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Distant Dependent Measurement of Elastic Modulus of Polymer Nanocomposite Fibers via Atomic Force Spectroscopy

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ABSTRACT

In order to study the mechanical properties of nanofibers, a method based on atomic force spectroscopy is introduced. The ability of the atomic force microscope to measure the forces with subnanoNewton sensitivity and nanometer-scale lateral resolution has led to using it as a powerful tool to measure the mechanical properties of nanostructured materials. In this work, composite fibers were produced by electrospinning solution of polyacrylonitrile with carbon nanofibers dispersed in dimethylformamide, which is an effective solvent for carbon nanofibers. Distance dependent measurements were performed on reinforced composite fibers. To quantitatively measure the elastic modulus of nanocomposite materials, measurements were carried out on different points on the surface of the sample and force-distance curves were then plotted. The obtained results fairly agree to previously measured values. The great improvement in elastic modulus was achieved without sacrificing the mechanical strength and stiffness of the polymer, and with minimal weight penalty.

1 Introduction

Nanocomposite fiber materials, particularly those constructed with uniform reinforcements, have been sought for a long time in materials science. The hoped-for enhancements of the properties of polymer–nanofiber composites have remained elusive, owing in part to the difficulties in mechanical properties measurement. In order to study and manipulate material on an atomic scale there needed to be a development in new instrumentation.

During the 20th century a world of atomic and subatomic particles opened new avenues. The scanning tunneling microscope (STM), the first member of scanning probe microscopes (SPM) family), was developed in the early 1980s by Binnig, Rohrer, and co-workers (Bennig, Quate et al. 1986). One of the most commonly used systems in this family is atomic force microscope (AFM). Invented in 1986, AFM has undergone many developments. Though transmission electron microscopy and X-ray diffraction (Sawyer and Grubb 1987) have been mostly used in the field of polymer nanotechnology, AFM has now proven itself to be one of the most convenient tools for the characterization of nonconductive materials providing an obvious advantage for polymer surfaces. Unlike traditional microscopes, the AFM does not rely on electromagnetic radiation such as photon or electron beams to create an image (Sawyer and Grubb 1987), so it can be reliably employed to investigate the polymer materials without anxiety of their degradation.

AFM operates by scanning an ultra small tip (radius<10nm), supported on a 100-200 µm long force-sensing cantilever, over the sample and thereby producing a three-dimensional image of the surface (Cappella and Dietler 1999). The force between a nanoscopic tip and the surface is measured with a force sensor. The output of the force sensor is then sent to a feedback controller that then drives a Z motion generator. X-Y motion generators then move the probe over the surface in the X and Y axis. The motion of the probe is monitored and used to create an image of the surface.

AFM studies can be divided into two main categories. The first is the imaging mode, generating an image of the surface of the sample to observe its structural or dynamic features, which has been employed very effectively on a wide variety of surfaces, including semiconductors, biological systems and polymers, with resolution in the micrometer to sub-nanometer range. The second is the spectroscopy mode, one of the most promising and interesting research areas related to SPM, allowing the study of surface interactions between a tip and the surface of the sample from a theoretical point of view by means of force-distance curves which measure forces as a function of distance (Safanama, Marashi et al. 2009). Distance dependent measurements (DDM), measuring forces as a function of distance, can be employed for the study and measurement of numerous properties of materials such as elasticity, Hamaker constant, surface charge densities and degrees of hydrophobicity and also for the characterization of all different types of surface forces (Cappella and Dietler 1999). One of the primary reasons that AFM is a particularly powerful microscopy technique is that digitally stored data can readily be treated mathematically to have quantitative determination of the surface characteristics (Leiete and Herrmann 2005).

