CODEN IEJMAT *Internet Electronic Journal of Molecular Design* **2006**, *5*, 135–143 ISSN 1538–6414
BioChem Press http://www.biochempress.com

Inter*net* Electronic Journal of Molecular Design

March 2006, Volume 5, Number 3, Pages 135–143

Editor: Ovidiu Ivanciuc

Proceedings of the **International Symposium on Carbon Materials – Theoretical and Experimental Aspects**, Budapest, October 24–26, 2005

# Nanoindentation Investigation of Carbon Nanotube–Polymer Composites

Peter M. Nagy,[1] Dora Aranyi,[1] Peter Horváth,[1] Petra Pötschke,[2] Sven Pegel,[2] and Erika Kálmán [1]

[1] CRC–HAS, Department of Surface Modification and Nanostructures, Pusztaszeri u 59–67, Budapest, H–1025, Hungary
[2] Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, D–01069 Dresden, Germany

Received: December 16, 2005; Revised: January 24, 2006; Accepted: February 7, 2006; Published: March 31, 2006

**Citation of the article:**
P. M. Nagy, D. Aranyi, P. Horváth, P. Pötschke, S. Pegel, and E. Kálmán, Nanoindentation Investigation of Carbon Nanotube–Polymer Composites, *Internet Electron. J. Mol. Des.* **2006**, *5*, 135–143, http://www.biochempress.com.

**Inter*net* Electronic Journal of Molecular Design**

**BioChem Press**
http://www.biochempress.com

# Nanoindentation Investigation of Carbon Nanotube–Polymer Composites #

Peter M. Nagy,[1,*] Dora Aranyi,[1] Peter Horváth,[1] Petra Pötschke,[2] Sven Pegel,[2] and Erika Kálmán [1]

[1] CRC–HAS, Department of Surface Modification and Nanostructures, Pusztaszeri u 59–67, Budapest, H–1025, Hungary
[2] Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, D–01069 Dresden, Germany

Received: December 16, 2005; Revised: January 24, 2006; Accepted: February 7, 2006; Published: March 31, 2006

*Internet Electron. J. Mol. Des*. **2006**, *5* (3), 135–143

**Abstract**

Polymer–carbon nanotube (CNT) composites are promising structural materials due to high formability, good mechanical properties and high electrical conductivity. The main targets of polymer–CNT composite research are to reach a homogeneous distribution of the CNT in the polymer, and to achieve a high adhesion between CNT and polymer. The resulting properties were less frequently investigated till now, for example nanoindentational hardness and Young's modulus have not been studied to our knowledge. Nanoindentation was chosen as method of investigation, because it requires a small piece of sample material and it is nearly damage free. Beside an MWNT free reference samples with 2, 4, and 6 wt% of multiwalled carbon nanotubes (MWCNT) were produced using the master batch dilution method starting from a composite with 15 wt% MWCNT. Nanoindentation investigations showed an increase in hardness and Young's modulus of the samples by increasing the MWCNT concentration. This increase was about twice the weight fraction of MWCNT in the nanocomposite samples.

**Keywords.** Nanocomposite; carbon nanotubes; multiwalled carbon nanotubes; polycarbonate; nanoindentation; hardness; Young's modulus; nanomechanical properties; pile–up.

**Abbreviations and notations**

| | |
|---|---|
| AFM, atomic force microscopy | HB, hardness |
| CVD, chemical vapour deposition | $h_c$, contact depth |
| CNT, carbon nanotube | PC, polycarbonate |
| $E_r$, Young's modulus | MWCNT, multiwalled carbon nanotubes |
| ISE, indentation size effect | |

## 1 INTRODUCTION

Polymer–carbon nanotube (CNT) composites are promising candidates to exploit the outstanding properties of carbon nanotubes in construction materials with high mechanical [1–5] and good electrical properties [6–7]. The main target of CNT–polymer composite research nowadays is to

# Presented in part at the International Symposium on Carbon Materials – Theoretical and Experimental Aspects, Budapest, October 24–26, 2005.

