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Nanotechnologies — Characterization of multiwall carbon nanotubes — Mesoscopic shape factors

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Foreword

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Introduction

Multiwall carbon nanotubes (MWCNTs) synthesized by chemical vapor deposition (CVD) are of growing interest for use in polymer composites and conductive coatings. In many cases, MWCNTs synthesized by CVD have static (permanent) bend points randomly distributed along their axis. Physical and chemical properties of mass-produced MWCNTs are strongly dependent on the statistical distribution of mesoscopic shapes and sizes of the individual MWCNT (see ISO/TS 80004-3), among other parameters, that comprise the mass produced product (see References [3] to [5]). It is therefore crucial to characterize the mesoscopic shapes of MWCNTs in order to help ensure that the final properties are reproducible for use in a wide range of materials including composites and other dispersions, as well as for Environment, Health and Safety (EHS) issues[6].

This Technical Specification provides methods for the characterization of mesoscopic shape factors of MWCNTs, including sample preparation procedures. In particular, it provides a statistical method for characterizing MWCNTs produced by the CVD method. During MWCNT synthesis, axial structures are not perfectly linear but include permanent bend points. This Technical Specification provides methods for determining a statistical quantity, representing a maximum straight length that is not deformed by permanent bending called the “static bending persistence length” (SBPL). The SBPL gives information regarding the relationship between the MWCNT mesoscopic shape and size. If two MWCNTs of equal length have different SBPL, their overall sizes (e.g. radius of gyration or an equivalent diameter such as a hydrodynamic diameter) will also be different from one another. In practical applications, the variation in SBPL affects both chemical reactivity and physical properties[3][4][5].

Electrical conductivity and dimensional stability of MWCNT-polymer compounds are also strongly dependent on the SBPL of the MWCNT used to make them[3][4][5]. Various properties might be affected by SBPL, including electrical percolation threshold[5][7], toxicity[6], thermal conductivity[8], rheological property[9], and field emission property[10]. SBPL could be useful for estimating the loading of a polymer CNT matrix to achieve electrical conductivity (percolation limit) and should also assist with modelling the mechanical properties of polymer-CNT composites with different loadings.

Prior to commencing any work, readers are advised to familiarise themselves with the latest guidance on handling and disposal of MWCNTs, particularly in relation to the use of appropriate personal protective equipment. Information on current practices is available in ISO/TR 12885.

Nanotechnologies — Characterization of multiwall carbon nanotubes — Mesoscopic shape factors

1 Scope

This Technical Specification describes methods for the characterization of mesoscopic shape factors of multiwall carbon nanotubes (MWCNTs). Techniques employed include scanning electron microscopy (SEM), transmission electron microscopy (TEM), viscometry, and light scattering analysis.

This Technical Specification also includes additional terms needed to define the characterization of scattered bending persistence length (SBPL). Two approximation methods are given for the evaluation of SBPL (which generally varies from several tens of nanometers to several hundred micrometers).

Well-established concepts and mathematical expressions, analogous to polymer physics, are utilized for the definition of mesoscopic shape factors of MWCNTs.

2 Terms, definitions and abbreviations

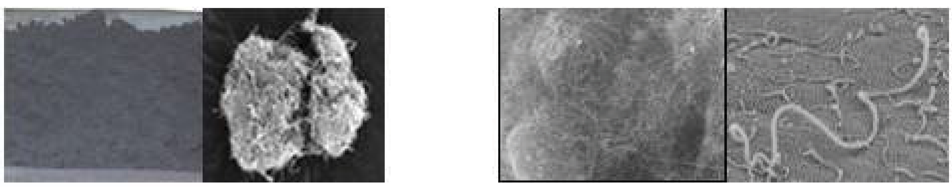
2.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

NOTE Equations for terms and definitions are given in Annex A.

