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Surface modified multi-walled carbon nanotubes in CNT/epoxy-composites

Florian H. Gojny [a], Jacek Nastalczyk [a], Zbigniew Roslaniec [b], Karl Schulte [a,*]

[a] *Polymer Composites, Technical University Hamburg-Harburg (TUHH), Denickestraße 15, D-21073 Hamburg, Germany*
[b] *Technical University Szczecin, Al. Piastów 48, Pl-70310 Szczecin, Poland*

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Abstract

Multi-walled carbon nanotubes (MWCNTs), produced by arc-discharge method, were treated with oxidising inorganic acids. The surface modification of the oxidised nanotubes (o-MWCNTs) was achieved by refluxing the tubes with multi-functional amines. The functionalised nanotubes were embedded in the epoxy resin and the resulting composite was investigated by transmission-electron microscopy (TEM). The functionalisation led to a reduced agglomeration and evidences are given for improved interaction between the nanotubes and the epoxy resin.
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1. Introduction

Since the first observation of carbon nanotubes in 1991 by Iijima [1] and the awareness of their novel mechanical and electrical properties [2–4], an extensive research in the field of CNT/polymer-nanocomposites has started. The introduction of carbon nanotubes as a structure element in nanocomposites should improve the material properties and therefore a large variety of applications, such as devices in nanoelectronics, field emitters or reinforcing materials are imaginable. However, due to their limited availability together with the high purchasing costs, only a few of these applications have been realised, yet. The progress in bulk synthesis and purification [5–7] make carbon nanotubes available in larger quantities at falling prices.

The progress in developing nanocomposites with carbon nanotubes approves their function as a reinforcing structural element. Studies using MWCNTs in polymer-composites reported an increased storage modulus [8,9].

The interfacial interaction between the nanotubes and polymer is one of the issues of nanocomposites. First experimental work focusing on the interfacial interaction in MWCNT/epoxy-nanocomposites was performed by Cooper et al. [10]. They investigated the detachment of MWCNTs from an epoxy matrix. In a special pull-out test for individual nanotubes values for the interfacial shear strength were determined varying from 35 to 376 MPa. This large variation and the fact that no

* Corresponding author. Fax: +49-40-42878-2002.
E-mail address: schulte@tuhh.de (K. Schulte). *URL:* http://www.tu-harburg.de/kvweb.

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Samsung Ex. 1014, Page 1 of 5
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00357

dependence on the size of interface and the shear strength could be observed requires further investigations.

Our research is focused on the evaluation of nanotube/epoxy-composites. The realisation of nanotube reinforced epoxies requires a homogeneous dispersion and strong interfacial interaction between the nanotubes and the polymer. We suppose that the use of MWCNTs as reinforcing elements in epoxies suffers from weak interfacial interactions.

An enhancement of the compatibility to the composite material can be achieved by a chemical modification of the MWCNTs, which could link nanotubes directly to the matrix. This linkage can be achieved by a reaction of functional groups with the epoxy, which enables a stress transfer between the polymer and the CNTs. The effect of a linkage between the nanotubes and the polymer, which should lead to improved interfacial interactions, is confirmed by calculations by Frankland et al. [11]. They predict that a functionalisation of less than 1% would improve the interaction between nanotubes and the polymer without decreasing their strength significantly.

In this Letter we present a procedure for a surface modification of carbon nanotubes which leads to a reduced agglomeration and furthermore, some evidences are given which indicate an improved interfacial interaction between the functionalised CNTs and the epoxy resin.

2. Experimental

The multi-walled carbon nanotubes used in this studies were arc-grown material produced at TUHH or obtained by MER Inc. The nanotubes were heated with an excess of a mixture of sulphuric and nitric acid in order to remove impurities of carbon black and graphite nanoparticles. These oxidised MWCNTs were separated by centrifugation and membrane micro-filtration (Millipore Durapore Membrane) and washed with distilled water and acetone.

