

Nanomechanical Properties of Silica Coated Multiwall Carbon Nanotubes – Poly(methyl methacrylate) Composites

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ABSTRACT

Nanomechanical properties of polymer composites, reinforced with silica *coated* multiwall carbon nanotubes (MWNT), have been studied using the nanoindentation technique. The nanohardness and the Young's modulus have been found to increase strongly with the increasing content of these nanotubes in the polymer matrix. Similar experiments conducted on thin films containing MWNT, but *without* silica shell, revealed that the presence of these nanotubes does not affect nanomechanical properties of the composites. While carbon nanotubes (CNT) have a very high tensile strength due to small nanotube stiffness, composites fabricated with CNT may exhibit inferior toughness. The silica shell on the surface of a nanotube enhances its stiffness and rigidity. Our composites, at 4wt% of the silica coated MWNT, display maximum hardness of 120 ± 20 Mpa, and the Young's modulus of 9 ± 1 GPa. These are respectively 2 and 3 times higher than those for the polymeric matrix.

Keywords: carbon nanotubes, nanoindentation, silica coating, nanohardness, elastic modulus, composites.

1 INTRODUCTION

The unique mechanical, electrical and optical properties [1-2] of MWNT make them very attractive for the fabrication of new advanced materials, particularly polymer composites with improved performance, or with new properties. Due to exceptionally high strength, and axial Young's modulus [1, 3], MWNT have been commonly considered as reinforcing fillers for high-strength materials. In this context, various polymers have been used as matrix materials, and different preparation techniques employed [4, 5]. In general, the tensile modulus and ultimate strengths of the CNT composites are reported to increase, although below the level of expectation.

The nanoindentation technique has been proven as a useful tool for determination of the mechanical properties of thin films, including polymers [6]. Pavoort et al. studied nanomechanical behavior of MWNT/polyelectrolytes composites produced by using the layer-by-layer (LBL)

assembly deposition technique [7]. Utilization of the LBL technique has been proven to be an efficient method for incorporating CNT to a polymer matrix, with reduced phase segregation, high homogeneity, good dispersion and interpenetration of the nanocolloids and polymers, and high CNT concentration [5]. The nanoindentation studies of Ref. [7] showed that the hardness and Young's modulus of thin LBL MWNT/ poly(allylamin hydrochloride) (PAH) films are comparable to that of PAH. The individual MWNT can be displaced easily during indentation, leading to poor nanomechanical properties, close to those of the surrounding matrix.

In this study we perform a nanomechanical characterization of composites, reinforced with the silica coated MWNT (MWNT@SiO₂), within the poly(methyl methacrylate) (PMMA) matrix. Individual carbon nanotubes were coated with a uniform, thick layer of silica, and incorporated into PMMA. The CNT-SiO₂/PMMA composites were spin-coated on a silicon wafer substrate, and subsequently investigated by the nanoindentation technique. The hardness and elastic modulus were measured and compared with values obtained for the films made of uncoated MWNT in the PMMA matrix.

2 MECHANICAL CHARACTERISATION

Nanomechanical tests were carried out using the atomic force microscope (AFM) (NanoScope IV Digital Instruments) with conjugated TriboScope Nanomechanical Test Instrument from Hysitron Inc. The diamond conical and Berkovich tips were employed in this study as indenters. The calibration of indenters was carried out on soft material: poly(methyl methacrylate) was used as a standard material with an elastic modulus equal to 3.6Gpa.

A series of indentations were performed for each material throughout whole area, but in reasonable distance from the sample edges to avoid the edge influence on the mechanical properties of tested composites. In a typical experiment trapezoidal loading pattern was used. The peak loads were varied from 100μN to 1400μN, while the load/unload time was varied from 3s to 45s to maintain constant load/unload rate equal to 40uN/s. In general, indents with a contact depth ranging from 60-500nm were

performed for each sample. To minimize the effect of the material creep, the hold time was incorporated at the maximum load. In all experiments, the 20s hold time was set. Prior to the indentation, the tip was used for a surface scanning, in order to find a reasonably smooth areas and to avoid large roughness influence on the mechanical properties. The in-situ imaging of the material's surface can also be used for visualization of the indent impressions into samples. To minimize any substrate contribution to the deformation response of tested materials, the thin films were indented within maximum displacement lower than 15% of the films thickness.

The data from the indents, performed under the same maximum load, were averaged to obtain the mean and the standard deviation for all samples. The fluctuations in the measured displacement, that occurred under the same maximum load are in the range of 1-15nm but not included in the graphs simply for reasons of clarity.

