
**Nanotechnologies — Clay
nanomaterials —**

Part 1:

**Specification of characteristics and
measurement methods for layered
clay nanomaterials**

Nanotechnologies — Nano argiles —

*Partie 1: Spécification des caractéristiques et des méthodes de mesure
des nano argiles en couches*



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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.

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Introduction

Layered clay nanomaterials are a subgroup of clay materials with the external dimension (thickness) or the internal structural dimension (interlayer distance) in the nanoscale. Clay itself, as most important group of layered nanostructured silicates, refers to naturally occurring or synthetic material composed primarily of fine-grained minerals, which show plasticity through a variable range of water content and will harden when fired or dried. The minerals found in clay are generally silicates of less than 2 micrometres in lateral size. Clays are very abundant at the earth's surface; they form rocks known as shales and are a major component in nearly all sedimentary rocks. The small size of the particles and their unique crystal structures give clay materials special properties, including cation exchange capabilities, plastic behaviour when wet, catalytic abilities, swelling behaviour, and low permeability^[1].

Other than the structure and composition, there are several additional factors which are important in determining the properties and applications of clays and clay nanomaterials (see [Annex A](#)). These are the mineral impurities, the presence of organic materials, the type and amount of exchangeable ions and soluble salts, and the morphological aspects^[2].

Natural and modified clays as layered structured minerals are very important industrial materials. In pristine form, clay materials are normally subnano spaced layers, structured in bundles and in exfoliated state; they are nano-objects with thickness in the nanoscale while in intercalated form they are structured nanomaterials with interlayer space in nanoscale.

Modification of clay with change in its characteristic such as its hydrophobicity, interlayer distance, exchangeable ion, and surface connected groups leads to the extension of its applications e.g. for high performance nanocomposites, effective rheological modifier, or biomedical applications. A small quantity of well dispersed intercalated or exfoliated organo-modified layered clay nanomaterials in polymeric composites (see [Annex B](#)) is proved to show superior impacts on properties such as barrier, tensile modulus, mechanical strength, and flame retardancy.

There are numerous industrial applications for layered clay nanomaterials. Purified and modified clays are used as; coatings on paper to enhance whiteness and to allow the proper absorption of ink, the life time extender of rubber in tires, in concrete, as catalysts in many industries. Moreover, they can also be used in oil purification, pharmaceuticals, ceramic industry, soil stabilization, porcelains and barriers for nuclear and chemical wastes because of their cation-exchange capabilities, low permeability, and long-term structural stability. In addition, layered clay nanomaterials are utilized in purification industries, in agricultural and food engineering applications, polymeric nanocomposites, deodorizer, insecticide carrier, pesticides carrier, drilling fluids, desiccant, detergents, plasticizer, emulsion stabilizer, food additives, cosmetic applications, environmental remediation and many other miscellaneous applications^{[1][2]}.

For such a wide range of clay nanomaterial applications, various fundamental characteristics (as shown in [Table 1](#)) play undeniable roles. These characteristics are measured and reported by the provider of the layered clay nanomaterials. In fact, the determinations of these fundamental and basic characteristics will facilitate the communication between sellers and buyers of these nanomaterials for different applications. These characteristics are considered for all industrial layered clay nanomaterial applications such as nanocomposites, paper, ink, purification, and catalysts. In addition to fundamental characteristics, presented in [Table 1](#), some other optional characteristics of layered clay nanomaterials as shown in [Table 2](#) are measured and reported subject to the agreement between sellers and buyers.

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Nanotechnologies — Clay nanomaterials —

Part 1:

Specification of characteristics and measurement methods for layered clay nanomaterials

1 Scope

This document specifies characteristics to be measured of layered clay nanomaterials in powder form and chemically modified ones, and describes their relevant measurement methods.

This document does not deal with health, safety and environmental issues.

2 Normative references

There are no normative references in this document.

3 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

aspect ratio

ratio of the sheet length to the sheet width

[SOURCE: ISO 8336:2017, 3.13]

3.2

bulk density

ratio of the mass of an untapped powder sample and its volume including the contribution of the interparticulate void volume

3.3

cation exchange capacity

amount of exchangeable cations per defined mass of clay nanomaterial sample

3.4

clay

naturally occurring or synthetically manufactured material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired

Note 1 to entry: Taken from Reference [3].

Note 2 to entry: Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fired. Associated phases in clay may include materials that do not impart plasticity and organic matter. Different disciplines have uniquely defined the size of clay particles, and it is for this reason that “fine grained” is used in the definition rather than a precise value. However, because of these size variations from discipline to discipline, it is important that the particle size be specified in the context of the application.

3.5
clay nanomaterials

material composed predominately of clay with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale

3.6
exchangeable ion

ions bearing in clays which can be exchanged with other ions

Note 1 to entry: See Reference [4].

3.7
exfoliated clay

state of separating clay layers and distributing individual layers

Note 1 to entry: Usually exfoliation of layered clay nanomaterials is conducted in liquid suspension by giving shear forces.

Note 2 to entry: See Reference [5].

3.8
film formability

ability of clay to form self-standing films (uniform and ordered lamination of clay layers)

Note 1 to entry: See Reference [6].