In a second step the oxidised nanotubes were heated with an excess triethylenetetramine, again separated by centrifugation and membrane micro-filtration, and finally washed with acetone. For the preparation of the nanocomposites, a suspension of oxidised MWCNTs in acetone and of amino-functionalised nanotubes in acetone were sonicated for 30 min and finally slowly dispersed in heated epoxy resin (Ruetapox 0164/LV). After cooling down to room temperature the hardener Ruetadur Teta was added to each of the two samples and finally cured for 24 h at room temperature.

3. Results and discussion

Our procedure to improve the interaction with the matrix is comparable to previous work by Chen et al. [12] using an ionic functionalisation to improve the stability of single wall carbon nanotube (SWCNT) suspensions. In order to remove amorphous carbon, we treated the nanotubes with oxidising inorganic acids. Besides the fast removal of these thermodynamically less stable impurities, a much slower oxidation of the nanotubes, starting at structural defects and at the caps of the tubes, occurs [13]. Through this treatment the outer shells were destructed to some extent, but carboxylic groups appear on the surface. The reaction of the oxidised nanotubes with triethylenetetramine leads to a mixture of covalently and ionically bonded amines on the surface of the nanotube. The ionic form of the functionalised nanotubes can be transformed into the covalent bonded amide by removing water while heating in vacuum. The main reasons for the choice of this functionalisation are: (i) the advantage of high yields and (ii) in particular the possibility of scaling up this procedure to larger scales, which is necessary for a potential technical application. The investigation via TEM showed that the agglomeration could be reduced by the introduction of functional groups. The steric and electrostatic repulsion of the functional groups lead to a better dispersion of the nanotubes (Fig. 1).

The presence of carboxylic acid groups on the surface enables a better dispersion of CNTs and reduces the amount of impurities. The nanotube/matrix interactions of oxidised MWCNTs and the epoxy resin seem to be still weak and as a conse-

Samsung Ex. 1014, Page 2 of 5
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00357

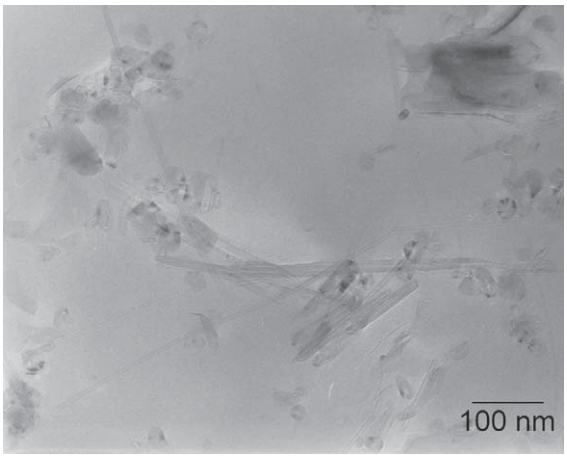

Fig. 1. TEM image of oxidised MWCNTs embedded in epoxy resin. The tubes are completely dispersed in the matrix due to the appearance of carboxylic groups on the surface.

quence of this, the stress transfer from the matrix to the tube is low and pull-outs of the CNTs from the surrounding matrix were observed (compare Fig. 2).

A further chemical derivatisation seems to be useful in order to make the outstanding properties of the carbon nanotubes accessible for an application as a reinforcing filler in epoxies.

This derivatisation of the oxidised MWCNTs was achieved by a reaction with triethylenetetramine. These introduced functional groups lead to covalent bonds with the epoxy resin. The TEM-micrographs (Fig. 3) of functionalised nanotubes in the same epoxy resin shows CNTs that are completely covered with matrix. A further evidence for a strong interaction is telescopic pull-out, which is a typical damage mechanism for MWCNTs under tensile load (Fig. 3e). The outermost layer, which is directly bonded to the matrix, remains in the matrix, while the inner-tube bridges the crack. The interactions between the shells of a MWCNT seems to be weaker than those to the matrix, as we can assume only van-der-Waals forces between the shells [14].

