Mechanical Properties of Individual Composite Poly(methyl-methacrylate) -Multiwalled Carbon Nanotubes Nanofibers

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Abstract. Multiwalled carbon nanotubes with their superb mechanical properties are an unique filler material for polymer composites. Here, we present an investigation of mechanical properties of electrospun Poly-(methyl-methacrylate) multiwalled carbon nanotubes composite nanofibers. The method of electrospinning was used to fabricate suspended individual Poly-(methyl-methacrylate) multiwalled carbon nanotubes nanofibers. In order to reinforce the nanofibers, different high concentration of multiwalled carbon nanotubes were used. Transmission electron microscopy measurements reveal a successful filling of the nanofibers. The different types of nanofibers were deposited at SiO₂ substrates. Which were previously etched, to create trenches for bend tests. Followed by fixing the nanofiber with a focus ion beam platinum deposition at the trench edges. An atomic force microscopy was used to perform the mechanical nanofiber bending tests over trenches. The results were compared with pristine Poly-(methyl-methacrylate) nanofibers to nanofibers with 15 weight% and 20 weight% multiwalled carbon nanotubes composite fibers. We observed that pristine nanofibers have Young’s modulus of 136 MPa, while for composite nanofibers with 15 weight% have 2.65 GPa and with 20 weight% have 6.06 GPa (at room temperature and air ambiance). This corresponds to an increase of Young’s modulus of 19 fold between the pristine nanofibers and the 15 weight% MWCNT filled nanofibers. Therefore the increase of the Young’s modulus compared between the pristine and the 20 weight% MWCNT filled nanofibers corresponds to 45 fold.

1. Introduction
Nanocomposites combine a few nanomaterial components in order to introduce new functionalities in a matrix or fiber to harness some of their characteristics. Such components as carbon nanotubes composite materials have attracted great attention from academia and
industry alike, due to their novel mechanical, electrical and thermal characteristics [1-6]. The application range of nanofibers is vast and can be extended with the use of novel nanofillers such as carbon nanotubes, TiO\textsubscript{2} [3]. Among the various application fields for nanofibers is the field of sensors for chemical detection, optical sensors [7-9] or sensors for biomedical uses. Notable works in the biomedical fields are for virus removal filters [10] or tissue engineering [11]. These examples provide a strong evidence for the future wide field of applications. Other applications like air filter systems sold by United Air Specialists Inc. [12] have matured into the industrial level. We present an investigation of mechanical properties of individual composite Poly(methyl-methacrylate) (PMMA) -Multiwalled Carbon Nanotubes (MWCNT) nanofibers. We used a concentration of 15 weight\% and 20 weight\% MWCNT embedded in PMMA nanofiber. Atomic force bending test with pristine PMMA nanofibers, with 15 weight\% and 20 weight\% MWCNT reinforced composite nanofibers were performed. We present different Young's moduli measurement methods of pristine polymer nanofibers and compare the results with the composite MWCNT-PMMA nanofibers. Finally we discuss the strong mechanical reinforcement with MWCNTs nanofillers. We observe a 45 fold increase of the Young’s modulus with 20 weight\% MWCNT-PMMA composite nanofiber compared to the pristine nanofibers.

2. Experiment
A single-side polished 4 inch standard silicon wafers were used as basic material. A cleaning step with H\textsubscript{2}SO\textsubscript{4}+H\textsubscript{2}O\textsubscript{2} was realized and followed by H\textsubscript{2}O dehydration baking. A primer (Hexamethyldisilazan) was used to improve the adhesion between the wafer surface and the later positive photo resist (AZ1514H). The resist was spun on with a height of 1.5 \textmu m and followed by prebake, lithography and postbake. The resist was developed afterwards with MIF 326. Deep Silicon Etching (BOSCH-process) was used to create high aspect ratio trenches. After etching the resist stripping and H\textsubscript{2}SO\textsubscript{4}+H\textsubscript{2}O\textsubscript{2} cleaning was performed again. A 670 nm thick SiO\textsubscript{2} layer was deposited on the wafer and was realized with a wet oxidation process at 1000 °C. Different concentrations of MWCNTs (From Bayer-Baytubes C150 [13]) were dispersed in dimethyl acetamide (DMAC, Carl Roth, GMBH) and with hydroxypropyl cellulose (HPC) (from Aldrich). The solution was sonicated for 30 minutes. 3 g of PMMA (from Aldrich Mw) were dissolved in acetone. A Sonopuls HD3100 sonicator (from Bandelin GmbH) were used. The dispersions were performed at 10 kHz and 100 W output power. Both solutions were mixed together and dispersed by sonication for additional 30 minutes. Electrospinning was processed to create the different types of nanofibers over Si/SiO\textsubscript{2} substrates and carbon layered copper Transmission Electron Microscope (TEM) grids. That was realized by using Yflow R2.2.D-300 lab - scale electrospinning unit with single-nozzle electrospinning (Yflow Sistemas y Desarrollos S.L). With injector-collector distances for the various fiber types of 15-16 cm, an applied voltages of +6 / -8.5 KV, +9.5/-8.0kV, and a flow rate of 2ml/h. Before operating the bending tests, a TEM imaging with already manufactured grids were operated, to analyze the CNT distribution and to check the successfully filling of PMMA-matrices with MWCNTs. Fig. 1 illustrates TEM images of a created 15 weight\% MWCNT-PMMA composite nanofiber.
Figure 1. Transmission electron microscopy images of 15 weight% MWCNT-PMMA composite nanofiber