3.9
gallery thickness

distance between clay layers

3.10
intercalated clay

clay in which heterogeneous material (atoms, molecules and nanoparticles) is inserted into a host structure (crystal lattice or other macromolecular structure)

3.11
interlayer distance

distance between identical adjacent layers of clay which is sum of gallery thickness (height) and thickness of a single sheet of clay (d_s)

3.12
layer

discrete material restricted in one dimension, within or at the surface of a condensed phase

[SOURCE: ISO/TS 80004-11:2017, 3.1.2]

3.13
layered clay nanomaterial

clay nanomaterial composed of one or more structural layer

3.14
loss on ignition

dried sample's weight loss during a heat treatment up to 1 000 °C

3.15**moisture content**

ratio of the mass of water contained in a sample to that of the sample

3.16**nanocomposite**

solid comprising a mixture of two or more phase-separated materials, one or more being nanophase

[SOURCE: ISO/TS 80004-4:2011, 3.2]

3.17**nanostuctured**

having internal or surface structure in the nanoscale

[SOURCE: ISO/TS 80004-11:2017, 3.1.8]

3.18**organoclay**

modified clay by exchanging the original interlayer cations for organic cations

3.19**phyllosilicate**

silicate mineral, such as mica, the tetrahedral silicate groups of which are linked in sheets

Note 1 to entry: See Reference [7].

3.20**smectite**

clay mineral (e.g. bentonite) which undergoes reversible expansion on absorbing water

3.21**specific surface area**

absolute surface area of the sample divided by sample mass

[SOURCE: ISO 9277:2010, 3.15]

3.22**tap density**

mass of the powder divided by its volume after tapping the sample in powder form

3.23**total surface area**

sum of external and internal surface area

4 Abbreviated terms

AFM	Atomic force microscopy
BET	Brunauer-Emmett-Teller
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectrometry
ICP-MS	Inductively coupled plasma - mass spectrometry
ICP-OES	Inductively coupled plasma - optical emission spectrometry
LOI	Loss on ignition

SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UV-Vis	Ultraviolet-visible spectrophotometry
XPS	X-ray photoelectron spectrometry
XRD	X-ray diffraction
XRF	X-ray fluorescence

5 Characteristics and measurement methods

5.1 General

This clause provides both fundamental and optional characteristics of layered clay nanomaterials and their relevant measurement methods. Relevant standards describing measurement protocols for individual characteristics are also listed in this clause. However, it should be noted that these standards have not yet been fully validated for application to layered clay nanomaterials.

5.2 Fundamental characteristics

[Table 1](#) lists the fundamental characteristics that are commonly used for material specifications of layered clay nanomaterials. The characteristics for measurements shall be selected from [Table 1](#) based on the agreement between sellers and buyers. [Table 1](#) additionally provides information on units suggested to be used for expressing the measurement results of individual characteristics, measurement methods recommended to be used, and other measurement method suggested to use when the recommended measurement methods are not available and existing standards for measurement protocols.

Table 1 — Fundamental characteristics and the relevant measurement methods

Characteristic		Units	Recommended measurement method(s)	Other measurement methods	Relevant measurement protocols
1-1	Chemical composition content	kg/kg	ICP-MS	ICP-OES or XRF	—
1-2	Mineral composition content	kg/kg	XRD	—	—
1-3	Interlayer distance	Nm	XRD	TEM or FESEM	—
1-4	Thickness	Nm	AFM	XRD, TEM or FESEM	—
1-5	Aspect ratio	—	AFM	SEM, FESEM or TEM	—
1-6	Bulk density	kg/m ³	Gravimetry and volumetry	—	Japanese Pharmacopoeia: 3.01 ^[14]
1-7	Cation exchange capacity	cmol+/kg	Schollenberger method	—	ISO 23470:2018
1-8	Loss on ignition	kg/kg	Thermogravimetry	Heating and weighing method	ISO/TR 18230:2015
1-9	Water absorption capacity	kg/kg	Water absorption method	Enslin-Neff method	ISO 10769:2011
1-10	Moisture content	kg/kg	Thermogravimetry	Oven-drying method	ISO 10769:2011

5.3 Optional characteristics

In addition to the fundamental characteristics which shall be measured ([Table 1](#)), there are some other important characteristics which could be related to specific applications. The optional characteristics listed in [Table 2](#) should be measured subject to the agreement between buyers and sellers. [Table 2](#) additionally provides information on units suggested to be used for expressing the measurement results of individual characteristics, measurement methods recommended to be used, other measurement method suggested to use when the recommended measurement methods are not available and existing standards for measurement protocols.