Fig. 4 gives some examples with matrix remaining on the caps and along sidewalls of the CNT. Initial points for the oxidation of the MWCNTs are the caps and structural defects along the sidewalls, where accordingly the density of functional groups is higher than on the non-oxidised sidewalls, which enables the matrix bonding.

It has to be mentioned that the oxidation leads, besides the introduction of functional groups, to structural defects, which may decrease the potential strength of the nanotubes. We suppose that the

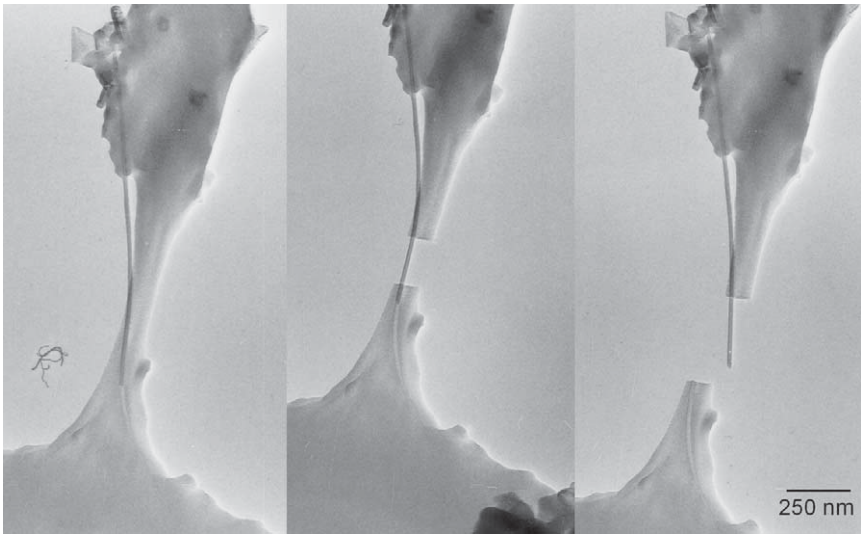

Fig. 2. A weak interaction between the epoxy matrix and the nanotube leads to pull-out.

Samsung Ex. 1014, Page 3 of 5
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00357