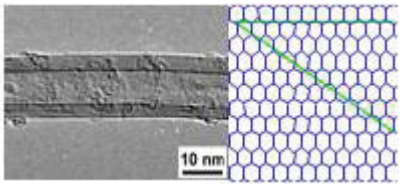
2.1.1
mesoscopic shape
description of shape at the observation scale for an individual multiwall carbon nanotube (MWCNT)

NOTE 1 Mesoscopic shape factors describe the average size and shape of individual MWCNTs, while “macroscopic” describes the shape and size of MWCNT aggregates or agglomerates. “Atomic scale resolution” describes the shape of an MWCNT at the atomic level (see Figure 1).



a) Macroscopic (aggregates) **b) Mesoscopic (individual)**

Figure 1 — Shape of MWCNTs at various scales (*continued*)



c) Atomic scale resolution

NOTE 2 See Reference [3].

NOTE 3 Copyright (c) 2010 ACS.

Figure 1 — Shape of MWCNTs at various scales

2.1.2
regular shape
⟨MWCNTs⟩ property of having regular pattern along tube axis

NOTE Correlations in the direction of the tangent show a periodical shape for MWCNTs of regular shape. Both straight and coil-shaped MWCNTs are typically classified as MWCNTs of regular shape.

2.1.3
random shape
⟨MWCNTs⟩ property of having static, or permanent, bend points distributed randomly (Gaussian) along their axis

2.1.4
SBPL
static bending persistence length
l_{sp}
maximum straight length without static bending

2.1.5
contour length
L
total length of an MWCNT along its axis

2.1.6
weighted average contour length
$\overline{L}_w$
average of contour length which is assigned a weight

2.1.7
end-to-end distance
R
straight distance between the two ends of an MWCNT

2.1.8
bending ratio
D_b
ratio between mean-squared end-to-end distance and squared contour length

2.1.9
intrinsic viscosity
$[\eta]$
description of an MWCNT's contribution to the viscosity of MWCNT dispersion

2.2 Abbreviated terms

CVD chemical vapor deposition

DDLS depolarized dynamic light scattering

DLS dynamic light scattering

DMF dimethylformamide

SEM scanning electron microscope

SBPL static bending persistence length

TEM transmission electron microscopy

3 Sample preparation methods

3.1 Ball mill cutting

Place 200 mg of MWCNTs and 20 ml of ethanol and zirconia balls into a zirconia pot (150 ml) and ball-mill 500 r/min for 2 h.

Pour the ball-milled MWCNT dispersion from the zirconia pot into a 50 ml conical centrifuge tube at 5 000 r/min.

Centrifuge the ball-milled MWCNT dispersion to separate the MWCNTs and then freeze-dry the separated MWCNTs for 24 h. Dry the MWCNTs at 300 °C for 30 min while exposed to air to remove unwanted volatile components.

Grind the dried MWCNTs by pestle and mortar.

NOTE When higher r/min and longer ball-milling time is applied than those described here, the structure of MWCNTs might be destroyed.

3.2 Dispersion method

Disperse 0,02 g of milled MWCNTs in 200 ml dimethylformamide (DMF) using an ultra-sonicator at 40 W for 3 h. Pour the MWCNT dispersion into a 50 ml conical centrifuge tube and centrifuge at 3 000 r/min for 30 min. Filter the dispersion with a paper filter to eliminate any non-dispersed parts that might remain.

NOTE DMF is the best solvent for CNT dispersion (see Reference [3]).

3.3 Sample preparation for scanning electron microscope

Use additional DMF to dilute the MWCNT dispersion to 10x. Drop 1 ml of the 10x dispersion onto a 0,02 µm ceramic filter and filter it under vacuum. Dry the ceramic filter, containing the MWCNTs, at 60 °C for 24 h.

NOTE This procedure is recommended for Method 1 (see 4.1.2.1) and Method 3 (see 4.1.2.3). As-synthesized MWCNTs can be used for Method 2 (see 4.1.2.2).

4 Experimental procedure

4.1 Measurements of the SBPL using SEM

4.1.1 SEM

4.1.1.1 General

High resolution SEM images allow closely spaced features to be examined at a high magnification.

4.1.1.2 Preparing SEM images

Cut the ceramic filter containing the MWCNTs into small pieces and place on a sample holder, to which conductive tape is applied. Dry the sample holder under vacuum at 40 °C for 1 h. Sputter coat the dried sample with iridium for 1 min. Gold or platinum may be used if an iridium source is not available. Take three or more SEM images at a magnification of 10 000x. Take three or more representative high resolution images at 20 000x.

