TECHNICAL SPECIFICATION

ISO/TS 21236-2

First edition
2021-05

Nanotechnologies — Clay nanomaterials —

Part 2: **Specification of characteristics and measurements for clay nanoplates used for gas-barrier film applications**

Nanotechnologies — Nano argiles —

Partie 2: Spécification des caractéristiques et des mesures pour les argiles en nanofeuillets utilisées dans des applications de films barrières aux gaz

Reference number
ISO/TS 21236-2:2021(E)

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

A list of all parts in the ISO 21236 series can be found on the ISO website.

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

The barrier property in polymeric materials has become progressively more important in recent years with the widespread use of plastic films and rigid plastics for food packaging, medical packaging, electronic devices, construction, agriculture and so on. All polymeric materials have varying degrees of gas permeability. Therefore, the required level of gas barrier performance varies depending on the application. Barrier films often consist of multilayers or coated films designed to be impervious to gas and moisture migration, as single-layer films are in general quite permeable to most gases. Food packaging films are required to have oxygen gas barrier properties and water vapour barrier properties. A transparent gas barrier film obtained by applying a silica or alumina vapour deposition method on a PET or nylon film is generally used for food packaging, pharmaceutical packaging, industrial product packaging and so on. Recently, a film with a higher level of gas barrier properties has been required for organic light emitting diode displays. These high gas-barrier properties cannot be achieved by simply using conventional barrier film for food packaging.

High gas-barrier films are expected to be used in a wide range of fields, such as electronics, pharmaceutical packaging and hydrogen storage. Various approaches can be taken to improve barrier properties in plastics packaging. There is a method of adding gas-impermeable nano-objects to plastic to make nanocomposites. One of the most common types of polymer nanocomposites contains clay nanoplates. These clay nanomaterials improve barrier properties. Many reports predict the market expansion of nanocomposite materials.

There are many scientific papers and patents on gas barrier composite material using clay nanoplate. Gas barrier properties are improved by mixing clay nanoplates into the polymer. The high gas-barrier phenomenon is described in Nielsen's tortuous model. There are lots of clay products in suspension or powder forms and the effect of loading is different in each. Different production processes bring various characteristics to clay-containing materials. Various clay products are available to buy, including smectite, talc, kaolinite and mica. Some are suitable for gas barrier properties while others are not. Among them, clay products having a high aspect ratio and high affinity with plastic are preferable. Users of clay nanoplate products should check the characteristic data described in the catalogue, as these are important for selecting high-quality clay nanoplates for gas-barrier films.

ISO/TS 21236-1 specifies characteristics of layered clay nanomaterials in powder form, as well as chemically modified ones, and describes their relevant measurement methods.

This document specifies the characteristics to be measured of clay nanoplate and specifies industrially available measurement methods used to determine these characteristics. In addition, measurement protocols are described. It provides a sound basis for the research, development and commercialization of clay nanoplate materials for the application of barrier films for water vapour and dry gases.

Nanotechnologies — Clay nanomaterials —

Part 2: Specification of characteristics and measurements for clay nanoplates used for gas-barrier film applications

1 Scope

This document specifies characteristics to be measured and measurement methods for clay nanoplate samples in powder and suspension forms used for gas-barrier films. In addition, measurement protocols for the individual characteristics are described.

This document does not deal with characteristics of post-manufacturing modification of clay nanoplates. This document does not cover considerations specific to health and safety issues either during manufacturing or use.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 80004-6, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-6 and the following 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
gas barrier film
film that reduces gas diffusion

3.2
nanoplate
nano-object with one external dimension in the nanoscale and the other two external dimensions significantly larger

[SOURCE: ISO/TS 80004-2:2015, 4.6, modified]

3.3
clay nanoplate
nanoplate composed of clay

3.4
polymer clay nanocomposite
polymer matrix nanocomposite with a nanostructured clay phase

[SOURCE: ISO/TS 80004-4: 2011, 3.2.1.1]

3.5
film formability
capability of forming a film without additives from a suspension

Note 1 to entry: See Reference [10].

4 Abbreviated terms

AAS atomic absorption spectroscopy

AFM atomic force microscopy

DLS dynamic light scattering

EPMA electron probe micro analysis

ICP inductively coupled plasma spectrometry

SEM-EDX scanning electron microscopy-energy dispersive X-ray spectroscopy

TEM transmission electron microscopy

TGA thermogravimetric analysis

UV-Vis ultraviolet-visible spectrophotometry

XRD X-ray diffraction

XRF X-ray fluorescent analysis

5 Characteristics and measurement methods

5.1 General

The characteristics of clay nanoplate samples to be measured or identified and the applicable measurement methods are listed in Tables 1 and 2. The characteristics listed in Table 1 shall be measured by using the listed measurement methods. The characteristics listed in Table 2 should be measured by using the listed measurement methods. The middle columns in Tables 1 and 2 indicate the form of test specimen, powder or suspension used for measurements of the individual characteristics. Test specimens in the specified form are prepared from the suspension or powder sample of clay nanoplates.

