POLYMER COMPOSITES
From Nano- to Macro-Scale
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Klaus Friedrich
Stoyko Fakirov
Zhong Zhang
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Preface

The use of polymer composites in various engineering applications has become state of the art. This multi-author volume provides a useful summary of updated knowledge on polymer composites in general, practically integrating experimental studies, theoretical analyses and computational modeling at different scales, i.e., from nano- to macroscale. Detailed consideration is given to four major areas: structure and properties of polymer nanocomposites, characterization and modeling, processing and application of macrocomposites, and mechanical performance of macrocomposites.

The idea to organize this volume arose from a very impressive workshop — The First International Workshop on Polymers and Composites at IVW Kaiserslautern: Invited Humboldt-Fellows and Distinguished Scientists, which was held on May 22-24, 2003 at the University of Kaiserslautern, Germany. The contributing authors were invited to incorporate updated knowledge and developments into their individual chapters within a year after the workshop, which finally led to these excellent contributions. The success of this workshop was mainly sponsored by the German Alexander von Humboldt Foundation through a Sofja Kovalevskaja Award Program, financed by the Federal Ministry for Education and Research within the “Investment in the Future Program” of the German Government. In 2001, the Humboldt Foundation launched this new award program in order to offer outstanding young researchers throughout the world an opportunity to establish their own work-groups and to develop innovative research concepts virtually in Germany. One of the editors, Z. Zhang, was among the 29 award winners in total, who was supported to establish an independent research team between 2001 and 2005 at the Institute for Composite Materials (IVW), University of Kaiserslautern, hosted by K. Friedrich.

The importance of promoting better knowledge in the field of polymer composites is demonstrated by the contents of this volume, which contains 18 independent chapters. The first part of this volume deals with the topic of structure and properties of polymer nanocomposites. In Chapter 1, Schulte et al. review the state of the art of carbon nanotube-reinforced polymers. The opportunity to apply carbon nanotubes as a filler for polymers and the improvement of the mechanical and functional properties are discussed. The application of non-layered nanoparticles in polymer modification is described by M. Q. Zhang et al. in Chapter 2. A grafting polymerization technique is applied to inorganic nanoparticles, which helps to provide the composites with balanced performance. Chapter 3, authored
 Preface

by Haupert and Wetzel, focuses on the reinforcement of thermosetting polymers by the incorporation of micro- and nanoparticles. Homogeneously distributed inorganic nanoparticles possess the potential to improve the mechanical performance of epoxy at very low filler contents. Privalko et al. present some interesting results concerning the synthesis and structure-property relationships of polyimide reinforced with a sol-gel derived organosilicon nanophase in Chapter 4, which suggest a good potential of low dielectric permittivity materials of this nanocomposite. Chapter 5 by Varghese and Karger-Kocsis focuses on the layered silicate/rubber nanocomposites via latex and solution intercalations. The structure-property relationships are discussed based on the dispersion state of the clay and the aspect ratio of the silicate layers. In Chapter 6, Sreekala and Eger report the property improvements of an epoxy resin by nano-silica particle reinforcement. The incorporation of SiO₂ nanoparticles into a reactive epoxy resin via a sol-gel process generated a new class of nanocomposites with perfect nanoparticle dispersion.

Part II focuses on some special characterization methods and modeling in the field of polymer composites. Chapter 7 by Goda et al. deals with micro-scratch testing and finite element contact and debonding analysis of polymer composites. A finite element macro/micro contact model has been introduced with the displacement coupling technique in order to study wear and failure mechanisms in real fiber-reinforced composites. Chapter 8, authored by Lauke et al., concentrates mainly on the determination of the interface strength of polymer-polymer joints by a curved interface tensile test. A new experimental method for the determination of the adhesion strength between two different materials is proposed and the stress concentration at the interface as a function of applied load is derived by the finite element method. In Chapter 9, Evstatiev et al. present the manufacturing and characterization of microfibrillar reinforced composites from different thermoplastic polymer blends. Various examples of the manufacturing and processing of this new type of polymer-polymer composites are given and their structure-property relationships are investigated. Z. Zhang and Friedrich review the state of the art of the tribological properties of micro- and nanoparticle reinforced polymer composites in Chapter 10. Nanoparticles have a significant influence on the wear performance of polymers and composites.