Table 2 — Optional characteristics of layered clay nanomaterials and relevant measurement methods

Characteristic		Units	Recommended measurement method(s)	Other measurement methods	Relevant measurement protocols
2-1	Brightness	—	Reflectometry	—	TAPPI T646
2-2	Colour	—	Colorimetry	—	—
2-3	Methylene blue adsorption capacity	mmol/100g	Filter paper method	UV-Vis spectrophotometry	ASTM C837 – 09 (2014)
2-4	Cohesion coefficient	kPa	Direct Shear test	—	ISO 17892-7:2017/ ASTM D3080/D3080M
2-5	Tap density	kg/m ³	Gravimetry and volumetry	—	Japanese Pharmacopoeia: 3.01 ^[14] and European Pharmacopoeia ^[15]

Table 2 (continued)

Characteristic		Units	Recommended measurement method(s)	Other measurement methods	Relevant measurement protocols
2-6	Specific surface area	m ² /g	Gas adsorption method	Ethylene glycol monomethyl ether absorption method	ISO 9277: 2010
2-7	Film formability	—	Film casting and visual inspection	—	—
2-8	Electrical Resistivity	Ω·m	Four-point probe method	—	—
2-9	Modifier Type	—	IR or FTIR	Raman spectrometry, XPS or UV-Vis	—

5.4 Descriptions on characteristics and measurement methods

Below, descriptions of the characteristics as well as of the measurement methods listed in [Tables 1](#) and [2](#) are presented.

5.4.1 Chemical composition content

Chemical composition content is defined as the ratio of the mass of a constituent element included in a layered clay nanomaterial sample to that of the dried sample. The chemical composition content of a layered clay nanomaterial sample shall be measured using an appropriate measurement method. The measurement results are usually expressed as wt%.

Wet chemical analysis using ICP-MS can be applied to chemical composition content measurements for elements even at an impurity level. The method is such that ions are generated at a high temperature under the atmospheric pressure in argon plasma and detected using a mass spectrometer.

Layered clay nanomaterial samples can be decomposed using various dissolving agents, including mixtures of strong acids and or hydrogen fluoride. Lithium metaborate (LiBO₂) fusion is one of the main options to decompose silicate material, because it is effective even in dissolving the most refractory minerals. A plasma source could be also used to dissociate the sample into its constituent atoms or ions, and the analysis of the atoms is done either with mass spectrometry or by detecting the optical emission from the excited atoms (ICP-OES). In chemical composition report in addition to report of major elements, it is required to report impurities, too.

The XRF spectrometry is also a method for the qualitative and quantitative determination of the elemental composition content of a layered clay nanomaterial sample in both laboratory and industrial environments. This method is less time consuming but it has some limitation on minimum content detection and so it cannot be recommended for chemical composition content measurements at an impurity level.

5.4.2 Mineral composition content

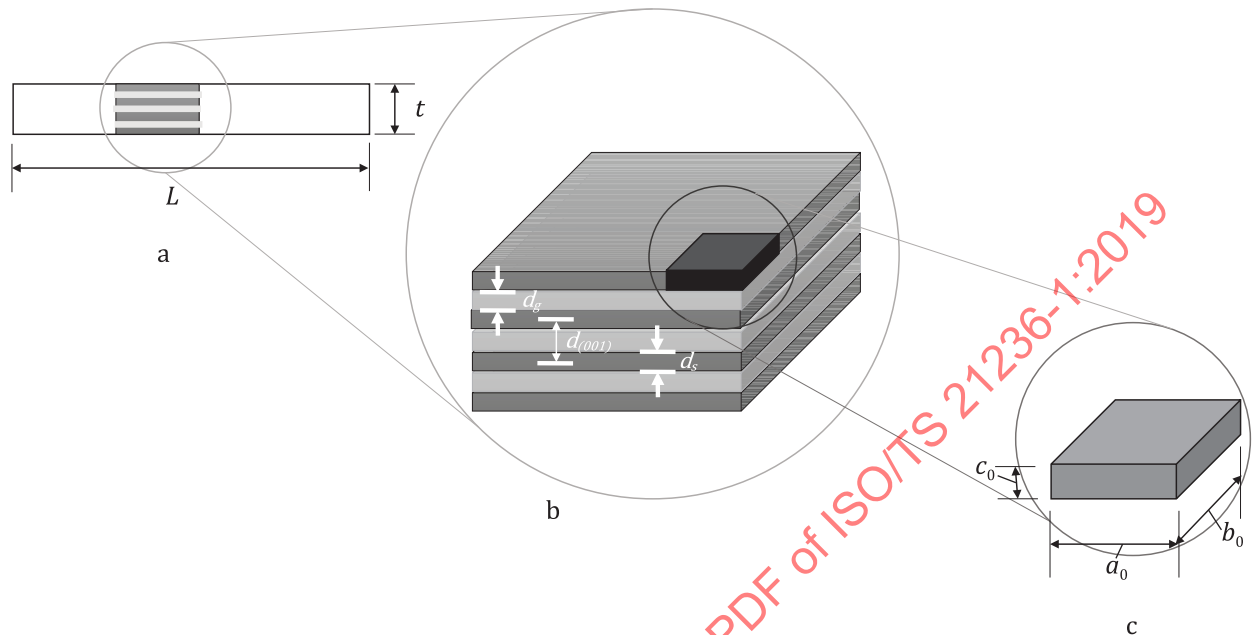
The mineral composition content is the ratio of the mass of a mineral composition included in a layered clay nanomaterial sample to that of the dried sample. The mineral composition content shall be measured using an appropriate measurement method. The measurement results are usually expressed as wt%.

