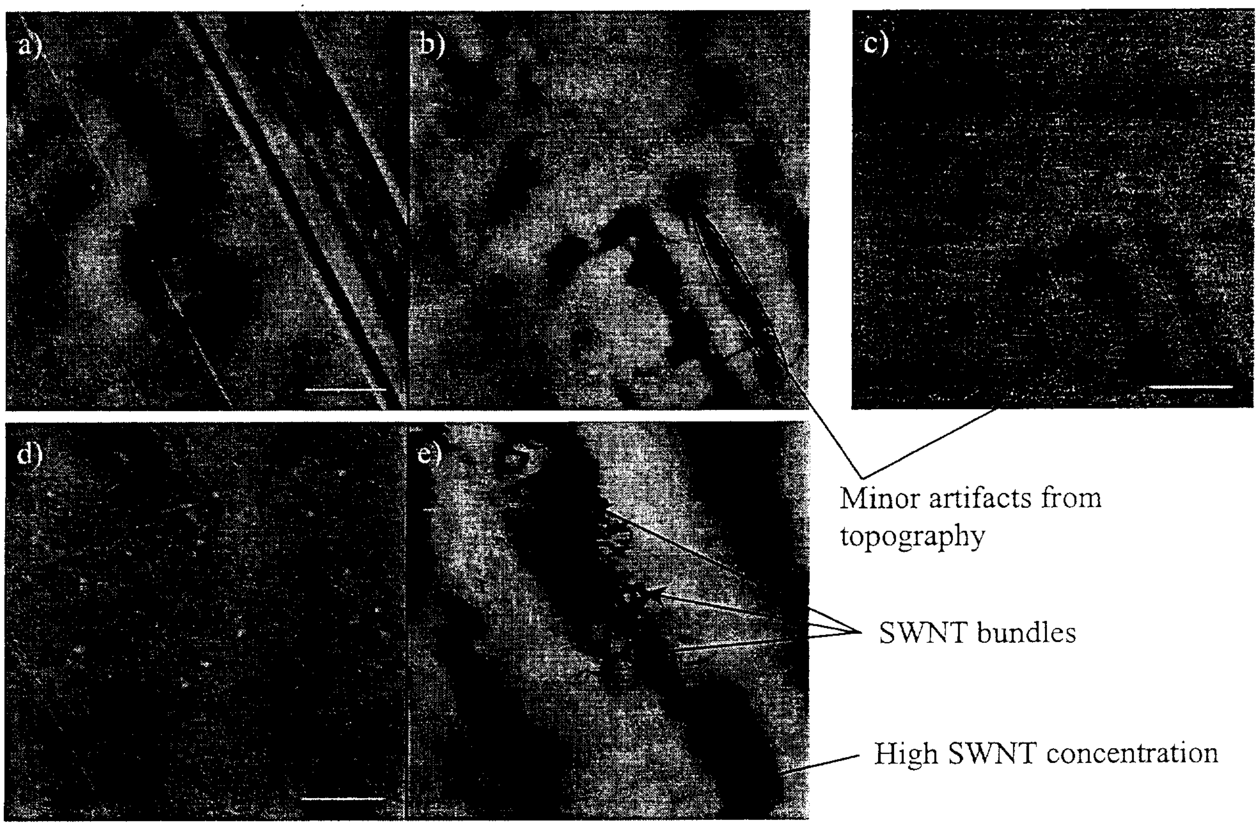

FIG. 3. *MFM and Electric Force Microscopy (EFM) images of two areas on a carbon nanotube polymer composite film; a-c) location 1 and d,e) location 2. a,d) Topography, b,e) Phase showing localized SWNT bundles via mapping the magnetic field gradient. c) Phase image of the same area as b) operated in EFM mode lacking the ability to resolve the nanotubes. Scale bar is 2.0 μm.*