"Macrocomposites: Processing and Application" is the topic of the third part of this volume. In Chapter 11, Nunes et al. consider the production of thermoplastic towpregs and towpreg-based composites. A purposely built powder-coating equipment was used to make thermoplastic matrix towpregs and pre-consolidated tapes (prepregs) from continuous fibers and a polymer powder. The mechanical properties of the composites were determined in order to assess the efficiency of this new process. Chapter 12 by Mitschang and Ogale deals with the manufacturing of tailored reinforcements for liquid composite molding (LCM) processes. Stitching and sewing processes exhibit high potential to generate various
advanced fiber-reinforced polymer composites based on LCM. Ye et al. describe the deconsolidation and reconsolidation of thermoplastic composites during processing in Chapter 13. A mechanistic model for void growth during thermal deconsolidation, and a transient heat analysis are introduced. An indicative void-closure model and a squeezed creep flow model are further discussed regarding to these important issues during thermoplastic composite processing. In Chapter 14, long fiber-reinforced thermoplastic composites and their automotive applications are discussed by Harmia et al. Advantages in processing and excellent performance suggest the use of these composites in the automobile industry.

In the last part of this volume, the mechanical performance of macrocomposites is considered. Chapter 15 deals with deformation mechanisms of knitted fabric composites. Duhovic and Bhattacharyya provide a general understanding of the sheet forming behavior of knitted fabric thermoplastic composites gained from tensile, dome-forming, cup-drawing and V-bending experiments. Numerical simulations are carried out as well. Chapter 16, entitled “Impact Damage in Composite Laminates”, is authored by Suemasu. A theoretical study, Rayleigh-Ritz approximation and finite element analysis are performed to obtain solutions on various levels of simplification for the damage problem and to clarify the mechanism of the initiation and growth of the low-velocity impact damage. Discontinuous basalt fiber-reinforced hybrid composites are discussed by Czigány in Chapter 17. Basalt fibers produced by melt blowing with proper surface treatments are recommended as a suitable reinforcement for both thermoplastic and thermoset polymers. An accelerated testing methodology for durability of polymer composites is the topic of Chapter 18, authored by Nakada et al. A prediction method of the fatigue strength of polymer composites and structures is introduced, which is applied to various fiber-reinforced plastics (FRP) and FRP/metal joints.

Various groups of readers may find particular interests in this volume: those who are active or intend to become active in the research on some aspects of polymer composites (material scientists, physical chemists, and mechanical engineers); those who have encountered practical problems in using polymer composites and wish to learn more updated approaches to their solution (designers, engineers and technologists in industries dealing with polymer composites’ selection, processing and application); and teachers and students at universities.

Finally, the editors would like to thank all the contributing authors for their excellent chapters. Special gratitude is due to Dr. Greg Franklin, Springer, who contributed strongly to the publication of this volume. We would like also to thank the team in Sofia, Bulgaria, who helped the editorial work.