To clamp the nanofibers permanently at the trench edges, a Focus Ion Beam (FIB) platinum deposition was operated. A Zeiss FIB Leo 1540XB with a Gemini column was used. Pt pads of 3 by 3 µm were deposited with current of 100 pA. The pad height of ≈ 315 nm were realized and was determined afterwards using atomic force imaging with an XE150 AFM (from Park Systems). Figure 2 show the fix composite nanofiber over an etched trench.

Figure 2. An electron microscope image of a 15 weight% MWCNT-PMMA composite nanofiber fixed with Pt pads on Si/SiO₂ trench structure

The AFM was equipped with a suitable contact-mode PNP-TR tip from Nanoworld [14]. All AFM bending test were performed at room temperature and air ambiance. Each nanofiber was investigated at three different positions along its length. In total two samples of pristine PMMA, 3x 15 weight%-MWCNT-PMMA and three samples of 20 weight%-MWCNT-PMMA were measured.

| Pristine PMMA Nanofiber | 1     | 2     |
|-------------------------|-------|-------|
| average Young’s modulus [GPa] | 1.21E-01 | 1.87E-01 |
| average Young’s modulus +Δ[GPa] | 8.92E-02 | 5.88E-02 |
| average Young’s modulus -Δ[GPa] | 5.74E-02 | 5.69E-02 |

Table 1. Average Young’s modulus of each pristine PMMA nanofiber at different positions
Table 2. Average Young’s moduli of each 15 and 20 weight%-MWCNT-PMMA Nanofiber at different positions

| Nanofiber Type | 1          | 2          | 3          |
|----------------|------------|------------|------------|
| 15 weight%-MWCNT-PMMA | 3.54E+00  | 1.90E+00  | 2.08E+00  |
| average Young’s modulus [GPa] |           |            |            |
| average Young’s modulus +Δ[GPa] | 2.30E+00  | 4.20E-01  | 8.11E-01  |
| average Young’s modulus -Δ[GPa] | 1.22E+00  | 4.28E-01  | 9.46E-01  |
| 20 weight%-MWCNT-PMMA | 8.96E+00  | 4.48E+00  | 6.20E+00  |
| average Young’s modulus [GPa] |           |            |            |
| average Young’s modulus +Δ[GPa] | 2.46E+00  | 5.90E+00  | 3.27E+00  |
| average Young’s modulus -Δ[GPa] | 3.49E+00  | 2.59E+00  | 3.27E+00  |

3. Results

Fig. 3 illustrates the determined Young’s moduli of separated nanofiber types. The results were calculated with Eq. 2, which was derived from the sample construction using differential beam theory [15–18]. Where E is the effective Young’s modulus, a - force position, F - applied force, L - fiber length, I - moment of inertia, R- fiber radius and ω as the fiber displacement.

\[ I = \frac{\pi R^4}{4} \]  
(1)

\[ E = \frac{Fa^3[L - a]^3}{3I\omega L^3} \]  
(2)

