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Nanotechnologies — Carbon nanotube suspensions — Specification of characteristics and measurement methods

Nanotechnologies — Suspensions de nanotube de carbone — Spécification de caractéristiques et méthodes d'essais

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Carbon nanotubes (CNT) have attracted great interest due to their wide scope of possible applications, such as composite reinforcement material, hydrogen containers, super-capacitors, molecular sensors and scanning probe tips. Offering attractive mechanical, electric and thermal properties, CNTs could achieve a significant improvement in bulk properties by adding low weight percentages.

The performance of nano-objects can be degraded with the formation of agglomerates or aggregates in post-processing. Suspensions of the appropriate fluids and additives will stabilize nano-objects, preventing agglomeration and reducing losses to the environment during handling. It is widespread practice in the manufacturing industry to pre-treat nano-objects by making suspensions before delivery to the downstream customers. Industrial products based on CNT suspensions are a good example.

Since CNT suspensions containing multi-walled carbon nanotubes (MWCNTs) are widely supplied nowadays, it is timely to develop appropriate specifications. Such specifications would facilitate the communication between interested parties and the commercialization of CNT suspensions, and help to generate consistent performance in the final products.

A number of characterization documents related to CNT have been developed by ISO/TC 229, in which measurement methods and procedures for characteristics including morphology, impurities, volatile components, etc. are specified. This document specifies the characteristics to be measured of CNT suspension samples and describes their measurement methods. ISO/TR 10929 describes the characteristics to be measured of bulk samples of MWCNTs and their measurement methods. ISO/TR 13097 provides guidelines on how to characterize the stability of suspensions. It includes general guidance on how to specify the suspension in terms of its physical and chemical characteristics, which might affect its performance or subsequent processing.

Nanotechnologies — Carbon nanotube suspensions — Specification of characteristics and measurement methods

1 Scope

This document specifies the characteristics to be measured of suspensions containing multi-walled carbon nanotubes (CNT suspensions). It includes the essential and additional characteristics of the CNT suspension, and the corresponding measurement methods.

Characteristics specific to health, environmental and safety issues are excluded from this document.

WARNING — The use of this document can involve hazardous materials, operations and equipment. It does not purport to address all of the safety or environmental problems associated with its use. The execution of this document is entrusted to appropriately qualified and experienced people.

2 Normative references

There are no normative references in this document.

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1.1
agglomerate
collection of weakly or medium strongly bound particles where the resulting external surface area is similar to the sum of the surface areas of the individual components

[SOURCE: ISO/TS 80004-2:2015, 3.4, modified — Notes 1 and 2 to entry have been deleted.]

3.1.2
aggregate
particle comprising strongly bonded or fused particles where the resulting external surface area is significantly smaller than the sum of surface areas of the individual components

[SOURCE: ISO/TS 80004-2:2015, 3.5, modified — Notes 1 and 2 to entry have been deleted.]

3.1.3
carbon nanotube
CNT
nanotube composed of carbon

Note 1 to entry: Carbon nanotubes usually consist of curved graphene layers, including single-wall carbon nanotubes and multi-walled carbon nanotubes.

[SOURCE: ISO/TS 80004-3:2010, 4.3]

3.1.4
carbon nanotube suspension
CNT suspension
suspension containing multi-walled carbon nanotubes

Note 1 to entry: Single-wall carbon nanotubes may be included in the suspension.

3.1.5
representative sample
random sample selected in such a way that the observed values have the same distributions in the sample as in the population

[SOURCE: ISO 3534-2:2006, 1.2.35, modified — EXAMPLE and Notes 1 and 2 to entry have been deleted.]

3.1.6
shelf life
recommended time period during which a product (CNT suspension) can be stored, throughout which the defined quality of a specified property of the product remains acceptable under expected (or specified) conditions of distribution, storage, display and usage

[SOURCE: ISO/TR 13097:2013, 2.14, modified — "(CNT suspension)" has replaced "(dispersion)".]