Klaus Friedrich
Stoyko Fakirov
Zhong Zhang
Editors Biographies

Klaus Friedrich – born in 1945, graduated in Fabrication Technology and in Mechanical Engineering before receiving his Dr.-Ing. (PhD) degree in Materials Science in 1978 from the Ruhr-University Bochum (RUB) in Germany. In addition to his industrial experience as a design engineer and his function as “Chief-Engineer” at the Institute for Materials, RUB, he was associated in 1980 as a Visiting Assistant Professor with the Center for Composite Materials, University of Delaware, USA. After that, he worked for eight years as a Professor of Polymers and Composites at the Technical University Hamburg-Harburg. Since August 1990, K. Friedrich became Research Director for Materials Science at the Institut für Verbundwerkstoffe GmbH (Institute for Composite Materials), University of Kaiserslautern. His major research interests include the fatigue and fracture properties as well as the friction and wear behavior of fiber-reinforced polymeric materials. Recent works are concentrating on fundamental aspects in the manufacturing of high performance composites with thermoplastic matrices. Prof. Friedrich was included in the Advisory Committees of many international conferences, and is a Scientific Board Member of various international journals in the fields of materials science, composites and tribology. In addition, he acted as consultant to various industrial companies within Europe and the USA. Together with his co-workers and students, he has published more than 600 papers in refereed journals and conference proceedings. Further, he is the Editor of three books on Friction and Wear of Polymer Composites, Application of Fracture Mechanics to Composite Materials, and Advances in Composites Tribology, respectively. In 1995, he was appointed as an Honorary Visiting Professor of the Zhongshan University, Guangzhou, China, for his achievements in the field of polymer tribology. At the end of 1996, his research group was awarded the innovation prize of the State of Rhineland-Palatine for applied research in the field of manufacturing of thermoplastic composite components. Besides, Prof. Friedrich has a long established track record in successful grant application from the German Science Foundation (DFG) and other research supporting establishments in Germany and Europe. In March 2001, he received an Honorary Dr. degree (Dr.h.c.) from the Budapest University of Technology and Economics, Hungary, and in June 2004, he was awarded the title of an Honorary Guest Professor of the University of Science and Technology of China, Hefei, which is among the best universities in China.
Stoyko Fakirov – got his MS degree in Chemistry from the Sofia University, Bulgaria, in 1959 and his PhD degree on Structure of Amorphous Polymers (1965) under the guidance of Prof. V. A. Kargin from the Lomonossov State University in Moscow. He received his DSc degree in 1982. In 1972, he became Associate Professor and in 1987, Full Professor of Polymer Chemistry. He is a co-organizer of the polymer education at the Sofia University (with obligatory courses on polymers for all chemistry students), as well as a founder and Head of the Laboratory on Structure and Properties of Polymers at the same university. He acted also as a Vice-Rector of this university for 3 years. Worth mentioning awards are Humboldt Fellow (1971, 88) and Humboldt Research Award Recipient (2000), Fellow of the Ministries of Education of Egypt, India, Spain, Turkey and Portugal, of the Japan Society for Promotion of Science, of the US Information Agency, of NATO-Spain, Member of the Advisory Board of the Institute for Polymer Research Dresden, Member of the Editorial Boards of three international journals on polymers. He has published about 300 papers in international polymer journals, has 11 US patents and contributed to about 150 international polymer meetings as well as delivered more than 100 invited seminar talks worldwide on his areas of interest: structure-properties relationships in polymers and composites, reactions in solid and molten condensation polymers, chemical healing, microfibrillar- and microplate-reinforced composites, microhardness of polymers, gelatin- and starch-based biomaterials. In addition, he acted as author, co-author, editor, co-editor and always as a contributor to 11 books on polymers, as for example, *Transreactions in Condensation Polymers* (1999), *Handbook of Thermoplastic Polyesters* (2002), *Handbook of Condensation Thermoplastic Elastomers* (2004) (all three of Wiley-VCH, Weinheim), *Microhardness of Polymers* (2000), Cambridge University Press, London, *Structure Development during Polymer Processing* (2000) Kluwer, Dordrecht. He was a Visiting Professor at the Universities of Mainz (Germany), Delaware, Newark (USA), Bosphorus, Istanbul (Turkey), Minho (Portugal), Kaiserslautern (Germany), CSIC, Madrid (Spain), NJIT, Newark, NJ (USA), and currently – Auckland (New Zealand). Here, he is focusing on new application opportunities of the concept of microfibrillar-reinforced composites (as developed in joint projects with the University of Delaware and the Institute for Composite Materials of the University of Kaiserslautern). These applications include commodity materials (with improved barrier properties), biomedical materials (scaffolds for tissue engineering and carriers for controlled drug delivery), materials for microelectronics (conductive elements), manufacturing of nanofibrillar reinforced composites, as well as the development of composites based on geopolymers.