The superior properties exhibited by CNFs, if harnessed, can be utilized to synthesize a novel class of structural composites which can be employed to fulfill the new increasing demand of structural fiber materials (Ko, Gogotsi et al. 2003). Electrospinning has emerged in recent years as a relatively easy, efficient, and robust method for making ultrafine continuous fibers from a variety of materials. Electrospinning is a nanofiber assembly technique that utilizes an external electrostatic field to generate high surface areas on small fibers with diameters on the nanometer scale.

The objective of this study is to present a new approach toward the characterization of Electrospun Polyacrylonitrile (PAN)-derived nanofibers loaded of different percentage of carbon nanofibers (CNFs) employing AFM. Distance dependent measurements were carried out on different points on the surface of the sample nanofibers and elastic modulus was measured using force-distance curves.

2 Materials & Methods

Pre-selected amount of PAN with an average molecular weight of 80000 g/mol (obtained from Polyacryl Iran Corporation) was dissolved in N, N-dimethylformamide (DMF) obtained from MERCK, and was stirred vigorously to obtain 12 wt% PAN solutions. The final spinning solution was prepared by ultrasonication of 5 and 10 wt% CNFs in DMF (99%, Wako Pure Chemical Industries Ltd.) for 30 min. PAN was then added to the CNF/DMF solution and stirred for 4 h.

Topography images of samples were obtained using the non-contact mode of AFM, Dualscope/ Rasterscope C26, DME, Denmark. For these measurements, triangular Si_3N_4 cantilevers of 145 µm long, with a spring constant of 24 N/m were used. Force-distance curves (both approach and withdrawal curves) were plotted on different points of the surface of the sample using DDM (Figure 1). From the contact lines of the force-distance curves, it was possible to draw information about the elasto-plastic behavior of materials once they are considered as ideally elastic materials (Bhushan 2004). During the approach curve, the tip went into the sample of a depth δ, causing a deformation. By studying the amount of deformation under different amount of applied forces, the mechanical behavior of the sample can be investigated.

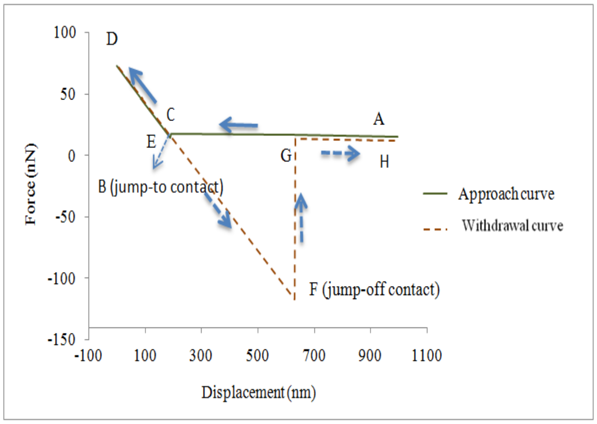

Figure 1. Typical force-distance curve illustrating the points where jump-to-contact (approach) and jump-off-contact (withdrawal) occur and the maximum values of the attractive force (pull-on force and pull-off force)

The elastic modulus of the fibers was determined using AFM, based on Kracke and Damaschke (Krake and Damaschke 2000) approach:

$$^{dF}/_{d(\Delta z)} = \left(^{2}/_{\pi^{1/2}}\right).E^{*}.A^{1/2}$$

(1)

where, dF/d(Δz) is the slope of contact region in force-distance curve, A is the contact area, E* is the effective Young’s modulus of the contact as defined by

$$^{1}/_{E^{*}} = {}^{(1-\upsilon_1^2)}/_{E_1} + {}^{(1-\upsilon_2^2)}/_{E_2} \qquad (2)$$

Here, E_1, E_2, υ_1 and υ_2 are the elastic modulus and the Poisson’s ratios of the sample and the tip, respectively. This method is applicable here due to the fact that the diameter of the fibers measured is much larger than the diameters of the contact area. The elastic modulus and the Poisson’s ratio of the tip are assumed to be 130 GPa and 0.27, respectively (Frank 2003). The radius of the contact area is 5 nm, as estimated from the shape of the tip.