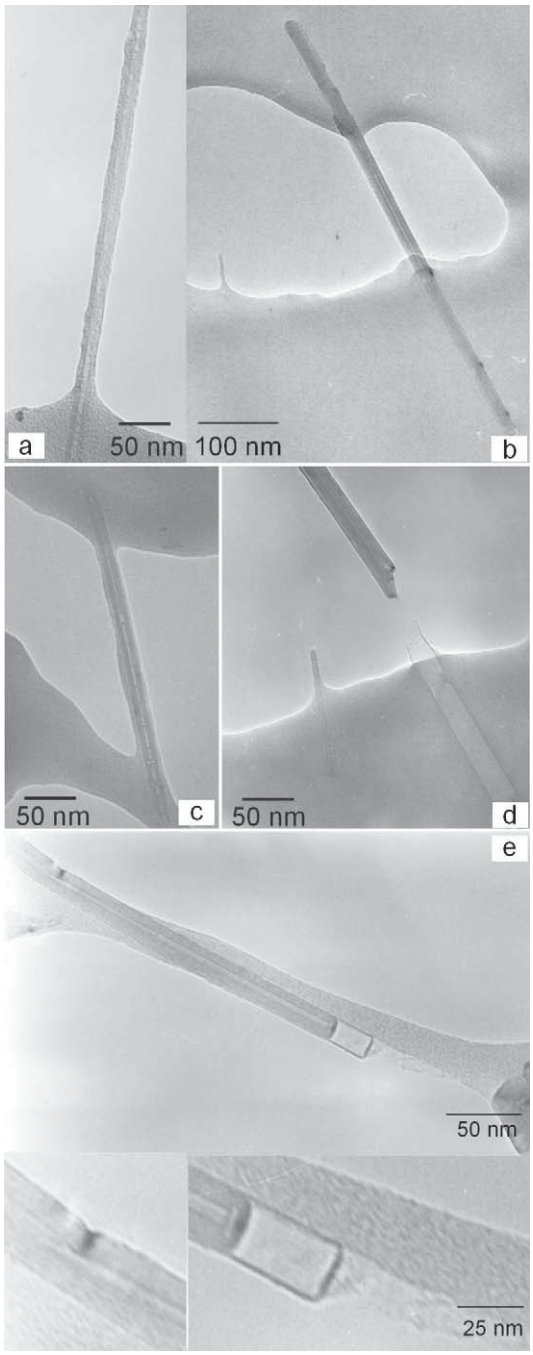

Fig. 3. TEM image of functionalised MWCNTs. (3a) Matrix covers the surface of the carbon nanotubes which indicates an improved interaction. (3b and 3c) Nanotubes should improve the fracture toughness by bridging micro-cracks and pores in the matrix. (3d and 3e) Telescopic pull-outs substantiate the evidence of improved interactions.

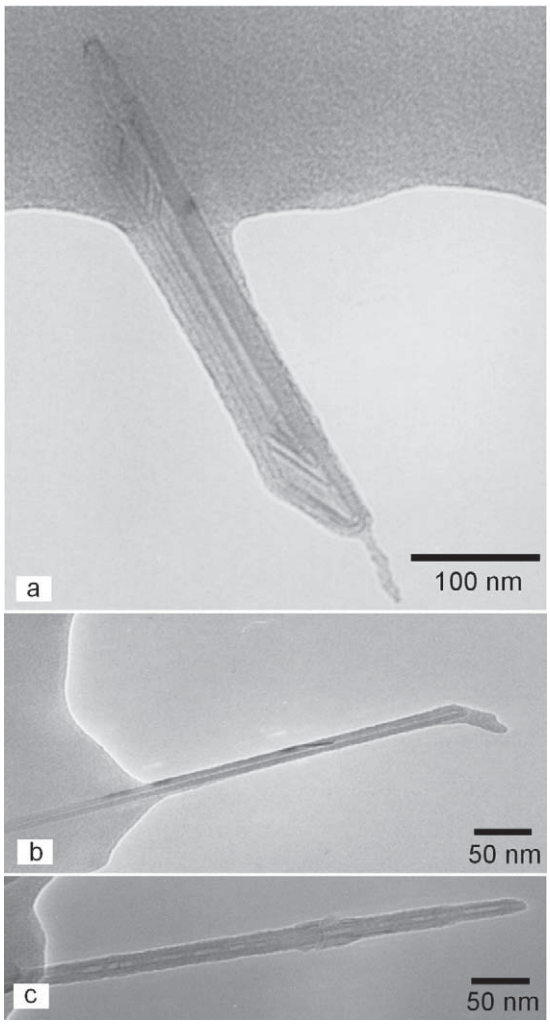

Fig. 4. Initial points for oxidation are the tensile caps and structural defects.

degree of oxidation and accordingly, the degree of functionalisation has a certain influence on the mechanical properties of the resulting composite. A widely destructed surface leads to a debonding of the nanotube whereas the inner concentric tubes are pulled out and parts of the outer shells, which are bonded to the matrix, remain in the matrix.

4. Conclusion

A chemical functionalisation of MWCNTs can be a useful tool to improve the dispersion of the

Samsung Ex. 1014, Page 4 of 5
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00357

nanotubes in an epoxy system. The investigation of the CNT/epoxy-nanocomposites via TEM gives evidences for improved interfacial interaction between the functionalised nanotubes and the matrix. These interactions should be strong enough to potentially increase the mechanical properties of carbon nanotube reinforced epoxy-composites. The investigation of the effect of surface modification of the CNTs on the mechanical properties of CNT/epoxy-nanocomposites is part of the ongoing research.

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Samsung Ex. 1014, Page 5 of 5
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00357