Zhong Zhang – born in 1968, is a Guest Professor and a group leader at the Institute for Composite Materials (IVW) of the University of Kaiserslautern, Germany. He obtained his BS, MS, and PhD degrees from the University of Science of Technology of China, Hefei, China in 1990, 1996, and 1999, respectively. His
main research area involves the processing-structure-property relationships of polymers and composites. His research activities were mainly sponsored by the National Natural Science Foundation of China when he worked at the Cryogenic Laboratory (Beijing), Chinese Academy of Sciences between 1990 and 1996. In 1997 and 1998, he joined some world leading institutions, e.g., Karlsruhe Research Centre, Germany, and Rutherford Appleton Laboratory, England, concentrating on low-temperature properties of polymers and composites. Parts of these results on failure processes in resins were of importance to support the design of large (11 m diameter) superconducting magnets for the Atlas experiment at CERN. He started to work at the IVW as an Alexander von Humboldt research fellow in September 2000. In 2001, he obtained a distinguished award from the same foundation, the Sofja Kovalevskaja Award financed by the Federal Ministry for Education and Research within its “Investment in the Future Program”, and especially created for young and highly talented scientists. Zhong Zhang was selected in a worldwide competition as the only one from China, and one of only two in the field of Engineering Science, among 29 Sofja Kovalevskaja Award winners in total. The foundation has granted him one million Euros to establish an independent research team at the IVW from 2001 to 2005. The objective of his research is to investigate the long-term behavior (e.g., tribological, creep and fatigue properties) of short fiber/nanoparticle-reinforced polymer composites, finally leading to an accelerative use of these materials in various industrial applications. Artificial neural networks are also used in his project to predict the performance of these materials as a function of their compositions and testing conditions. Dr. Zhang gave more than 20 invited lectures at world leading institutions, and some keynote and plenary lectures at international meetings. So far, he published more than 80 scientific papers in refereed journals and international conference proceedings.
Part I

Nanocomposites: Structure and Properties
1 Introduction

The investigation of fullerenes and especially of carbon nanotubes (CNT) has opened a totally new window for the development of polymer matrix composites with novel properties and applications. CNT, which have a number of unexpected properties, both mechanical and electrical, seem to have huge potentials as a filler, i.e., as a reinforcement in nanocomposites. With the addition of only 0.05 vol.% of CNT, the authors could achieve an electrical conductivity of less than $10^{-2}$ S/m in an epoxy matrix.\textsuperscript{1,2} With the discovery of carbon nanotubes, the research efforts initially concentrated on the better understanding of their processing conditions, modification, and properties. Initially, the application of CNT as a filler material in matrix polymers in order to improve their properties has not been in the focus of research. However, the CNT potential of quite high mechanical properties gave rise to the assumption that the fracture mechanical properties and, especially, the fracture toughness of polymers can be improved. The extremely low diameter of CNT and their high aspect ratio make them an ideal material to improve the properties of the polymer matrix, compared to glass, carbon, or aramid fibers.
This should lead to a reduced sensitivity to delaminations, as the CNTs, having a diameter which is a couple of hundred times smaller than that of carbon fibers, can reinforce the tiny area in between the fibers of a laminated composite. They should also improve the elastic modulus of the matrix material itself. This last statement is mainly based on theoretical calculations and simulations, which predict a high fracture strength and elastic modulus for carbon nanotubes.\textsuperscript{3,6}

In this chapter, we report technologies to produce CNT-nanocomposites, their resulting microstructures, and their mechanical properties. Tests were performed on various epoxy-based matrices, which were reinforced with catalytically and arc-grown multiple-wall carbon nanotubes (MWCNT). The arc-grown CNT were produced in a furnace, developed at the Technical University Hamburg-Harburg (TUHH), while the catalytically grown CNT were received from various sources. Carbon nanotubes were used as-received, but also after the application of chromatographic filter methods and oxidative chemical treatment. The latter enables a cleaning from the soot and can be used as a first step in the functionalization of the CNT surfaces. The oxidative treatment leads to the formation of carboxylic groups, which support via steric hindrance the dispersion of the tubes and stabilize them in solution or in the matrix material. This is an important step for the homogenous distribution of the CNT in polymers.

For the homogenous dispersion of the CNT in the matrix, a number of techniques were used. The quality of the nanotube distribution in the matrix was inspected by high resolution transmission electron microscopy (TEM).