* Correspondence author; E–mail: nagyp@chemres.hu.

reach a homogeneous distribution of the CNT in the polymer and to achieve an adequate adhesion between CNT and polymer [8–10].

In context with the availability and prices of CNT, there is a need for methods using small sample amounts in order to get information about the mechanical performance of such composites. For standard mechanical test methods, like tensile testing, it is not easy to work out the required number of standard samples when having only small amounts of CNT and the corresponding nanocomposites. Consequently, alternative methods are often used for determining mechanical properties [1,4,9,11]. In this work, nanoindentation was used to determine hardness (HB) and Young's modulus ($E_r$) of the samples.

In ancient times, hardness was used to determine the purity of valuable materials: pure gold and silver are extremely soft if really pure, gemstones are in contrary extremely hard. The first hardness scale, the Mohs empirical hardness scale was established to determine the hardness of minerals. Modern hardness test was developed around 1900 as a materials testing instrument, first of all to determine the quality of construction materials. A hard indenter body is pressed by a predefined load into the sample, and the so called contact pressure is calculated. This quantity is the quotient of the maximal load over the cross sectional (in some standards the whole surface) area of the relaxed indent crater. The contact area is determined optically by measuring the dimensions of the indent's impression [12–14]. In hardness test a rule of thumb exists: in order to obtain correct data, the sample should have a ten times higher thickness than the indent's depth. As the thickness of the tested plates or coatings decreased in the past decades, the technique has been changed for enabling measurements with smaller and smaller penetration depts. Milestones of this development are the development of micro–hardness test by combining an optical microscope with the hardness tester, and the development of the nanoindentation as a depth sensing test method [15–16]. In nanoindentation experiments the indenter is pressed into the sample according to a predefined load–time program. The area of contact is calculated from the contact dept. This is the depth where the load is getting zero on the unloading arm of the load curve. The Young's modulus of the sample is also determined in these experiments, and it is proportional to the slope of the unloading curve at maximal load.

The aim of this work was to investigate the mechanical properties of CNT–polymer composites by nanoindentation. The nanoindentation was chosen as method of investigation, because this method uses small pieces of sample material, and it does not require specially machined samples. It is shown that the hardness and Young's modulus of the composite is increasing with the multiwalled carbon nanotubes (MWCNT) content. AFM images of the indents were also taken which indicated that the deformation of the samples changes slightly with the variation of MWCNT concentration.

# 2 MATERIALS AND METHODS

## 2.1 Nanocomposite preparation

Beside an MWNT free reference polymer composites containing 2, 4 and 6 wt% of MWCNT were prepared by melt extrusion starting from a commercially available master batch of polycarbonate with 15 wt% MWCNT (provided by Hyperion Catalysis Intern. Inc, Cambridge, USA). The MWCNT are produced by chemical vapor deposition (CVD) and have diameter in the range of 10–15nm consisting of 8–15 graphite layers [17]. The composite granules as well as the base polycarbonate (PC) have been subsequently compression molded at 260°C into plates with a diameter of about 70mm and a thickness of about 1mm. Prior to processing the materials were dried at 120°C in vacuum for 4h. The polycarbonate used has a zero shear viscosity of 600 Pa s at 260°C. It has to be mentioned that all the samples filled with MWCNT were electrically conductive [18] having volume conductivities higher than 0.01S/cm. This indicates a kind of percolated network of MWCNT within the polycarbonate matrix, which is expected to get denser at higher MWCNT loading. The dispersion of MWCNT in the samples is quite homogeneous, as described in work of Satapathy *et al*. [19].