3.1.7
dry solid content
mass fraction of substances remaining after completion of a specified heating process

Note 1 to entry: Adapted from ISO 13580:2005, 3.1.

3.1.8
suspension
heterogeneous mixture of materials comprising a liquid and a finely dispersed solid material

[SOURCE: ISO/TS 80004-6:2013, 2.13]

3.1.9
viscosity
measure of the internal friction of a fluid when caused to flow by an external force

[SOURCE: ISO 13503-1:2011, 2.14]

3.1.10
volume resistivity
quotient obtained when the potential gradient is divided by the current density

[SOURCE: ISO 472:2013/Amd.1:2018, 3.17, modified — Note 1 to entry has been deleted.]

3.2 Abbreviated terms

CNT	carbon nanotube
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-OES	inductively coupled plasma-optical emission spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
MWCNT	multi-walled carbon nanotube
SEM	scanning electron microscopy
TEM	transmission electron microscopy

4 Characteristics and measurement methods

Given the various applications of CNT suspension, the characteristics to be measured are different for desired applications. These characteristics in this document are classified into two categories:

a) the essential characteristics of CNT suspension that shall be measured for all applications;

b) the additional characteristics of CNT suspension that should be measured depending on specific applications.

The essential characteristics of both a CNT suspension and its constituent CNTs listed in Table 1 shall be measured and reported to the buyer. The additional characteristics of CNT suspension listed in Table 2 should be measured depending on applications.

The measurement method for each characteristic is provided in Tables 1 and 2.

The CNT suspension characteristics are summarized in Annex A.

Table 1 — Essential characteristics of CNT suspension and measurement methods

Characteristics	Measurement methods
Outer diameter	See 6.1
Specific surface area	See 6.2
Homogeneity	See 6.3
Morphology	See 6.4
Dry solid content	See 6.5
CNT content	See 6.6
Viscosity	See 6.7

Table 2 — Additional characteristics of CNT suspension and measurement methods

Characteristics	Measurement methods
Fineness	See 6.8
Elemental impurity content[a]	See 6.9
pH value[a,b]	See 6.10
Water content[a]	See 6.11
Thermal conductivity[c]	See 6.12
Volume resistivity[b,c]	See 6.13
Shelf life	See 6.14
[a] Applicable to Li-ion battery application.	
[b] Applicable to composite material application.	
[c] Might be used in some adhesives, e.g. silicone.	

5 Sampling

5.1 Sampling principle

The representative sample should be taken from the CNT suspension and original CNT powder products. The amount of samples should be sufficient for the subsequent measurements. The detailed sampling method should conform to ISO 15528.

5.2 Sampling devices

When taking samples from a suspension product, the sampling devices should be able to take suspension samples from all layers of the product in the container (top, middle and bottom). Disposable pipettes are recommended so that different levels (top, middle and bottom) of the sample can be taken from the suspension product.

5.3 CNT retrieving

When a CNT test specimen in powder form is needed for measuring the characteristics, the test specimen is retrieved from the suspension sample by heating the suspension to fully remove the liquid. In cases where the CNT test specimen in powder form cannot be retrieved from the CNT suspension sample, the original CNT powder sample before dispersion can be used for measuring the characteristics.

6 Description of characteristics and measurement methods

6.1 Outer diameter

The outer diameter of a fibrous object is the distance on a two-dimensional microscopic image between the two outer edges on a cross-sectional line orthogonal to the longitudinal direction of fibre. One datum of outer diameter is obtained for each fibrous object. Each diameter datum is randomly obtained from the fibrous object without deliberately measuring the narrower or wider area of the image of the fibrous object. The target fibrous objects to be measured shall be representative of the fibrous solid objects contained in a CNT suspension sample, i.e. all types of fibrous objects on an image shall be equally selected for measurements. The number of diameter data may be agreed between the interested parties.

The diameter shall be measured by TEM or SEM. SEM can be used when the spatial resolution is precise enough for the target CNT diameters. When a test specimen for measurement is prepared, the CNT concentration of the suspension is adjusted to be dilute enough.