3 EXPERIMENTAL SECTION

MWNT (CVD method, purity > 95%, diameter 10-20 nm, length 5-20 μm) were obtained from NanoLab (Newton, MA). In this study we produced two different composites, based on multiwall carbon nanotubes in PMMA, Mw=320000). The first one is based on functionalized MWNT that were blended with PMMA. In the second composite we employed silica coated MWNT, that were incorporated into a polymer (PMMA) matrix.

The first sample was prepared by an amide functionalization of MWNT in order to obtain soluble carbon nanotubes in organic solvents. To solubilize the MWNT, we used sample preparation according to the method of Ref. [8]. The MWNT dispersed in chloroform and the appropriate amount of poly(methyl methacrylate) (Mw=320000) were mixed in order to obtain the desired weight concentration of CNT with respect to PMMA. For nanomechanical tests we prepared five MWNT/PMMA samples with 1, 2, 3, 4 and 5wt% of MWNT.

In another sample silica-coated MWNT were used as a filler in the poly(methyl methacrylate) polymer. The coating process steps are as follows. The MWNT were functionalized with poly(allylamin hydrochloride) (PAH). CNT (50mg) were dispersed in a 0.5wt% PAH (Mw=70000) salt solution (0.5M NaCl, 500ml) and sonicated for 5h. Excess of polymer was removed by centrifugation (5 times) and washed with water. A residual black solid was re-dispersed in water, forming a stable, homogenous CNT suspension. The CNT water dispersion was transferred to silica sol (mixture of TEOS, H₂O, ethanol; mass ratio 2:1:4) in a 5:1 volume ratio. To prevent phase separation of TEOS and MWNT/water, the mixture was sonicated. After 2h the solution became homogenous and was set aside overnight at room temperature. After 12h, the mixture was centrifuged (4 times) to wash the carbon nanotubes with ethanol. The sediment was re-dispersed in a

solution of ammonia in ethanol (4.2 vol. % ammonia (28 wt % in water) in ethanol). Immediately after this, TES solution (10 vol. % in ethanol) was added under stirring (5ml of TES in 500ml ethanol solution of CNT). The reaction mixture was stirred for another 8h and sonicated from time to time. Finally the CNT were washed with ethanol (4 times centrifuged) and again re-dispersed. The process described above leads to the formation of a uniform and thick layer of silica on every individual MWNT (Fig. 1). The modified MWNT were subsequently transferred to chloroform by functionalization with 3-aminopropyl trimethoxysilane (97%). An appropriate amount of PMMA was added to the silica-coated MWNT - chloroform solution to obtain the desired concentration of CNT. This mixture was further homogenized in an ultrasonic bath for 1h. For nanomechanical investigation, 5 different silica-coated MWNT/PMMA (MWNT-SiO₂/PMMA) composites were prepared with 1, 2, 3, 4 and 5 wt % of CNT in a polymer matrix.

The chloroform dispersions of both MWNT/PMMA and MWNT-SiO₂/PMMA composites were spin-coated on a silicon wafer substrate. In general, thin films with a thickness greater than 3 μm were formed.

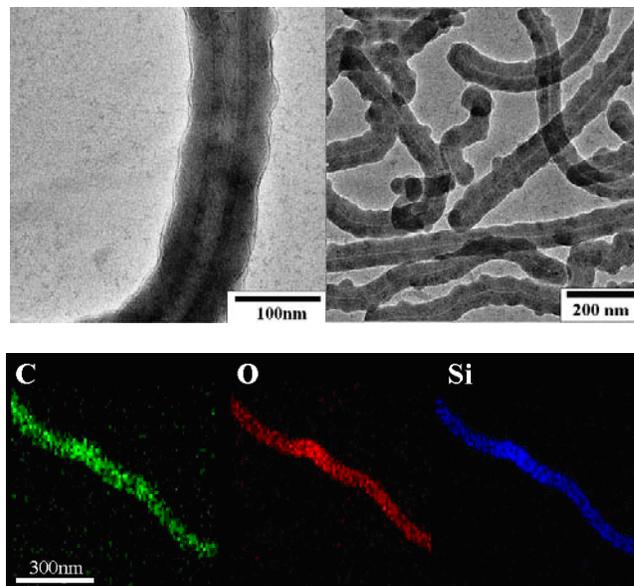


Figure 1 : TEM images and EDX mapping of silica coated multiwall carbon nanotubes.