## 2.2 Nanointendation

The nanoindentation instrument we used in this work was a Nanoscope IIIa scanning probe microscope equipped with a Dimension 3100 AFM head and with a Hysitron TriboScope nanoindenter head. It is possible to image the nanoindentation impression by replacing the two heads against each other. The Triboscope head is also able to image the sample surface with the indenter tip; this method however distorts the image slightly, and the imaging speed should be reduced considerably. The indentation samples were simply cut from the sample plates, and glued on stable steel sample holder using special wax glue.

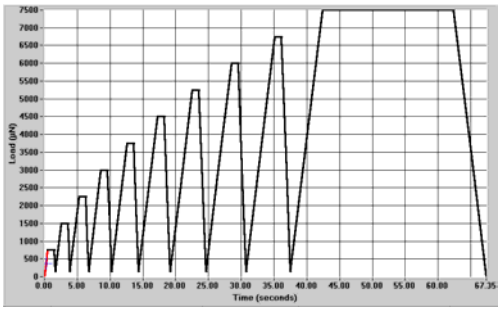


**Figure 1.** Cyclic loading program used in indentation experiments.

## 2.3 Cyclic indentation method

To obtain as much experimental data as possible, we used the so–called “cyclic loading” method. The indenter tip was first loaded to 10% of the nominal value, this load was hold for 5seconds, and unloaded to 5% of the nominal load. In the next cycle it was loaded to 20%, hold and unloaded to

5%, and so on, as it is shown in the load program in Figure 1. This cyclic loading method enables to evaluate the hardness and Young's modulus in all unloading arms of the loading curve, resulting in 10 data pairs in each indentation.