See Annex A for measurement protocols of individual characteristics.

Table 1 — Required characteristics of clay nanoplate samples for measurement or identification

Characteristics	Test specimen form	Measurement methods
Mineral composition content	Powder	XRD, Polarization microscopy
Chemical composition content	Powder	ICP, AAS, XRF, SEM-EDX or EPMA
Cation exchange capacity	Powder	Schollenberger method[12]

Table 1 *(continued)*

Characteristics	Test specimen form	Measurement methods
Particle size	Suspension	Laser diffraction method or DLS
Loss on ignition	Powder	Weight measurement or TGA

Table 2 — Recommended characteristics of clay nanoplate samples for measurement or identification

Characteristics	Test specimen form	Measurement methods
Methylene blue adsorption capacity	Powder	Filter paper method or UV-Vis
Aspect ratio	Powder	AFM, TEM or SEM
Film formability	Powder	Suspension casting method
Viscosity	Suspension	Viscometry

See Annex B for principles of a gas barrier using clay nanoplates. See Annex C for value chains of clay nanoplate materials.

5.2 Mineral composition

A clay nanoplate sample is usually composed of various minerals. Natural smectite clay can contain quartz, mica, feldspar and calcite. The mineral composition contents of a clay nanoplate test specimen are the ratios of masses of minerals in a clay nanoplate test specimen to that of the whole test specimen. The minerals shall be identified and the individual contents shall be measured. The measurement results of the mineral composition contents shall be expressed as wt % for individual mineral compositions.

The mineral composition shall be measured by XRD,[11] EPMA or polarization microscopy for a clay nanoplate sample in powder form. EPMA is a complementary method for clay nanoplate samples. Polarization microscopy is a supplementary technique, giving mineral phase information and not information on composition. This measurement is used as a complementary method to increase the reliability of mineral identification. A thin film sample is prepared for measurement by suspension casting or similar. When a sample is provided in suspension form, a test specimen in powder form is prepared from the suspension sample by drying at 100 °C. In cases of XRD, the mineral composition content is calculated from the peak intensity ratio of minerals. It is common practice to use internal standards such as reference materials. For measurement, a compacted sample with a flattened surface or a fixed oriented sample is prepared by suspension casting.

5.3 Chemical composition

The chemical composition consists of the elements contained in a clay nanoplate sample. The chemical composition shall be measured and the results expressed as wt % for individual elements.

The chemical composition shall be identified and its contents shall be measured by ICP, AAS, XRF, SEM-EDX or EPMA for a clay nanoplate sample in powder form. SEM-EDX is a complementary method for clay nanoplate samples. When a sample is provided in suspension form, a test specimen in powder form is prepared from the suspension sample by drying at 100 °C. For ICP and AAS measurement, proper concentration of aqueous suspension is to be prepared. For XRF measurement, proper size of dried solid specimen is prepared.

5.4 Cation exchange capacity

The cation exchange capacity is the number of exchangeable cations per defined mass of a clay nanoplate dry sample. The cation exchange capacity shall be measured by the Schollenberger method[12] and the results expressed in the unit of milliequivalent of hydrogen per 100 g of dry powder sample (meq+/100g), or in the SI unit centi-mol per kg (cmol+/kg). The Schollenberger method has been most commonly used in the measurement of cation exchange capacity of soils. The ion concentration can be calculated based on elemental analysis by ICP or AAS.[13]

5.5 Particle size

Dynamic light scattering (DLS) is a generally accepted method for particle size distribution.[14] ISO 22412 lists DLS as a method for the estimation of an average hydrodynamic particle size and the measurement of the broadness of the size distribution. The applicability to nanomaterials depends on several factors, both related to the material and to the test setup. DLS can give good information in a narrow size range and provides three-dimensional information instead of the two-dimensional information from microscopy techniques. The laser diffraction method is also applicable to the particle size measurements (ISO 13320). In the suspension, primary and agglomerate particles both exist. Care should be taken that larger agglomerates are formed when the concentration of the suspension is high. The applicability is limited to stable particle suspensions of monomodal and relatively narrowly dispersed size distributions, and the shape of the particles plays a role in the interpretation of the results. Clay samples whose lateral size is enlarged from their original size are often useful to improve the film property due to the large aspect ratio.[15] Suspension is made using a proper method such as stirrer mixing, shaking, rotating or revolution mixing.