2 General Problems in Nanocomposite Technology

The term \textit{nanocomposites} means to distribute as much as possible amounts of nanoparticles in a polymer matrix. It has been shown that, when using fiber-reinforced polymers, the maximum amount of fibers in the matrix is about 70 vol.\%.

Actually, the fiber volume fraction in these materials varies between 20 and 60\%. Figure 1 summarizes the values to be achieved for various fillers used in composites. In a volume element of 1 cm\(^3\), it was assumed that we have continuous fibers with a diameter of 10 \(\mu\)m, particles (e.g., talcum) with a diameter of 1 \(\mu\)m, and nanotubes with a diameter of 10 nm. The aspect ratios should be 20, 100, and 1000, respectively. If we further assume a volume content of 30\% for both the fibers and the particles, and only 3\% for the nanotubes, we already have quite interesting results:

The filler element numbers are \(\sim 10^6\) fibers, \(\sim 10^{10}\) particles, and \(\sim 10^{15}\) nanotubes, respectively. The surface area amounts to \(\sim 0.1\) m\(^2\) for the fibers, \(\sim 1\) m\(^2\) for the particles, and \(\sim 100\) m\(^2\) for the nanotubes. There is another important aspect to be found, and that is the distance between the filler elements. For the fibers we calculated a distance of \(\sim 10\) \(\mu\)m, for the particles \(\sim 1\) \(\mu\)m, and for the nanotubes \(\sim 100\) nm.
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Particle size 10 μm 1 μm 10 nm
Volume content 30% 30% 3%
Number of particles \( \sim 10^6 \) \( \sim 10^{10} \) \( \sim 10^{15} \)
Interface \( \sim 0.1 \text{ m}^2 \) \( \sim 1 \text{ m}^2 \) \( \sim 100 \text{ m}^2 \)
Aspect ratio \( \sim 20 \) \( \sim 100 \) \( \sim 1000 \)

Figure 1. Influence of particles on the surface area.

These values already show the problems to overcome. Nanotechnology means that one has to deal with huge surface areas, a vast amount of nanofillers, and a small distance between them.

Figure 2 shows a calculation of the distance between nanotubes depending on their volume fraction. For this example, we assumed to have single-wall carbon nanotubes (SWCNT) with a diameter of \( \text{ca.} \ 1 \text{ nm} \). At a volume fraction of 3%, the distance between two tubes is just two times the diameter (\( \text{ca.} \ 3.2 \text{ nm} \)). If we now assume to have isotactic polystyrene (iPS) as matrix polymer with a chain diameter of 0.8 nm, there is only a small gap for the polymer to penetrate between the tubes.

The main conclusion from this result is that it is extremely problematic to achieve high volume contents of nanotubes in a polymer matrix. All those who
report contents in the range of 10% or more might have agglomerates rather than a proper distribution.

3 Experimental

3.1 Manufacturing of Multiple-Wall Carbon Nanotubes

A number of methods have been developed to produce single- and multiple-wall carbon nanotubes. The most prominent are laser ablation, arc discharge, and catalytic growth (vapor deposition (CVD) and high pressure carbon monoxide (HipCO) process).

In the present chapter, the MWCNT were produced at the TUHH by the arc discharge method in a Klatschmer generator. This method has previously been developed for the production of fullerenes, but today it is a common method to produce MWCNT without having a catalyst. It is based on the ignition of an electric arc between two graphite electrodes. A direct current of 20 to 30 V between the electrodes, in a helium atmosphere at a pressure of about 500 mbar, produces a plasma in which carbon is vaporized from the anode and reorganized at the cathode, forming a cylindrical deposit. During the process, the distance between the electrodes and the current density have to remain constant. Inside the deposit, which has a hard shell of turbostratic graphite, MWCNT are formed. Figure 3 is a scanning electron micrograph showing the nanotube-containing core of such a deposit, produced in a joint venture of TUHH and Trinity College, Dublin. In case that an

Figure 3. Scanning electron micrograph of the core of a deposit produced in a Klatschmer generator. The outer shell, consisting of tropostratic graphite, has been removed. The amorphous core material contains up to 50% multiple-wall CNT.
ultra-fine metal powder (Ni, Fe, Co, Cr) is added to the anode, single-wall carbon nanotubes can be found on the walls of the reactor.