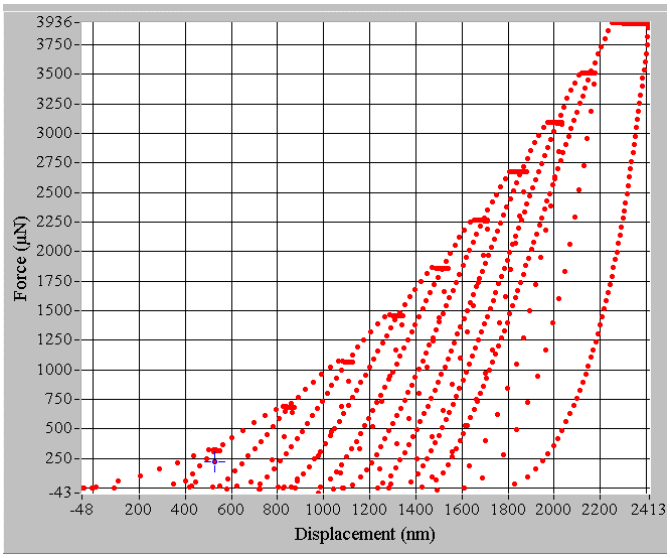


**Figure 2.** Load curve of an indentation experiment.

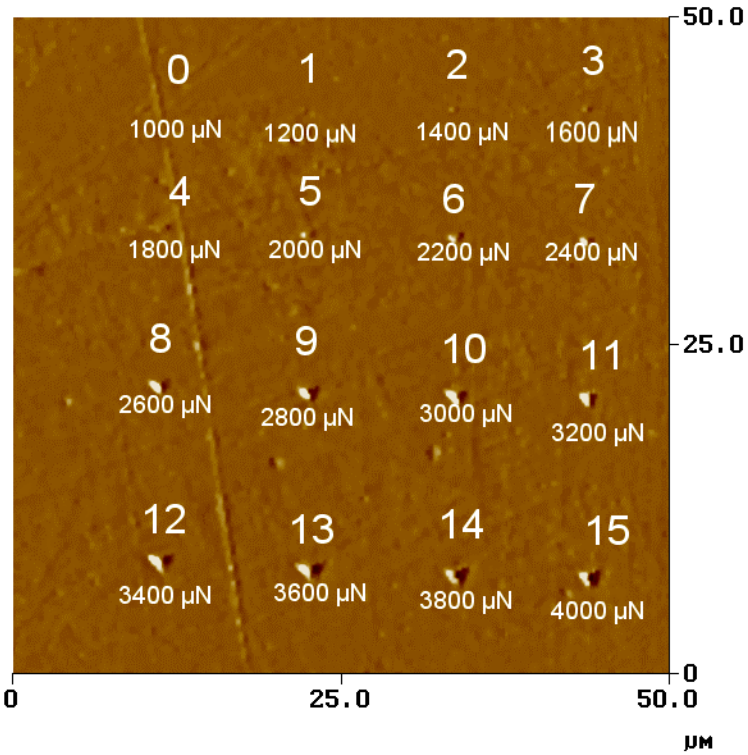


**Figure 3.** Principal schema of 4x4 array of indentations, numbers on each indentation triangle indicating order and maximum load in µN of the indentation.

The loading curve is shown in Figure 2 leading to a total time for each cyclic loading of about 70s. The method is applicable only to samples, which do not show the work hardening effect. For

polymer composites this requirement is fulfilled, consequently this cyclic method accelerated the work considerably without influencing the accuracy of the measurement. In each run sixteen cyclic indentation experiments were carried out on a 4×4 matrix of indentation sites covering an area of about 50×50μm (see Figure 3). During each run the maximal load increased from 1000 to 4000μN covering a broad range of indentation depths. Since positioning of the sample/indenter for the next cycle needed about 85s, the total time needed for each 4x4 matrix was about one hour. After each run the surface of the indented area was imaged in the AFM mode of the Hysitron nanoindenter showing the 16 impressions in the (sometimes considerably rough) surface of the sample (Figure 3) (this imaging took about one quarter of the time requirement of the experiment).

## 3 RESULTS AND DISCUSSION

The evaluation of each load curve delivers 10 different values of hardness, Young's modulus, and penetration– or contact–depth values. The hardness and the Young's modulus are plotted against the calculated contact depth in Figures 4 and 5, respectively.

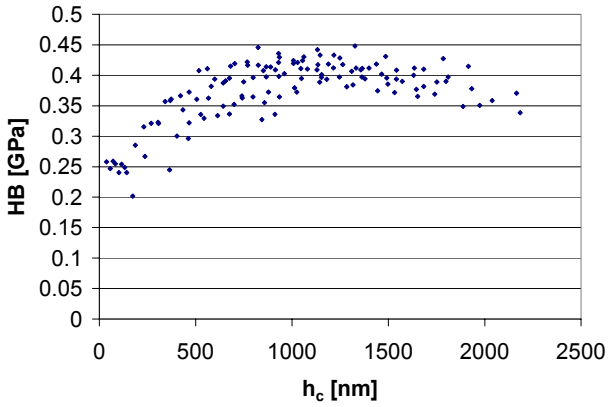


**Figure 4.** Hardness as function of contact depth in the sample with 2wt% MWCNT.

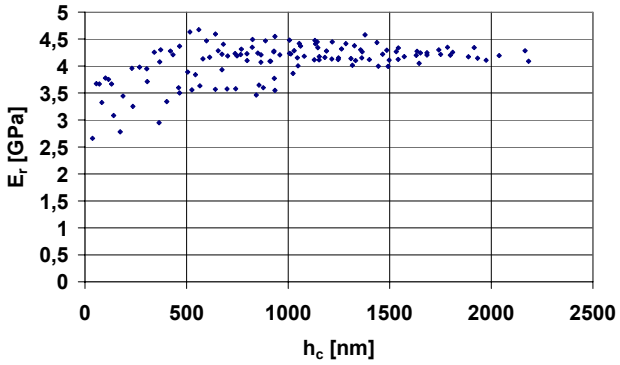


**Figure 5.** Young's modulus as function of contact depth in the sample with 2wt% MWCNT.

The data obtained for a sample with 2wt% MWCNT are shown in Figures 4 and 5, but all other samples show a similar behaviour: the hardness and Young's modulus is increasing with

penetration depth at low penetration under about 500nm, and reaches a constant value above about 1μm penetration. This effect is called the indentation size effect (ISE). It may have many influencing factors, as a soft surface layer on top of the sample, surface roughness, indenter tip rounding, and so on. All the data contain a considerably high spread due to the roughness of the samples. The increase in values with penetration depths at low depths is caused by a surface effect in the sample, but the increased spread of data in this range is due to intrinsic error caused by the surface roughness.