The contents of major mineral composition of a layered clay nanomaterial sample can be determined using XRD spectra of the dried sample. This technique could provide crystallographic information about a sample by observing the diffraction pattern due to an X-ray beam hitting the sample^{[8][9]}.

Although many quantification methods based on the XRD technique are highly accurate, sample preparation, data processing and the selection of standards are essential for the XRD quantification of layered clay nanomaterial samples^[10].

5.4.3 Interlayer distance

In [Figure 1](#), the thickness, length and some other structural parameters of layered clay nanomaterial are schematically presented.



Key

- L lateral size of layered clay
- t layered clay nanomaterial thickness
- d_s layer thickness
- d_g gallery thickness
- $d_{(001)}$ interlayer distance
- a layered clay nanomaterial
- b multilayer structure of intercalated clay nanomaterial
- c repetitive lattice cell

Figure 1 — Structural parameters of layered clay nanomaterial — (a) a layered clay nanomaterial, (b) the dark grey area represents a single sheet of clay material and the light grey area represents the spacing between two adjacent sheets, and (c) a_0 , b_0 and c_0 represent the lattice cell parameters

The interlayer distance of clay and clay nanomaterials can be calculated from Bragg's equation ($n\lambda = 2d \sin \theta$) using XRD spectrum, where in Bragg's equation d is the spacing between layers of the clay, λ the wavelength of X-ray, θ the angle at the peak and n is the layer number. In the Bragg's equation for case of $n = 1$ d is d_{001} which is the interlayer distance of a layered clay nanomaterial sample. A typical XRD spectrum of layered clay nanomaterial is shown in [Figure 2](#).

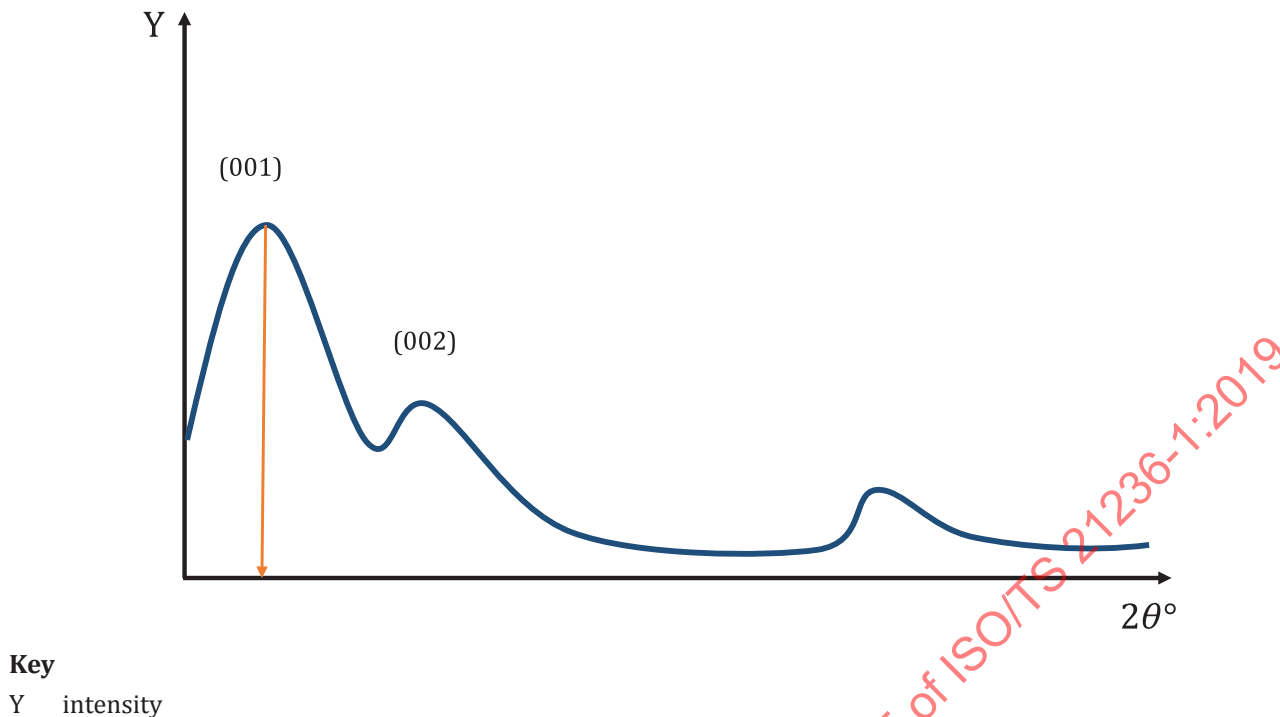


Figure 2 — Typical low angle XRD spectrum for a layered clay nanomaterial sample

XRD method is a preferable method for determination of the interlayer distance of a layered clay nanomaterial sample due to its simplicity and accessibility. However other methods such as TEM and FESEM, could be used for complementary and more detailed structural analysis of layered clay nanomaterials. TEM could be used for structural analysis of layered clay nanomaterials. This method produces images and diffraction patterns with a resolution in atomic scale by using an electron beam which passes through the sample and interacts with the sample to a detector.