It was observed, that pristine nanofibers have average Young’s modulus of 136\(±^{99}_{-72}\) MPa, while filled nanofibers, with 15 weight% have 2.65\(±^{4.2}_{-1.5}\) GPa and with 20 weight% have 6.06\(±^{5.36}_{-4.18}\) GPa. As fig 3 shows, a substantial of the Young’s modulus was observed, compared with pristine PMMA nanofiber to the 15 weight% and 20 weight% MWCNTs composite nanofibers. The average diameters with 436\(±^{9}_{-9}\) nm for pristine PMMA nanofibers, 330\(±^{24}_{-59}\) nm for 15 weight%-MWCNT-PMMA nanofibers and 284\(±^{7}_{-9}\) nm for the 20 weight%-MWCNT-PMMA nanofibers were determined.
4. Discussion

Clearly, it can be seen that the Young’s moduli increases significantly with the use of MWCNTs as filler material. The mean reinforcement from pristine PMMA nanofiber to 15 weight%-MWCNT-PMMA nanofiber was about 19.4 fold. Moreover, the reinforcement from pristine PMMA nanofiber to 20 weight%-MWCNT-PMMA nanofiber was even greater. The Young Modulus increase was here about the 44.5 fold, than without MWCNT as filler. This is a huge gain of the mechanical properties and highlights again MWCNTs as unique filler material. Furthermore the deviation values of the Young’s moduli increases even with the use of MWCNTs. There are many reasons for that deviance. One reason could be the randomized distribution of the MWCNTs in the polymer matrix, observed in TEM images. It was recognized, that the MWCNTs were not well aligned in the nanofiber. This causes different defects likewise, empty polymer nanofiber, short and long MWCNTs influenced by sonication [19], (compare fig. 1). Another reason is, that the nanofibers have non uniform diameters, due to MWCNT bundles or empty polymer matrices. The morphology of the pristine nanofibers were much more uniform compared to the composite nanofibers. During all steps humidity plays a significant role for stiffness of polymers. Water absorption results in swelling of polymers, detaching molecular chain apart leading to lower strength [20]. Another failure source could be, that the AFM tip might be not hit the fiber always exactly in the middle of its diameter. A slip or a tangential strike of the AFM tip during the bending tests is also a possible scenario affecting our results. The Young’s modulus of the pristine PMMA nanofiber with $136^{+109}_{-72}$ MPa and with a diameter of $436^{+9}_{-9}$ nm is quite small compared the Young’s modulus of bulk PMMA, which is in average 3 GPa [21]. This result was determined in past literature values [22]. Lu-Qi Liu et al. used electrospray PMMA nanofibers as well with diameters of $380^{+61}_{-61}$ nm and using a nano tensile tester [1, 23] and determined a Young’s modulus with $72.8^{+33.2}_{-33.2}$ MPa. At the tensile test the nanofibers were glued with liquid epoxy to an AFM tip and loaded in a SEM chamber with a micro manipulation system. The free end of the nanofiber were glued afterwards to the chamber stage. Then the tension test was realized by pulling the nanofiber end. Meanwhile the AFM cantilever was video-recorded and analyzed. The cantilever deflection was recorded and used to determine the force [24] using the thermal-noise calibration method of Sader et al. [25] and results in the Young’s modulus calculation. The small deviation of both Young’s modulus results, may be due to in the different measurement methods. The nano tensile Lu-Qi Liu et al. [22] used is more precise but also complicated, then the nano bending test. At the nano tensile test, the specimen only will be stressed with pull stresses. This eliminates the rise of shear forces. At the bending test performed here, shear forces cannot be completely excluded. It is assumed that the results with the tensile test are more accurate. But nevertheless the results of the Young’s modulus, which were determined in this work, are comparable to prior results in literature [22]. The smaller Young’s modulus of pristine PMMA nanofibers compared to bulk PMMA is justified with different reasons. Shearing forces during electrosprning decrease the molecular density and the rapid solidification leads to a mechanical stressed fiber [22]. These reasons bring about to a decrease of the nanofiber stiffness. Moreover the use of FIB induces strong thermal effects, which has extreme weakening effect on polymer stiffness. It has been demonstrated, that the Young’s modulus and tensile strength of electros spun nanofibers are generally lower, than at commercial scaled fibers. This is caused the unoptimized molecular orientation of the polymer matrix [26, 27].

5. Summary

In summary, we observed that MWCNT reinforced PMMA nanofibers present a higher Young’s moduli, compared with a pristine PMMA nanofiber. The reinforcement rises with the increasing weight percentage of MWCNT per nanofiber. Even the elastic behavior increases demonstrably in the composite nanofibers. The low Young’s modulus of the pristine PMMA nanofiber,
compared to the Young’s modulus of bulk PMMA, was indicated and compared to other research group.

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