The nanotubes were often found as agglomerates throughout the film. Individual nanotube bundles as well as regions of localized high nanotube concentration are clearly visible only in the MFM phase images, as indicated by the arrows, in Figure 3e. The ability to track the nanotubes in the polymer is a function of the magnetic field strength used to induce the magnetic field in the nanotubes. Qualitatively, the contrast between the nanotubes and the background is lost at 15 nm of lift height. The images were taken at a lift height of 10 nm, leaving at most a 5 nm depth of penetration. If the images were taken at a lift height smaller than 10 nm the phase image will have artifacts due to possible contact interactions of the probe with the sample. Some possible minor topographical or contact artifacts in the phase images are labeled in Figures 3b,c. It is important to note that these images are not reproducible without a magnetic tip, indicating that the response is indeed due to mapping the magnetic field gradient above the sample and not due to contact interactions. The electric field was mapped as well, but did not give contrast

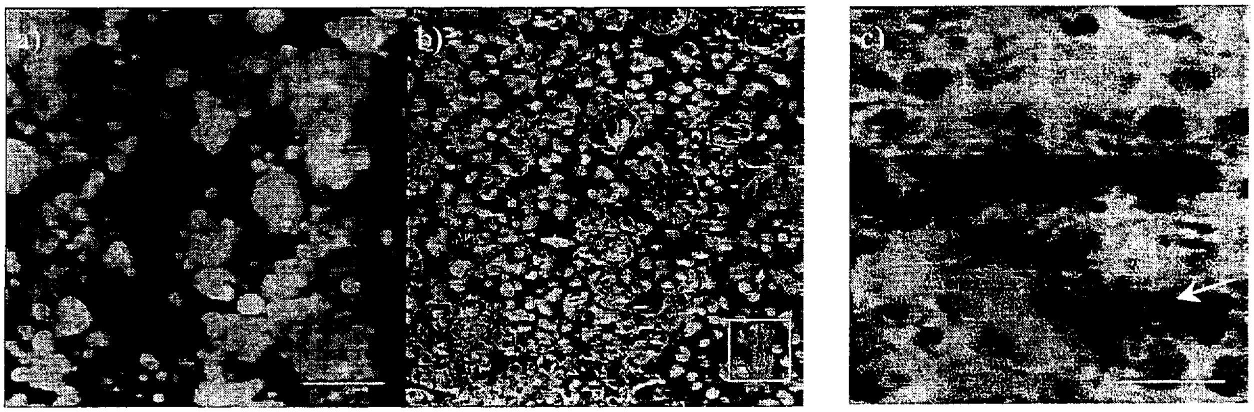

FIG. 4. *MFM image of a carbon nanotube polymer composite: a) Topography, b) Phase image showing distribution of carbon nanotubes in polymer matrix. Scale bar is 1.0 μm. c) Phase image from inset of b). Scale bar is 200 nm.*

between the nanotubes and the surrounding polymer matrix. The electric field map is shown in Figure 3c for the same region mapped in Figure 3b. This clearly indicates that the response shown in the phase map for the MFM images is due to long-range magnetic field interactions and not due to variations in electrostatic potential.

Greater detail was obtained in the MFM images for samples mounted in cross-section. Figure 4 shows topographical and phase images for a cross-section of a 1 vol% SWNT-CP2 composite film prepared by microtoming the film embedded in an epoxy with a diamond bladed ultramicrotome. The cross-sections of the nanotubes exposed at the microtomed surface appear as bright dots in Figure 4b due to the bundling of the tubes. Figure 4c shows a MFM image from the inset of Figure 4b. The nanotubes are visible as bright coils in the matrix and details on their wrapping are clearly evident. Some of the tubes can be seen disappearing, into the depth of the polymer, as indicated by the arrow in Figure 4c. The features visible in Figure 4c are due to very small bundle sizes. If the correction for the tip size is taken into account the bundles are less than 5 nm in diameter, giving an indication of just how powerful the MFM technique is for nanotube visualization.

4. Conclusion. The MFM has been able to map the nanotube dispersion in polymer films and film cross-sections to allow its use as a tool in composite fabrication characterization. Although questions remain regarding the depth of penetration that the MFM actually maps, these do not diminish the value of MFM as a rapid analysis tool for the characterization of the degree of dispersion of carbon nanotubes in a polymer matrix.

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