The measurement results shall be displayed as a histogram of the number of fibrous objects versus diameter at the interval of 1 nm. Also, the average (median) of diameter data of fibrous objects shall be expressed in the unit of nm. It should be noted that the measurement results may be qualitative with increased uncertainty when the observed microscopic images lack the representativeness of sample.

ISO/TS 10797 and ISO/TS 10798 specify the protocols for diameter measurement of single-wall CNTs by TEM and SEM, respectively. These documents can be useful for MWCNTs.

6.2 Specific surface area

Specific surface area (SSA) refers to the absolute surface area of the sample divided by the sample mass. The SSA is one of the fundamental characteristics of CNTs and affects the performance of products containing CNTs.

The original CNT powder samples are preferably used for the SSA measurement, irrespective of 5.3. The SSA shall be measured using the gas adsorption method. The results of SSA measurements shall be expressed in the unit of m^2/g.

The analysis technique based on the model developed by Brunauer, Emmett and Teller (BET) allows the specific surface area of a powder to be estimated by measuring the amount of gas that is adsorbed. The BET analysis is the standard method for determining the specific surface area from nitrogen adsorption isotherms. ISO 9277 applies to the measurement of the specific surface area. This document specifies the measurement procedures for the overall specific external and internal surface areas (diameter > 2 nm) of disperse or porous solids by measuring the amount of physically adsorbed gas according to the BET analysis. ISO 18757 provides some useful detailed information concerning specific materials. Measurement instruments for the BET method are commercially available. Metrological

traceability should be maintained. Reference materials are available for the application of the BET analysis to nanoparticles in powder form.

6.3 Homogeneity

Homogeneity of a CNT suspension sample is the measure of how uniformly distributed constituents of the CNT suspension are throughout a larger sample, as determined by measuring representative smaller samples.

The homogeneity of CNT suspension shall be examined by visual observation. A sample for examination is taken from the CNT suspension product into a transparent container. The container with sample is left statically for more than 24 h before examination. It is examined whether the colour is black and uniform over the surfaces of suspension sample and whether there is a phase separation and sedimentation. The examination results shall be reported qualitatively.

6.4 Morphology

Morphology of a CNT suspension sample refers to the shapes and structures of CNTs and other solid objects contained in the suspension sample. The morphology shall be measured qualitatively to observe the presence of CNTs and other solid objects contained in a CNT suspension sample.

Microscopic images of solid objects in a CNT sample shall be obtained by TEM or SEM. SEM can be used when the spatial resolution is precise enough for the target CNT sizes.

The CNT suspension sample is sufficiently diluted by adding anhydrous ethanol at an adequate concentration for the TEM and SEM measurements. Each image shall be accurately representative of the solid objects contained in a CNT suspension sample and be taken so that CNTs can be clearly observed. The scale bar is shown on each image.

More than five microscopic images shall be taken and reported.

6.5 Dry solid content

A CNT suspension sample may contain solid components other than CNTs and dissolved materials. The dry solid content can be an indication of CNT content in the suspension sample when impurities are negligible. The dry solid content of CNT suspension sample is the ratio of the mass of the CNT suspension after drying to that of the CNT suspension before drying.

Dry solid content shall be measured by the oven-drying method, which consists of drying the suspension sample to constant mass at temperatures between 100 °C and 120 °C and weighing. The measurement results of dry solid content shall be expressed as the mass percentage, in % mass fraction.

NOTE When dissolved materials in a CNT suspension sample are negligible, the dry solid content is closely equal to the solid content of the sample.

6.6 CNT content

A CNT suspension sample is predominantly composed of carbonaceous materials, which can be removed by combustion at appropriately high temperatures. The sample may contain metallic and inorganic impurities, which are left as ash after combustion. The ash content is measured by weighing the residue after combustion at 800 °C ± 25 °C using an electric furnace.

The CNT content of a CNT suspension sample is the difference between the dry solid content and the ash content, provided that the suspension has negligible non-CNT carbon and non-volatile organic matters. The results of CNT content should be expressed as the mass percentage, in % mass fraction.