The currently most successfully commercialized route is based on the CVD technique. Catalyst particles, such as Fe, Ni, or other metal catalysts, are introduced onto a substrate which is placed in a furnace. The growth of filaments (carbon nanotubes) is most sensitive to the reaction conditions, such as the pressure of the vaporized carbon source (benzene, toluene, etc.), the purity and flow rate of the carrier gas, the residence time for thermal decomposition, and the temperature of the furnace.

In addition to the arc-grown CNT produced at the TUHH, catalytically grown CNT, received from various sources, were also used.

3.2 Treatment of Carbon Nanotubes

The dispersion of the nanotubes was performed either via direct stirring of the CNTs into the epoxy using an Ultraturrax T-25 disperser, or via a sonication method. The sonicator, a Bandelin Sonoplus HD2200, generates a pulsed ultrasound whereby the nanotubes were dispersed in the epoxy resin.

A purification of the CNTs has been performed by oxidation using a mixture of sulfuric and nitric acid at 100 °C for 3 h. The separation of the oxidized nanotubes from the reaction solution was performed via centrifugation and membrane microfiltration.

The oxidized carbon nanotubes were then functionalized with different types of amines, such as triethylenetetramine, ethylenediamine and polyetheramines. The functionalization has been performed by refluxing a suspension of oxidized CNTs with the amine for 12 h to ensure a quantitative conversion. The separation of the nanotubes from the solution was again performed via centrifugation and membrane microfiltration.

3.3 Matrix Polymers

The epoxy resins Araldite LY556 with the hardener HY932 and Ruetapox LV 0164 with a polyetheramine hardener (Jeffamine® T-403) were used. The Jeffamine® T-403 can be used as hardener and/or as flexibilizer for epoxies and leads to thermosets with improved ductility.

3.4 Electron Microscopy

Transmission electron microscopy (TEM) was performed with an EM400 type microscope from Philips. Scanning electron microscopy (SEM) was performed with a Gemini GSMIC-848 apparatus.
3.5 Dynamic-Mechanical Thermal Analysis

The study of the thermo-mechanical behaviour was performed by dynamic-mechanical thermal analysis (DMTA), using a Gabo Eplexor 500 N equipment. Rectangular specimens, 50 mm long, 5 mm wide, and 2 mm thick, were prepared for the measurements. The tests were performed in tensile mode at a frequency of 10 Hz with a static strain of 0.6% and a dynamic strain of ±0.1%. The samples were measured between −120 °C and 150 °C at a heating rate of 3 °C/min.

4 Results

4.1 Comparison of the Multiple-Wall Carbon Nanotubes Studied

Arc-grown carbon CNT form relatively stiff rods consisting of concentric multiple-wall tubes (Figure 4). Due to this production process, graphitic nanoparticles can be observed next to the tubes. The amount of this so-called soot can exceed 30% of the total material. Therefore, a cleaning process is required before the use of CNT in the production of composites. The catalytically grown carbon nanotubes have not as much soot, but catalyst particle remains are present as dark spots. Figure 5 is a transmission electron micrograph of catalytically grown CNT (produced at the University of Cambridge); CNT are extremely long, highly entangled, and with a cotton-like appearance. The tubes are highly crystalline, but compared to the arc-grown ones, they have a very high defect concentration, mainly within the outer

![Figure 4](image)

*Figure 4. Transmission electron micrograph of arc-grown carbon nanotubes. A high amount of carbon nanotubes and the soot consisting of graphitic nanoparticles and carbon black are clearly seen.*
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Figure 5. Transmission electron micrograph of catalytically grown multiple-wall carbon nanotubes with less impurities, but with a higher defect density and strongly entangled layers, which should affect the mechanical properties. Figure 6 is a scanning electron micrograph of CVD-grown MWCNT; they grow perpendicular to the catalyst but are extremely parallel and, in addition, pronounced entanglements forming the cotton-like structure are seen. Figure 7 is a transmission electron micrograph of CVD-grown MWCNT; the catalyst particles and the high defect density are clearly seen. These two findings suggest that arc-grown carbon nanotubes have a much lower defect density than the CVD tubes. As they are less entangled, they can be more easily dispersed than the catalytically grown tubes.
4.2 Purification