FESEM is another technique that examines and analyses the surface of samples by scanning with a primary electron beam, which causes the ejection of secondary electrons, backscattered electrons, absorbed electrons and X-ray radiation. The images constructed by these signals can be used to determine the interlayer distance of a layered clay nanomaterial.

5.4.4 Thickness

Thickness of a layered clay nanomaterial is defined as the distance between the two edges on a cross-sectional line orthogonal to the layer surface. When the thickness varies over the surface of the nanomaterial, the largest value is recorded as the thickness. The thickness of a layered clay nanomaterial shall be measured using an appropriate method. There are two options for the measurement method. The recommended method is AFM and the other method is based on calculation using the structural parameters of the layered clay nanomaterial. The measurement results are expressed in the unit of nm.

An AFM image can be used for determination of the thickness of layered clay nanomaterial. The thickness of a layered clay nanomaterial can be measured as the step height on a three-dimensional image between the top of the nanomaterial and the substrate surface when the nanomaterial is deposited laterally on the substrate.

As one can see in [Figure 1 \(b\)](#), the internal structure of a layered clay nanomaterial is presented as a multi-layer stack containing N single silicate sheets with uniform interlayer spacing^[11]. The thickness

of a layered clay nanomaterial can also be obtained through the measurement data of structural parameters. The thickness t is given by the following formula;

$$t = (N-1) \times d_{001} + d_s$$

where

d_{001} is the silicate interlayer distance and can be calculated by XRD spectrum using Bragg's equation;

d_s is the thickness of a single silicate layer;

N is the average number of silicate layers per layer stack, which can be distinctly identified by analysing TEM or high resolution FESEM images.

5.4.5 Aspect ratio

Aspect ratio of a layered clay nanomaterial is defined as the ratio of the average lateral size to the average thickness of the layered clay nanomaterial^{[12][13]}. The aspect ratio of a layered clay nanomaterial shall be measured using an appropriate measurement method. The measurement results are expressed as a dimensionless number.

The lateral size and thickness of a layered clay nanomaterial can be measured by analysing images obtained by AFM, SEM, FESEM, or TEM.

5.4.6 Bulk density

Bulk density of a layered clay nanomaterial powder sample is the ratio of the mass of an untapped powder sample and its volume including the contribution of the interparticulate void volume. The bulk density shall be measured using an appropriate measurement method. The measurement results are expressed in the unit of kg/m³.

The bulk density of a layered clay nanomaterial powder sample depends on both the density of powder particles and the spatial arrangement of particles in the powder bed. Thus, the bulk density of a powder is often very difficult to measure with good reproducibility. So, it is essential to specify the measurement conditions for bulk density in reporting of results.

The bulk density of a layered clay nanomaterial powder sample can be determined using a graduated slenderer. In this method, the mass of a powder sample that may have been passed through a sieve into a graduated cylinder or cup with predetermined volume is determined. Details of the method could be found in many references including Japanese Pharmacopoeia and European Pharmacopoeia^{[14][15]}.

5.4.7 Cation exchange capacity

Cation exchange capacity is defined as the amount of exchangeable cations per unit mass of a layered clay nanomaterial powder sample. The cation exchange capability shall be measured using an appropriate measurement method. The measurement results of cation exchange capacity are expressed in the unit of milliequivalent of hydrogen per 100 g of air-dried layered clay nanomaterial (meq+/100 g), or the SI unit centi-mol per kg (cmol+/kg).

ISO 23470:2018 specifies a method for the determination of the cation exchange capacity and the content of exchangeable cations (Al³⁺, Ca²⁺, Fe²⁺, K⁺, Mg²⁺, Mn²⁺, Na⁺) in soils using a hexammincobalt trichloride solution as extractant. The method is applicable to all types of layered clay nanomaterial powder sample which have been prepared in accordance with ISO 11464.

5.4.8 Loss on ignition

LOI is referred to the weight loss of a dried layered clay nanomaterial sample during a heat treatment at 1 000 °C. The volatile materials lost from a layered clay nanomaterial sample consist of "combined water" (hydrates and labile hydroxy-compounds), organic and volatile inorganic materials including

organic modifier of layered clay nanomaterials. The LOI at 1 000 °C can be measured gravimetrically by TGA instruments using a pre-dried sample. ISO/TR 18230:2015 is not intended for determination of layered clay nanomaterial LOI but in the absence of any standards for these materials the procedures mentioned in the standards may be useful for measurement of LOI of layered clay nanomaterials. The measurement results of LOI are expressed as wt%.

5.4.9 Water absorption capacity

Water absorption capacity, W_A , is defined as the ratio of the mass of water, m_{wg} , absorbed by a layered clay nanomaterial sample through capillarity in the test apparatus to the dry mass, m_{wd} , of the sample.

$$W_A = \frac{m_{wg}}{m_{wd}}$$

where, m_{wg} is the limiting value of the absorbed water over the test period. The water absorption capacity should be measured using an appropriate measurement method. The measurement results of water absorption capacity are expressed as wt%. ISO 10769:2011 specifies the measurement procedures for water absorption capacity of bentonite.