The average particle size shall be measured by the laser diffraction method or the DLS method for a clay nanoplate sample. The analytical value obtained by these measurement methods is hydrodynamic size. The results shall be expressed in the unit of nm. ISO 13320 and ISO 22412 specify measurement protocols for general application of the laser diffraction method and DLS, respectively.

When the sample is provided in suspension form, the particle size is measured as it is. When the sample is provided in powder form, a test specimen in suspension form is prepared by dispersing the sample in a dispersion liquid.

5.6 Loss on ignition

The loss on ignition is the ratio of the difference between the mass of a clay nanoplate sample in dried powder form before and after a heat treatment up to 1 000 °C to the mass of the sample before the heat treatment. It attributes to decompositions of organic impurity and organic modifier, loss of structural water and phase changes of the clay minerals with mass loss. When the sample is provided in suspension form, a test specimen in powder form is prepared from the suspension sample by drying.

The loss on ignition shall be measured by the weight measurement method or TGA. The results shall be expressed as wt %.

The adsorbed water content in the nanoplate sample is indicated by moisture content (see Clause 6).

5.7 Methylene blue adsorption capacity

The methylene blue adsorption capacity of a clay nanoplate powder sample is the ratio of the maximum amount of methylene blue dye adsorbed to the dried powder sample having been dispersed in water to the mass of the dried powder sample before dispersing. When the sample is provided in suspension form, a test specimen in powder form is prepared from the suspension sample by drying.

The methylene blue adsorption capacity should be measured by using the filter paper method or the UV-Vis method[17] (see ISO/TS 80004-6) depending on the required measurement accuracy. The results should be expressed in the unit of mmol/100g.

5.8 Aspect ratio

The aspect ratio of a clay nanoplate sample is the ratio of the circle equivalent diameter of the planar object contained in clay nanoplate sample to its thickness.

The diameter and thickness should be measured by selecting appropriate methods from AFM[8,9], TEM[6,10] and SEM[20] and the results should be expressed in the unit of nm. For accurate measurements, it is recommended that sufficiently diluted test specimens are prepared so that there is no overlapping between planar objects on the image. A sample is prepared as follows: a sufficiently diluted suspension, such as 5×10^{-5} wt %, is prepared from the sample in powder or suspension form. The dilution is cast and dried on a flat substrate at the sub-nanometer level. Casting is performed by dropping droplets of the suspension with a pipette or similar. Drying is performed under as mild a condition as possible, not exceeding 100 °C.

The average diameter and the average height of the planar objects are measured. The aspect ratio is calculated by dividing the former by the latter. The data number of diameter and thickness measurements can be decided by agreement between buyer and seller.

5.9 Film formability

The film formability is the capability of forming a film without additives.[10] The film formability should be evaluated by visual observation and mandrel bend test of the obtained precipitate. The results should be expressed in the way defined by the method used. For evaluation protocols, see A.9.

5.10 Viscosity

The viscosity of a fluid is the rheological property that expresses resistance to shearing flows. Viscosity of a clay nanoplate sample in a suspension form should be measured by the viscometry and the results expressed in the unit of Pa·s. The dry matter content of the suspension sample should be reported and expressed in the unit of unity by mass. The name of suspension liquid and the measurement temperature should be reported.

When a sample is provided in suspension form, viscosity is measured as it is. When a sample is provided in powder form, a test specimen in suspension form is prepared by dispersing the powder sample in an appropriate dispersion liquid. Viscosity is sensitive to clay concentration. Therefore, if the sample is in powder form, the concentration shall be mentioned.

The type of viscometer used and measurement conditions can be adopted as agreed between buyer and seller.

6 Reporting

The reporting shall include the following. An example of the reporting format is shown in Annex D.

- Sample identification:
  - sample name;
  - manufacturer’s name;
  - lot number;
  - sample source;
  - storage conditions prior to testing.
- Name of the suspension liquid for a suspension sample. In the case of hydrophilic clay, the suspension liquid is water. In the case of organoclay, the suspension liquid is organic solvent.
- Dry matter content: the ratio of the mass of residues of a clay nanoplate sample in suspension or powder form after drying to reach constant mass to that of the sample before drying. For aqueous suspension samples, the drying temperature is 105 ± 2 °C (ISO 11465). The measurement results are expressed as wt %.
- Moisture content: the moisture content of a clay nanoplate sample in a powder form is measured by the weight loss method where the sample is heated or by TGA. The appropriate heating temperature is 105 ± 5 °C. The measurement results are expressed as wt % (ISO 15512).
- Name of additives, if any, such as surfactant and thickening agent.