We used the hardness and the Young's modulus averaged for the contact depths higher than 500nm as standard measure of hardness and Young's modulus of the sample. These data are shown in Figures 6 and 7 as function of the MWCNT concentration of the composite. Both mechanical properties are increasing with MWCNT content linearly, and the relative increase in mechanical properties is about twice the MWCNT weight concentration.

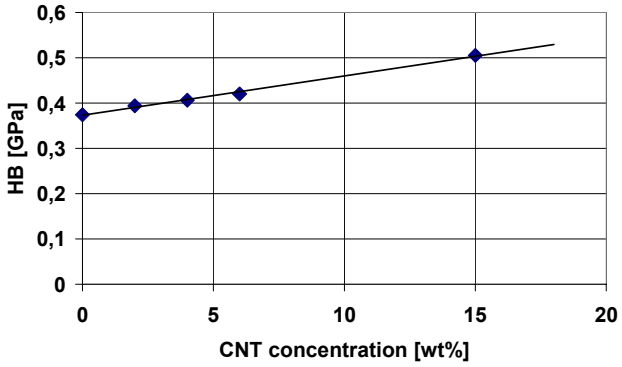


**Figure 6.** Hardness as function of MWCNT concentration in the nanocomposites.

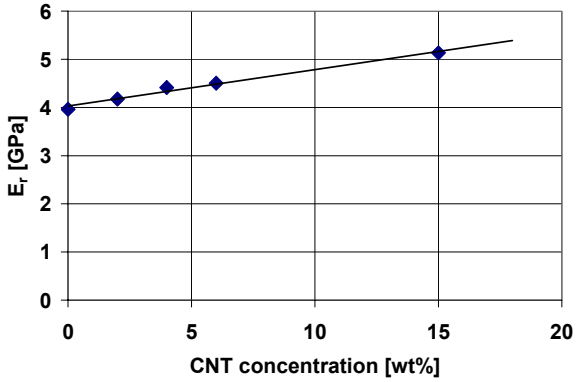


**Figure 7.** Young's modulus as function of MWCNT concentration in the nanocomposites.

The AFM images of indented areas are shown in Figure 8. So called pile–ups surround the indents in the PC sample as shown in Figure 8a. These small bumps are composed of the material pressed away by the indenter. This effect increases the measured hardness and Young's modulus in

depth sensing indentation experiments. The pile–up increases the contact area compared to the calculated one (based on the assumption of a flat sample surface), and in consequence the calculated hardness and Young's modulus values are larger than the real ones. This effect is the largest in Figure 8a, taken on the pure PC sample, more or less pronounced in Figure 8d and in Figure 8e taken on samples containing 6 and 15wt% CNT respectively, and the effect is small in Figure 8b and in Figure 8c with 2 and 4wt% CNT respectively. The effect should be investigated more in detail in order to evaluate the piling–up effect, and determine the exact hardness and Young's modulus values.