4 RESULTS AND DISCUSSION

Fig. 2 shows the nanomechanical characterization of MWNT/PMMA composites. The homogeneity of our samples is confirmed by the relatively small standard deviation of data points. The hardness and Young's modulus are shown as a function of the contact depth for different MWNT content. The nanoindentation studies reveal that the mechanical properties of the MNWT

composites are comparable to those of thin films of PMMA. Moreover, H and E_r as a function of contact depth exhibit exactly the same behavior as was shown for PMMA. There are no significant changes in H values with increasing concentration of carbon nanotubes in polymer. Young's modulus of thin films presents independent behavior on indentation displacement and E_r values are close to that obtained for PMMA.

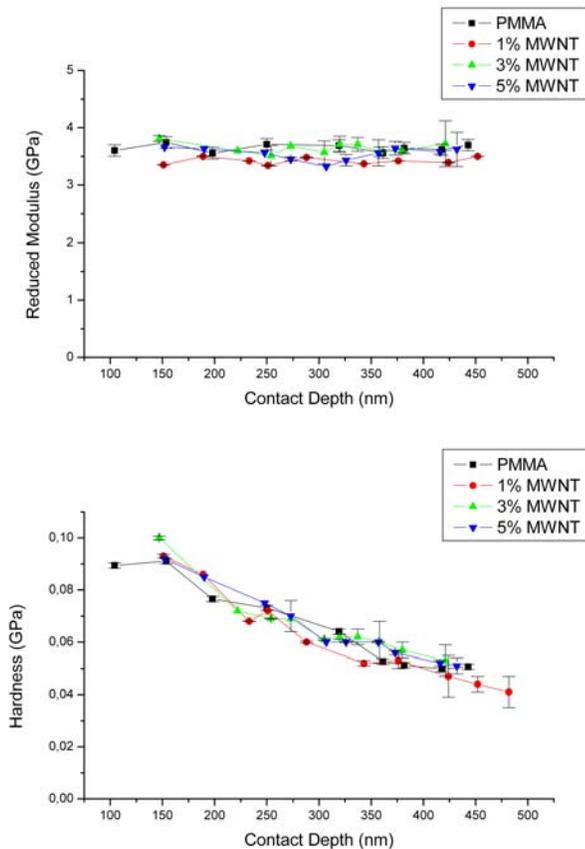


Figure 2: The elastic modulus and hardness for different CNT weight percentage content in MWNT/PMMA composites, as a function of the contact depth.

LBL technique has been proven an efficient method for incorporating carbon nanotubes into a polymer matrix, allowing for high composite homogeneity, good dispersion, interpenetration and high CNT concentration [5]. However, nanoindentation investigations of LBL - MWNT/PAH composites revealed, that the hardness and elastic modulus are close to those of the surrounding polymer matrix [7]. These results are consistent with our study, and confirm that high concentration and a homogenous distribution of CNT within a polymer matrix, as well as strong adhesion between the structural components do not ensure reinforcement of composites (in the nanomechanical sense). It was suggested, that flexibility of carbon nanotubes and their curvy morphology reduce the reinforcement action.

The indenter can easily displace carbon nanotubes due to their flexibility and bending properties. As a result, the indenter “feels” essentially only resistance of the surrounding matrix, and the mechanical response of the composite is close to that of the polymer matrix. Wong and Sheehan determined the average bending strength for MWNT to be 14.2 ± 8.0 GPa, i.e. several times smaller than for SiC nanorods [9]. Thus, nanomechanical improvement of a CNT/polymer composite examined by nanoindentation is limited by the relatively small bending strength of carbon nanotubes.

A completely different situation occurs for the silica coated CNT, as shown in Fig. 3. The MWNT@SiO₂ reinforced composites can exhibit much higher hardness and elastic modulus than PMMA. Both those quantities increase with increasing concentration of the coated MWNT in the polymer matrix. The results demonstrate the great influence of the silica reinforcing on the mechanical response of the CNT/polymer composite. Silica shell on a carbon nanotubes surface changes its mechanical properties. Such modified carbon nanotubes possess higher stiffness and are more rigid.