As both the CVD- and arc-grown carbon nanotubes have impurities (amorphous carbon or catalyst residues), they should be cleaned. A number of purification methods have been described in the literature. In addition to chromatographic methods, the oxidative technique has been successfully used,\textsuperscript{10-16} by taking into account the differences in the thermodynamic stability of carbon black, graphite, and the nanotubes. The wet chemical oxidation with a solution of sulfuric and nitric acids has been shown to be effective. In our studies, the nanotubes were refluxed in a solution of 3 parts of sulfuric and 1 part of nitric acid for 3 h at 130 °C. After centrifugation or membrane micro-filtration and washing with water, the nanotubes were refluxed for a couple of hours in a dilute sodium hydrogen carbonate solution to really eliminate the remaining acids. TEM clearly showed a reduction in impurities.

It could be also observed that, due to this purification process, the nanotubes start to be oxidized first at their caps and structural defects, and that functional groups (mainly carboxylic, which can be used for further modification) are formed on the surfaces (Figure 8). As this process injures the tubes, the caps of the
nanotubes can be opened or totally disappear (Figure 9), which is a disadvantage of the oxidative technique. The catalysts do not only help the formation and build up of CNT; in this special case, they also contribute to the degradation of nanotubes.

Figure 9. Transmission electron micrograph of oxidized carbon nanotubes. The opening of the caps due to the formation of functional groups is clearly seen.

4.3 CNT/Epoxy Composites: Dispersion, Matrix Bonding, and Functionalization

4.3.1 Dispersion

The use of nanoparticles as reinforcement elements in polymers is a common method to improve the mechanical and/or electrical properties of composites. The improvement of the fracture mechanics properties by the addition of particles can be achieved when a sufficiently good interaction between the nanoparticles and the matrix polymer takes place and when the particles are well dispersed within the matrix.

Our studies aimed at the improvement of the mechanical properties of epoxies by the addition of multiple-wall carbon nanotubes. The quality of the dispersion and the possible interaction between the CNT and the epoxy were investigated by light microscopy. For the homogeneous distribution of carbon black in an epoxy matrix, it was sufficient to use a high-speed disperser (Ultraturrax T-25), but for the dispersion of nanotubes this approach was not optimal (Figure 10a). The nanometer-scale size of the CNT and their aspect ratio make it necessary to develop new dispersion techniques in order to brake up the intermolecular bonds, leading to the formation of agglomerates.

In this respect, sonication has been found to be a promising alternative. A suspension of the CNT in an appropriate solvent (acetone) can be sonicated with a pulse ultrasound to break up the agglomerates. This suspension can later be mixed with the epoxy and the solvent is evaporated by simple heating. The nanotubes were sonicated for 20 min at a 30% amplitude, mixed with the epoxy resin and
sonicated again for 10 min. During sonication, the samples have to be cooled to avoid curing of the composite. Finally, the composites were cured for 5 h at 80 °C and for 3 h at 130 °C in vacuum for the post curing. This approach allowed to substantially reduce the size of the agglomerates (Figure 10b).

A further reduction of the agglomerate size can be achieved by a combination of sonication and oxidative cleaning. The functional groups which develop on the surfaces on the CNT lead to steric hindrance and electrostatic interactions with the solvent, hence to a better distribution of the nanotubes in the epoxy matrix (Figure 11).

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*Figure 10.* Light microscopy of a series of CNT/epoxy nanocomposites with different amounts of nanotubes: (a) CVD-grown CNT, 0, 0.1, 0.2, and 0.4 wt.%; (b) arc-grown carbon nanotubes, 0.4, 0.8, and 1.5 wt.%. The arc-grown carbon nanotubes tend to show less agglomerations than the CVD-grown CNT.

*Figure 11.* Transmission electron micrograph of a CNT/epoxy composite. Oxidation followed by sonication leads to an improved dispersion.