3 Results and discussion

AFM topography images are presented in Figure 2. Surface irregularities along the axis of the composite fibers can be observed. These irregularities can be associated with the change in the diameter of fibers due to the incorporation of CNFs into PAN fibers.

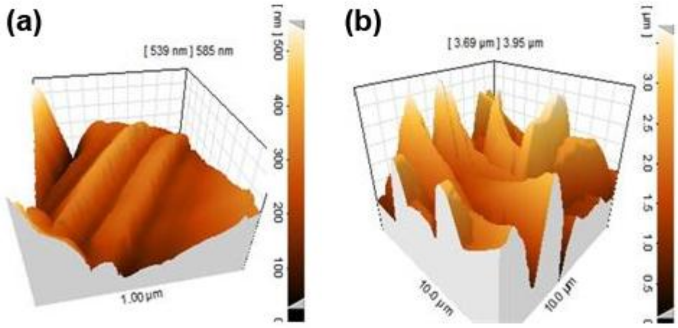

Figure 2. AFM topography images of (a) as-spun pure PAN fiber and (b) its counterpart composite fiber containing 10 wt% CNF

Figure 3 demonstrates a typical force-distance curve measured on the surface of the PAN nanofibers. The distance dependent measurements have been carried out on three different points under 15 different values of applied force. It was observed that the slope of the force-distance curves increases with the percentages of CNFs (Not shown here).

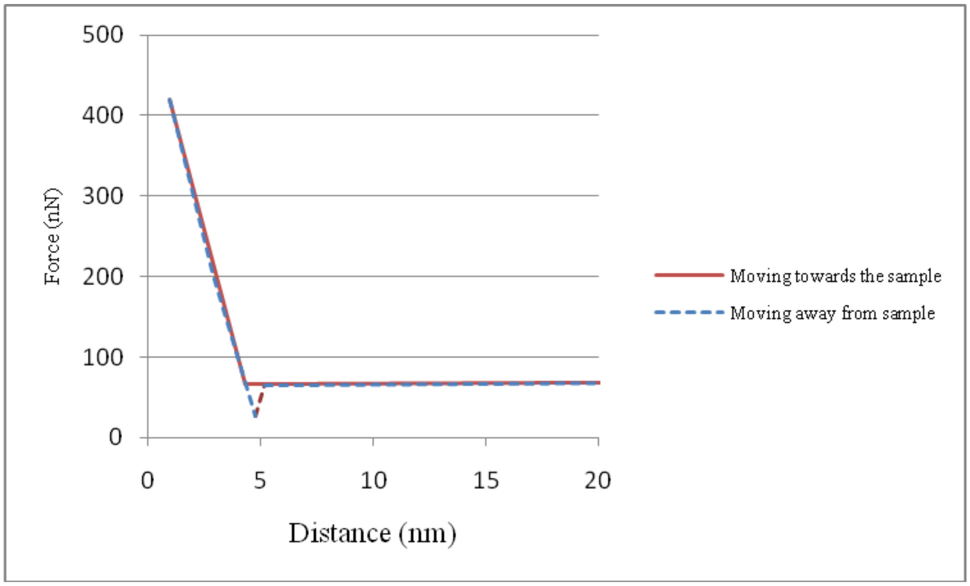

Figure 3. A typical force-distance curve plotted on the surface of the PAN fiber using DDM (applied force= 49.53 nN)

Force-deformation curve was plotted for each sample through measuring the deformation depth of each curve (Figure 4).