Water absorption capacity can be also measured using DIN 18132 which is according to modified Enslin-Neff method. The Enslin-Neff method is frequently used in the bentonite industry and civil engineering. The measurement results of Enslin-Neff method are expressed as the amount of exchangeable Na^+ and to a lesser extent by the smectite content^[16].

5.4.10 Moisture content

The moisture content of a layered clay nanomaterial shall be measured using an appropriate method. The measurement results of moisture content are expressed as wt%. The most common method used to determine the moisture content is the thermogravimetric method, where a sample of layered clay nanomaterial is dried at 110 °C to constant mass.

TGA is a commercial instrument that can measure the mass change of a sample as a function of time when heated isothermally in an inert gas atmosphere

Moisture content can be also determined oven-drying method where heating a sample at 110 °C in a convection oven to constant mass and weighing the remaining sample.

5.4.11 Brightness

Brightness is defined as the percentage of blue light reflected from the surface of a sample as measured at a specific effective wavelength of 457 nm (with a half-peak bandwidth of 44 nm). The brightness of layered clay nanomaterials can affect the brightness of the polymeric composites, paper and any materials in which layered clay nanomaterials are used. The measured brightness could be significantly affected by measuring methods. Actually, the measured value depends significantly on the manner of specimen preparation. Sample preparation, measuring and result reporting methods should be done according to TAPPI T646 or equivalent standard test methods.

TAPPI T 646 Mineral pigment brightness describes a procedure for determining the brightness of clay or other mineral pigment that has been pulverized under controlled conditions and made into a uniformly compacted pigment plaque. This method is for use with minerals normally used in the manufacture of paper and is not intended for highly coloured pigments. The instrument employed has the same spectral, geometric, and photometric characteristics as that described in TAPPI T 452 "Brightness of Pulp, Paper, and Paperboard (Directional Reflectance at 457 nm).

5.4.12 Colour

Colour is a physical property of layered clay nanomaterial that allows us to estimate some of its important characteristics, such as mineral impurity composition, existence of iron chemical

compounds and organic compounds. For many applications of layered clay nanomaterials including their applications in paper and polymer industries layered clay nanomaterials need to have no or controlled colours. Therefore, users of layered clay nanomaterials for such applications in addition to transparency and brightness should be aware of the sample colour.

Colour is measured by means of visual and spectrophotometry methods. The colorimeter can be used for measuring surface colours of samples. In process of measuring colour using a colorimeter, the specimens (in defined size like 4 cm × 4 cm) are placed on a white standard plate and the Hunter lab colour scale is used to indicate the colour^{[17][18]}.

5.4.13 Methylene blue adsorption capacity

The methylene blue adsorption capacity is a simply measurable index that provides an indication of clay activity and clay characteristics such as cation exchange capacity, dry bond strength, swell potential and casting rate. The methylene blue adsorption capacity of a layered clay nanomaterial sample is defined as the ratio of the maximum amount of methylene blue dye adsorbed to the dried sample having been dispersed in water to the mass of the dried sample.

The methylene blue adsorption capacity should be measured using an appropriate method. The measurement results are expressed in the unit of mmol/100 g. The methylene blue adsorption capacity is measured by using the filter paper method or the UV-Vis method depending on required measurement accuracy.

Methylene blue adsorption capacity measurement has attracted wide attention to being easily applicable and need no special equipment^[19]. ASTM C837-09(2014) gives measurement protocols for methylene blue adsorption capacity of clay materials.

5.4.14 Cohesion coefficient

The cohesion coefficient of a layered clay nanomaterial powder sample is related to the strength of the powder sample in shearing conditions. The cohesion coefficient should be measured using an appropriate method. The measurement results are expressed in the unit of kPa.

This characteristic of layered clay nanomaterials changes with its surface properties and water content. The test is performed by deforming a test specimen at a controlled strain rate on or near a single shear plane determined by the configuration of the apparatus. Generally, three or more specimens are measured, each under different normal loads, to determine the effects upon shear resistance and displacement, and strength properties of powder.

ISO 17892-7 and ASTM D3080/D3080M standards specify measurement procedures for cohesion coefficients of soils. Those standard documents could be used for cohesion coefficient measurement of layered clay nanomaterials.

5.4.15 Tap density

The tap density of a layered clay nanomaterial powder sample is dependent on the manner in which the particles are packed together. The principle of the measurement method is tapping a specified amount of powder sample in a container by means of a tapping apparatus until no further decrease in the volume of the powder sample takes place. The mass of the powder divided by its volume after the test gives its tap density. The standard method for measurement of tap density of materials in powder form can be found in References ^[14] and ^[15].

5.4.16 Specific surface area

The specific surface area of a layered clay nanomaterial powder sample which is the sum of external and internal surface areas is a factor that can relate grain-scale properties to macro-scale physical and chemical properties of the layered clay nanomaterial. The specific surface area should be measured using an appropriate method. The measurement results are expressed in the unit of m²/g.

Large surface areas lead to increased interaction of ions and molecules with the layered clay nanomaterials. Therefore the total specific surface area affects many physical and chemical properties of the clay and clay nanomaterials^{[20][21]}. The magnitude of the specific surface area of a layered clay nanomaterial powder sample depends largely on the type of clay minerals and its characteristics. Especially in fine-grained intercalated clays one can distinguish between an external and internal surface, the latter being the interlamellar space of the minerals. The internal surface is determined by measuring the total surface and subtracting from it the separately determined external surface^[22].