NOTE 1 This procedure is recommended for Method 1 (4.1.2.1) and Method 3 (4.1.2.3).

Alternatively, place an as-synthesized MWCNT on a sample holder, to which conductive tape is applied. Dry the sample holder under vacuum at 40 °C for 1 h. Sputter coat the dried sample with iridium for 1 min. Gold or platinum may be used if an iridium source is not available. Take three or more SEM images at a magnification of 10 000x. Take three or more representative high resolution images at 20 000x.

NOTE 2 This procedure is recommended for Method 2 (see 4.1.2.2).

4.1.2 Measurement methods for the SBPL

4.1.2.1 Method 1

From the SEM images, determine the contour lengths and end-to-end distances of at least 100 different individual MWCNTs. Classify the data using an interval of 100 nm for contour length. For each contour length range, calculate mean-squared end-to-end distance.

Obtain the bending ratio for each contour length range by dividing the mean-squared end-to-end distance by squared average contour length [see Equation (A.3)]. When the contour length is greater than 1μm, the value of contour length from the top view image may be underestimated by up to 15 %[3]. When more accurate values are required, measure the contour length and end-to-end distance using a 3-D image, which can be obtained by several side view images[3].

Plot the bending ratio with respect to the reciprocal contour length, measure the gradient and determine the SBPL using Equation (A.4). When the linear relationship between bending ratio and reciprocal contour length reaches the asymptotic limit, the resulting slope equals 2 times the SBPL.

NOTE 1 For MWCNTs of random shape, the end-to-end distance varies at constant contour length[3]. Therefore, various values of end-to-end distance could be measured for each contour length range. The distribution of end-to-end distance of MWCNT is Gaussian for each contour length range when MWCNT are in random shape. To obtain the mean-squared end-to-end distance, calculate the mean value of the squared end-to-end distance.

NOTE 2 Because well-dispersed MWCNTs are filtered prior to SEM imaging, 100 MWCNTs are sufficiently representative of the shape of the MWCNTs in the sample. This is supported by dynamic light scattering (DLS) and depolarized dynamic light scattering (DDLS) measurements as well as intrinsic viscosity measurements[3]. An approximate value for the SBPL can be obtained using Method 2 or Method 3.

4.1.2.2 Method 2

Measure the radius of curvature of at least 100 individual tubes from the SEM images of as-synthesized MWCNTs, then calculate the mean value of the radius of curvature. This mean radius is approximately equal to the value of SBPL.

4.1.2.3 Method 3

From the SEM image, select at least 10 MWCNTs with a contour length in the range of $2{,}0 \pm 0{,}2\ \mu m$. Measure the end-to-end distance of each MWCNT. The approximate value for SBPL can be obtained from the mean-squared end-to-end distance and the squared average contour length [see Equations (A.3) and (A.4)].

NOTE 1 Method 1 is the most accurate method but it is time consuming. The SBPL estimated by Method 2 has up to 20 % deviation compared to Method 1 (Method 2 has a tendency to underestimate the SBPL). The SBPL estimated by method 3 has up to 100 % deviation compared to the value obtained by Method 1. The order of magnitude of SBPL has consequences for many applications such as transparent conductive film, electrode and polymer composites.

NOTE 2 The values of SBPL obtained by Methods 1, 2, and 3 can be confirmed by the viscometry method (Annex B) and/or the light scattering method (Annex C).

4.2 Measuring inner and outer diameters of MWCNTs using TEM

Place a droplet of the diluted, MWCNT/DMF dispersion onto a carbon-coated copper grid. Dry the grid at 60 °C for 24 h. Take TEM images at 10 000x magnification. Take three or more high resolution images at 1 000 000x to 3 000 000x of the MWCNT.

In order to obtain averages, measure the inner and outer diameters at not less than three different positions along the axis for at least 10 different MWCNTs. At least 30 total measurements are required.

5 Test report

The test report shall contain the following information (see Annex D):

a) a full description of the sample preparation method(s) used;

b) average inner and outer diameter;

c) method used to determine SBPL;

d) SBPL;

e) all information necessary for evaluating the SBPL.

The test report may also include information relating to weighted average contour length and bending ratio (optional).