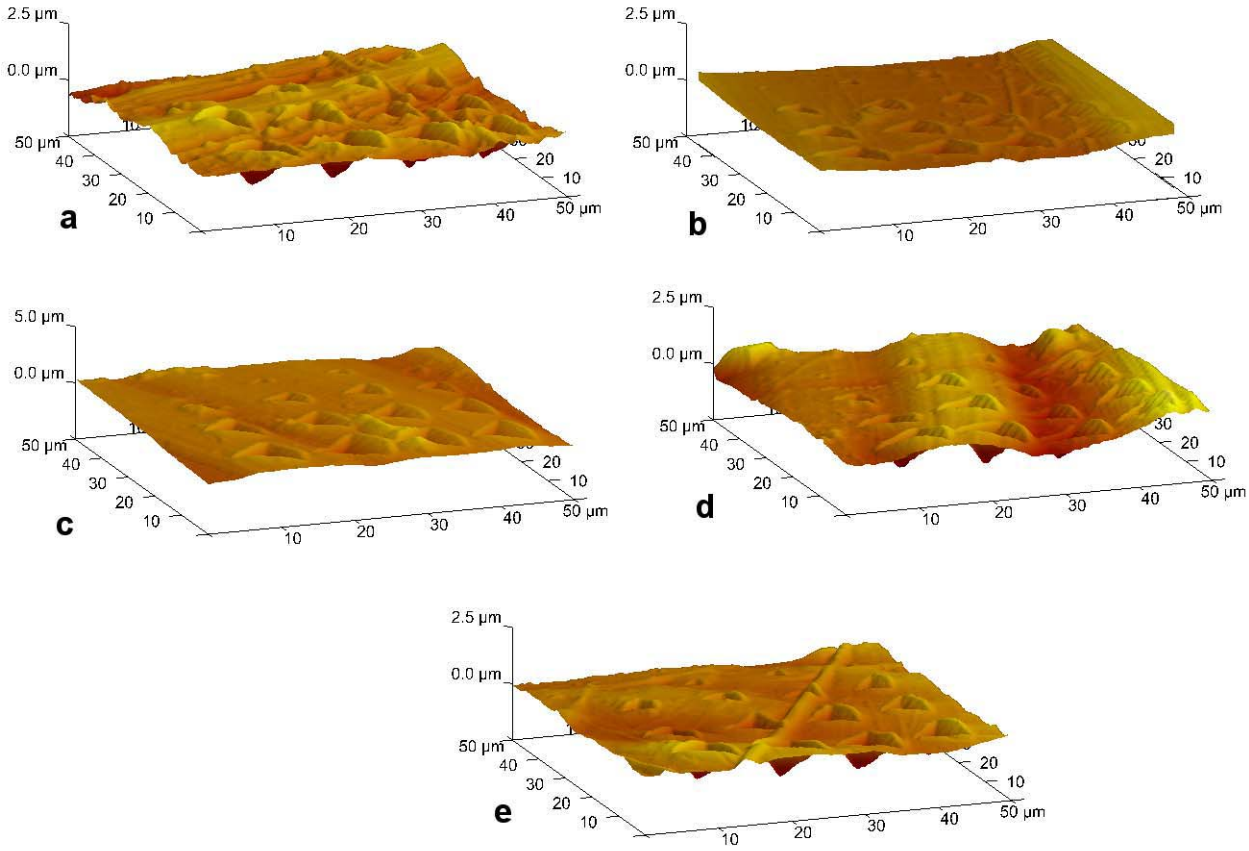


**Figure 8.** AFM images of the indented surfaces of pure PC (a), PC with 2wt% MWCNT (b), PC with 4wt% MWCNT (c), PC with 6wt% MWCNT (d), and PC with 15wt% MWCNT (e).

Pile–up is influencing the measured hardness and Young's modulus in depth sensing nanoindentation experiments. The pile–up increases the area carrying the load compared to the flat surface, consequently the measured hardness and Young's modulus of an indent surrounded by a pile–up bump are smaller than the real ones. Based on measurement of the pile–up height, the decrease of the measured values are less than 10%, which is in the range of the measurement error, so we do not carried out a correction for the pile–ups.