The specific surface area of a layered clay nanomaterial powder sample should be measured by the gas adsorption method using BET analysis. BET analysis determines the specific surface area of the adsorbent by means of an inert gas adsorption-desorption isotherm measured at defined temperature and pressure. The total surface area and macroscopic pore size distributions can be also calculated using BET and Barrett-Joyner-Halenda (BJH) desorption curves^[22]. ISO 9277:2010 specifies the determination of the overall specific external and internal surface area of the powder or porous solids by measuring the amount of physically adsorbed gas according to BET method.

However, BET method could have some limitation due to the lack of complete adsorption of gas on internal surfaces of pore. As an alternative method widely used in scientific research, ethylene glycol monomethyl ether (EGME) adsorption could be used for the total specific surface area measurement of layered clay nanomaterials^{[23][24]}.

5.4.17 Film formability

Film formability of a layered clay nanomaterial suspension sample refers to the ability of the suspension to form freestanding film after casting and drying. In some applications such as gas impermeable multilayer films of polymeric materials, this property is important and should be measured and reported. A finely dispersed suspension of 3 wt% of clay nanomaterials in water^{[6][25]} or other appropriate organic solvent, e.g. heptane for organo-modified layered clay nanomaterials, should be prepared with vigorous stirring and then degassed in an appropriate vacuum chamber. About 110 ml of degassed suspension should be poured into a polypropylene tray (200 mm × 140 mm × 25 mm), and dried at 60 °C for 1 day. The evaluation of film formability might be carried out as follows:

The produced film should be visually inspected and a manual peel test with relatively low speed test on it should be done. The films could be categorized in four different categories called A, B, C, and D, whereas A stands for the flexible freestanding film with excellent shape retention ability, and capacity of separation from substrate, B for the freestanding film with good shape retention ability, C for the non-uniform fragile film with poor retention ability, and D for the case in which no continuity in the dried sample could be observed. More information about film formability evaluation and its application to gas barrier film can be found in ISO/TS 21236-2¹⁾.

5.4.18 Electrical resistivity

Electrical resistivity of a layered clay nanomaterial sample is referred to the electrical resistance of a pelletized powder sample isotropically pressed for a given cross-sectional area and given length. The electrical resistivity should be measured using an appropriate method. The measurement results are expressed in the unit of $\Omega \cdot m$.

Many factor including moisture and organic contents can affect electrical resistivity of clay nanomaterials. The four-point or Kelvin, probe (See [Figure 3](#)) method is the most commonly used method for electrical resistivity measurement of low conductive materials. Two of the probes are used to source current and the other two probes are used to measure voltage. This technique involves bringing four equally spaced probes into contact with the sample of unknown resistance. The probe array is usually

1) Under preparation.

placed in the centre of the pelletized layered clay nanomaterial sample at an appropriate pressure, as shown in [Figure 3](#). The volume resistivity is calculated with the following formula [IEC 62899-202]:

$$\rho = F \times t \times \frac{V}{I}$$

where

ρ is the electrical resistivity ($\Omega \cdot m$);

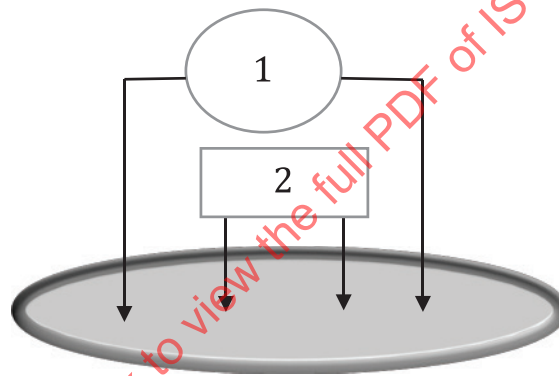
V is the measured voltage (volts);

I is the source current (amperes);

t is the sample thickness (m);

F is a correction factor.

It should be mentioned that pelletizing pressure should be reported in the test results. Mention should be made to the humidity condition and temperature too.



Key

- 1 current source
- 2 voltmeter

Figure 3 — Four-point collinear probe resistivity method

5.4.19 Modifier type

Modifier type is referred to the type of materials including typically quaternary alkylammonium ions that may be used to modify chemical or structural properties of clay (see [Annex B](#)). The modifier type of a layered clay nanomaterial should be identified using an appropriate method. Infrared (IR) or FTIR spectrophotometry is normally used for identification of modifier type. If they are not available due to any reason, Raman spectroscopy, XPS or UV-Vis spectrophotometry may be used.

IR and FTIR spectrophotometry, which are based on the absorption of IR-radiation by the chemical bonds, could be used to identify the composition of modifier of clay. The infrared spectrum of a clay material is sensitive to the chemical composition, isomorphous substitution. The method is best suitable for compounds with simple chemical formula.

6 Reporting

6.1 General

The manufacturer or provider shall report the relevant general information and the measurement results of fundamental characteristics of the layered clay nanomaterials. The optional characteristics could also be reported. The following items shall be reported.