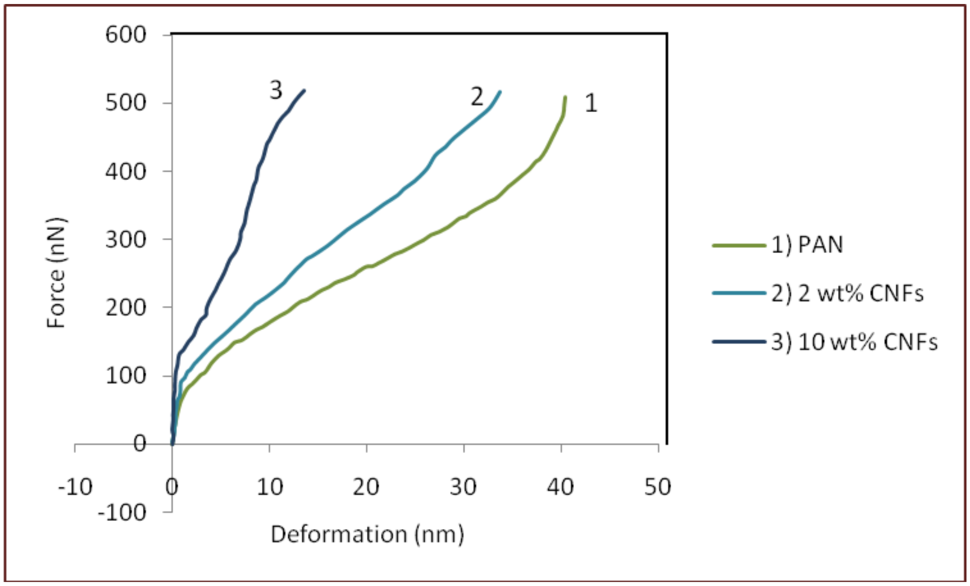

Figure 4. Force-deformation curve plotted from a set of experiments; (1) As-spun pure PAN fiber, (2) Composite fiber loaded by 2 wt% CNF, (3) Composite fiber loaded by 10 wt% CNF

The non-linear force-deformation relationship shown in the curve is contributed to the deformation of the fiber under large forces (Cappella and Dietler 1999). As can be seen in the figure, the slope of the curves increases with increasing the percentages of CNFs and one can expect the higher elastic modulus.

The elastic modulus of each sample has been calculated using Krake and Damasche equations (Figure 5). The samples are assumed to have a Poisson's ratio of 0.3 (Frank 2003).

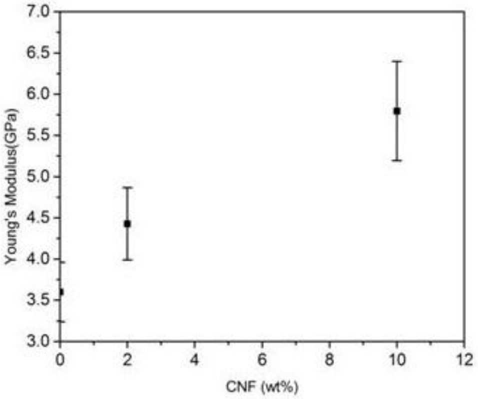

Figure 5. The elastic modulus measured for different percentages of CNFs

As shown in this figure, increases in composite moduli can be observed even for very low loadings of CNFs. This can be attributed to the higher elastic modulus of CNFs in which causes limitation in the deformation of fibers. Several papers have widely discussed the unique mechanical properties of CNFs (Treacy, Ebbesen et al. 1996; Falvo, Clary et al. 1997; Wong, Sheehan et al. 1997). It should be feasible to increase the modulus of a polymer/CNF composite up to and beyond that achievable with high modulus graphite fiber.

4 Conclusion

The ability of the atomic force microscopy in characterization of carbon nanofiber reinforced composite fibers via distance dependent measurement method was demonstrated. AFM studies showed surface irregularities along the axis of the composite fibers which can be associated with the change in the diameter of fibers because of the incorporation of CNFs into PAN fibers. Elastic modulus of the fibers was evaluated using force-distance curves and the results demonstrated great improvement in the composite moduli. Results obtained from this research confirm the reliability of AFM to investigate mechanical properties of materials.

5 Acknowledgement

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