# 4 CONCLUSIONS

Polycarbonate – MWCNT composites has been manufactured by melt extrusion starting from a commercially available masterbatch of PC with 15 wt% of MWCNT produced by CVD process. Extensive nanoindentation experiments were carried out on the samples cut from the PC–MWCNT composites. Young's modulus and hardness of polycarbonate nanocomposites containing MWCNT were found to increase nearly linearly with MWCNT content in the investigated range of concentration. The relative increase of these mechanical properties is about 2 times the MWCNT weight concentration of the composites. So–called pile–ups were revealed around the nanoindentation impressions by AFM investigation in all samples. These pile–ups were most pronounced in the pure PC sample, however within the nanocomposites, the samples with higher MWCNT concentration showed larger pile–ups. Piling–up is reducing the Young's modulus and hardness of the samples, but this effect is expected to be small (<10%). It could be also shown that nanointendation is a suitable method in order to characterize the mechanical properties of nanocomposites containing carbon nanotubes using small sample amounts.

**Acknowledgment**

The authors thank Hyperion Catalysis International Inc. (Cambridge, MA, USA) for providing the material used for sample preparation. We are also grateful for the support within the Carbon Nanotube Network (CNTnet), a thematic network supported by the European Commission. The authors also acknowledge the financial support of the Hungarian OTKA Foundation under contract number T037643, T037952 and T043577.

# 5 REFERENCES

[1] Cs. Balazsi, Z. Konya, F. Weber, L. P. Biro, P. Arato, Preparation and characterization of carbon nanotube reinforced silicon nitride composites, *Mater*. *Sci*. *Eng*. *C* **2003**, *23*, 1133.

[2] M. Cadek, J. N. Coleman, K. P. Ryan, V. Nicolosi, G. Bister, A. Fonseca, J. B. Nagy, K. Szostak, F. Beguin, W. J. Blau, Reinforcement of Polymers with Carbon Nanotubes: The Role of Nanotube Surface Area, *Nano*. *Lett*. **2004**, *4*, 353–356.

[3] L. Chen, M. Z. Qu, G. Zhou, B. L. Zhang, Z. Yu, PC–mediated shortening of carbon nanotubes, *Mater*. *Lett*. **2004**, *58*, 3737–3740.

[4] X. Li, H. Gao, W. A. Scrivens, D. Fei, X. Xu, M. A. Sutton, A. P. Reynolds, M. L. Myrick, Nanomechanical characterization of single–walled carbon nanotube reinforced epoxy composites, *Nanotechnol*. **2004**, *15*, 1416–1423.

[5] P. Pötschke, T. D. Fornes, D. R. Paul, Rheological behavior of multiwalled carbon nanotube/polycarbonate composites, *Polymer* **2002**, *43*, 3247–3255.

[6] O. Hjortstam, P. Isberg, S. Soderholm, H. Dai, Can we achieve ultra–low resistivity in carbon nanotube–based metal composites? *Appl*. *Phys*. *A* **2004**, *78*, 1175–1179.

[7] Y. J. Kim, T. S. Shin, H. D. Choi, J. H. Kwon, Y.–C. Chung, H. G. Yoon, Electrical conductivity of chemically modified multiwalled carbon nanotube/epoxy composites, *Carbon* **2005**, *43*, 23–30.

[8] Artifacts in SPM, TopoMetrix Pamphlet, **1994**, Santa Clara.

[9] C. A. Cooper, S. R. Cohen, A. H. Barber, H. D. Wagner, Detachment of nanotubes from a polymer matrix, *Appl*. *Phys*. *Lett*. **2002**, *81*, 3873–3875.

[10] K.–T. Lau, D. Hui, Effectiveness of using carbon nanotubes as nano–reinforcements for advanced composite structures, *Carbon* **2002**, *40*, 1597–1598.