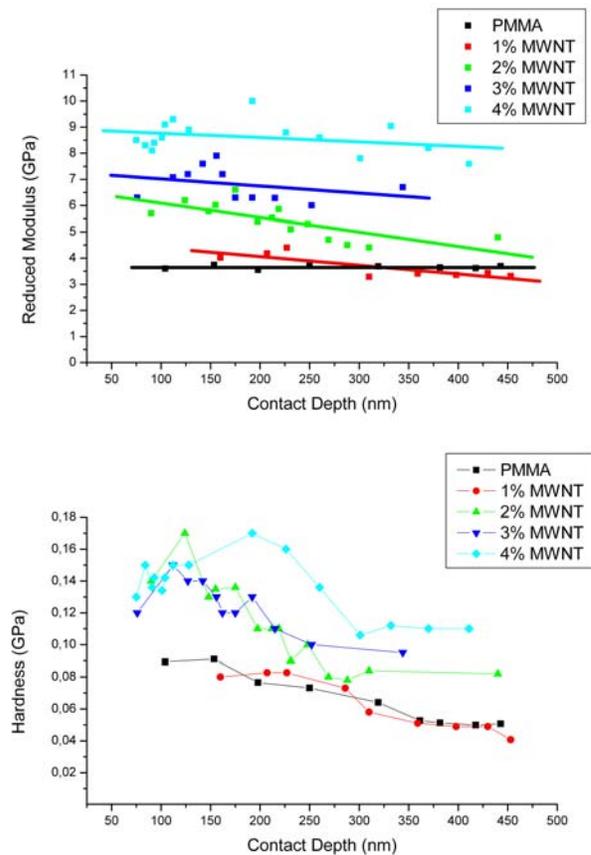


Figure 3: The elastic modulus and hardness for different CNT weight percentage content in silica coated MWNT/PMMA composites, as a function of contact depth.

Relatively large data scatter for the MWNT@SiO₂ films, as compared to MWNT/PMMA composites, indicate the presence of some inhomogeneities, and a nonuniform distribution of MWNT throughout samples (Fig. 4). The preparation method used in our study of MWNT@SiO₂/PMMA composite does not provide uniform distribution of CNT within the film, due to poor solubility of CNT@SiO₂ in chloroform. This leads to large errors in E_r and H. Nevertheless, the shown results demonstrate clearly a significant increase in the hardness and elastic modulus of MWNT@SiO₂/PMMA thin films, emphasizing the importance of the silica reinforcement of the carbon nanotubes. For example, Fig. 3 shows the Young's modulus for the 4wt% sample to be approximately 3 times as high as that for PMMA. For this CNT concentration, the hardness increases about two times in comparison to the polymer. We point out that this is not due to different preparation techniques used for the coated and uncoated CNT. Results of Ref. [7] clearly demonstrate, that even for a strong interconnectivity between components, and high homogeneity at very high wt% of CNT, the nanohardness and Young's modulus remain as low as that for a surrounding polymer. Presence of carbon nanotubes in polymeric materials does not improve nanomechanical properties due to high elasticity and small bending strength of CNT [9].

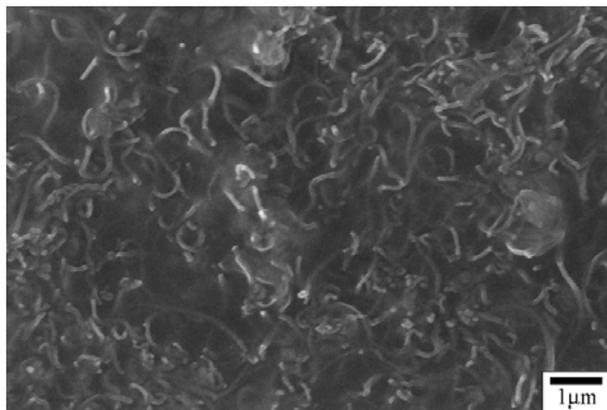


Figure 4: SEM image of the 3% silica coated MWNT composite.

5 CONCLUSIONS

The nanomechanical properties of the CNT/polymer composites (e.g. hardness) are not affected by the presence of CNT. We show, that silica coated MWCNT improve the nanomechanical properties of polymeric composites. Since the bending strength of CNT is improved by silica shell, the hardness and elastic modulus of MWNT/polymer composites increase with increasing content of MWNT in matrix. For example, a polymer composite at 4wt% of MWNT@SiO₂ displays an ultimate hardness of 120 ± 20

MPa and the Young's modulus of 9 ± 1 GPa. These are, respectively, 2 and 3 times higher as compared to those for the polymeric matrix. Silica coating of MWNT opens up possibilities for production of new advanced, reinforced materials for variety of applications. Since silica is an insulator, a coated CNT can be used as a coated nanowire for some nano-electrical applications. The electrical, as well as dielectric properties, of composites containing silica coated CNT are strongly affected by the insulator layer on each nanotube. It was recently shown [10], that a super-dielectric can be made this way, which has a very large, low frequency dielectric constant, and low dielectric loss. This may lead to novel applications in biology, medicine and nanoelectronic devices.

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