[11] O, Lourie, H. D. Wagner, Evidence of stress transfer and formation of fracture clusters in carbon nanotube–based

composites, *Compos*. *Sci*. *Technol*. **1999**, *59*, 975–977.
[12] P. Laquerriere, A. Grandjean–Laquerriere, M. Guenounou, D. Laurent–Maquin, P. Frayssinet, M. Nardin, Correlation between sintering temperature of hydroxyapatite particles and the production of inflammatory cytokines by human monocytes, *Colloids and Surfaces B* **2004**, *30*, 207–213.
[13] E. Meyer, Untersuchungen über Härteprüfung und Härte, *Z. Ver*. *Dtsch*. *Ing*. **1908**, *52*, 645–654.
[14] D. Tabor, Indentation hardness: Fifty years on – A personal view, *Phil*. *Mag*. *A*, **1996**, *74*, 1207–1212.
[15] M. F. Doerner, W. D. Nix, A method for interpreting the data from depth–sensing indentation instruments, *J. Mater*. *Res*. **1986**, *1*, 601–609.
[16] W. C. Oliver, G. M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater*. *Res*. **1992**, *7*, 1564–1580.
[17] Carbon nanotubes for static dissipation. *Plastics Additives & Compounding* **2001**, *9*, 20–22.
[18] B. K. Satapathy, R. Weidisch, P. Pötschke, A. Janke, Tough–to–brittle transition in multiwalled carbon nanotube(MWNT) / polycarbonate nanocomposites, *Compos*. *Sci*. *Technol*. **2006** accepted.
[19] B. K. Satapathy, R. Weidisch, P. Pötschke, A. Janke, Crack toughness behavior of multiwalled carbon nanotube (MWNT) / polycarbonate polymer nanocomposites, *Macromol*. **2005**, *26*, 1246–1252.

## Biographies

**Dr**. **Peter M**. **Nagy** is senior scientist at the Chemical Research Centre of the Hungarian Academy of Science, Budapest, Hungary. He is the head of the laboratory for AFM and Nanoindentation investigations within the Department of Surface Modification and Nanostructures. He got his Ph.D. in solid state physics from the Loránd Eötvös University Budapest, Hungary. In 1999 he joined the Chemical Research Centre as an expert in scanning probe microscopy. In recent years his research interest has been widened in direction of nanomechanical testing and nanotribology.

**Dora Aranyi** is Ph.D. student at the Department of Surface Modification and Nanostructures. She obtained her MSc degree at the University of Szeged in Physics. Her main research area is SPM metrology and nanotribology.

**Peter Horvath** is Ph.D. student at the Department of Surface Modification and Nanostructures. He obtained his MSc degree at the Technical University of Budapest in Physics of Condensed Materials. His main research area is SPM metrology and relaxation of nanoindentation impressions.

**Prof**. **Dr**. **Erika Kálmán** is head of Department of Surface Modification and Nanostructures at the Chemical Research Centre of the Hungarian Academy of Science, Budapest, Hungary, Professor at the Technical University Budapest and director of Bay Zoltan Institute for Materials Science.

**Dr**. **Petra Pötschke** is scientist at the Leibniz Institute of Polymer Research Dresden, Germany and heads a working group on melt processed nanocomposites based on carbon nanostructures within the Department of Polymer Reactions and Blends. She got her Ph.D. degree in mechanical engineering from the Technische Universität Dresden, Germany. In 1988 she joined the Institute of Polymer Technology Dresden, now renamed into Leibniz Institute of Polymer Research Dresden. In 2000 and 2001 she was a visiting scholar with Prof. D.R. Paul, Department of Chemical Engineering, University of Texas at Austin, USA, having a grant of the Max–Kade–Foundation. During this time she has started to work in the carbon nanotube composite field. Her main working areas are morphology development in immiscible melt mixed blends, melt rheology, and composites and blends with carbon nanostructures.

**Sven Pegel** is Ph.D. student in Dr. Pötschkes group at the Leibniz Institute of Polymer Research Dresden, Germany. He got his diploma from the Technical University Hamburg–Harburg under the supervision of Prof. Karl Schulte. He performed his work partially at the University of Cambridge, UK and cooperated there with Prof. Alan Windle, Dr. Milo Shaffer and Dr. Jan Sandler. His main working areas are carbon nanotube based melt mixed composites and their characterization using different techniques.