6.2 Information

- Product name
- Batch and lot number
- Manufacturer or provider name
- Production date

6.3 Measurement results

- Chemical composition content
- Mineral composition content
- Interlayer distance
- Thickness
- Aspect ratio
- Bulk density
- Cation exchange capacity
- Loss on ignition
- Water absorption capacity
- Moisture content

6.4 Example of table format

[Table 3](#) is an example format for reporting and may or may not be used. The optional characteristics described in [Table 2](#) may be added to the reporting items.

Table 3 — Example table format for reporting the fundamental characteristics of layered clay nanomaterials by the manufacturer or provider

General		Manufacturer or Provider name			
Batch No.		Lot No.			
Production date					
	Characteristic	Unit	Value	Measurement method	Standard deviation
1	Chemical composition content				
2	Mineral composition content				
3	Interlayer distance				
4	Thickness				
5	Aspect ratio				
6	Bulk density				
7	Cation exchange capacity				
8	Loss on ignition				
9	Water absorption capacity				
10	Moisture content				

Annex A (informative)

Basic information on layered clay nanomaterials

A.1 General

Clays are a family of layered hydrous aluminium/magnesium silicates in which the gallery thickness may vary from subnano in its original form to a few nanometres in expanded or modified intercalated structure. Single or few layer clay nanomaterials may be obtained in exfoliated state of clay. Clay nanomaterials are composed predominately of clay with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale.

A.2 Structural aspects

The clay's sheet structure is mainly composed of 2 types of unit cells, silica tetrahedrons (SiO_4) and alumina or other metal octahedrons (MetO_6). In silica tetrahedrons, one silicon atom is attracted by four oxygen atoms and arranging them near each other and bonding with shared oxygen atoms makes tetrahedral sheets. In the metal octahedron, one metal atom is attracted by six oxygen atoms and arranging them near each other and bonding with shared oxygen atoms forming octahedral sheets. Layered arrangement of silica and metal oxide sheets together results in different clays.

In the case that each octahedral sheet surrounded by one tetrahedral sheet m:n structure is 1:1 (e.g. kaolinite).

In the case of sandwiching each octahedral sheet by two tetrahedral sheets m:n structure is 1:1 (e.g. smectites). Here, there is a considerable interlayer space due to the lack of strength of H-bonding to hold layers together. This structure is expanding clay, and a number of water molecules and ions determine the thickness of interlayer space and results in shrinking and swell.

A.3 Gallery

Gallery is a space between clay layers. The Gallery is generated by the presence of cations, water molecules and other molecules which could be intercalated between clay layers. Generally, when isomorphous substitution (and broken edges) causes clay to be negatively charged, cations would gather here. The distance between two adjacent sheets of clay is referred as gallery thickness or gallery height of clay.

A.4 Isomorphous substitution

In isomorphous substitution, one or more ions in tetrahedral or octahedral sheets are replaced with different ions. In the case of replacement of Al^{3+} with Mg^{2+} (as an example), the resulting extra negative charge could attract appropriate cations, leading to the clay modification. Substitution of Al^{3+} for Si^{4+} in tetrahedral sheets results in positive charge which could be also used for further clay modification too.

A.5 Modification

Most layered silicate clays are naturally hydrophilic. This makes them poorly suited for mixing and interacting with most polymer matrices which are mostly hydrophobic^{[26][28]}. Moreover, the stacks of clay layers are held tightly together by electrostatic forces. For these reasons, the clay shall be treated before it can be used to make a polymeric nanocomposite (See [Annex B](#)). Making a composite out of

untreated clay would not be very effective because most of the clay would be unable to interact with the matrix. An easy method of modifying the clay surface is traditional ion exchange method. The cations are not strongly bound to the clay surface, so small molecule cations can replace the cations present in the clay. By exchanging ions present between layers with various organic cations, montmorillonite clay can be compatibilized with a wide variety of matrix polymers. At the same time, this process helps to separate the clay platelets so that they can be more easily intercalated and exfoliated.

By exchanging of exchangeable cations for organic cations that are also called surfactants, the surface energy of clay decreases and the gallery thickness expands. The resulting material is called organo modified clay nanomaterial or organoclay. The basal spacing of the resulting layered organoclays depends on the chemical structure of the surfactant, the degree of cation exchange, and silicate layer thickness^[29]. Organo-chemically modified montmorillonites have been widely studied fundamentally and in practical applications in the area of organic-inorganic hybrids, composites and nano-scale composites^[30]. Ammonium surfactants used in commercially available organoclays usually incorporate short aliphatic chains and benzyl groups^{[30][34]}. Phosphonium surfactants have been also used in the preparation of organoclays^{[35][39]}. Phosphonium surfactants are more thermally stable than ammonium surfactants (see [Annex B](#)).

Annex B (informative)

Organo-modified layered clay nanomaterials (Organoclay)

Organoclay is an organically modified phyllosilicate, derived from a naturally occurring clay mineral. By exchanging the original interlayer cations for organocations (typically quaternary alkylammonium ions) an organophilic surface is generated, consisting of covalently linked organic moieties (see [Figure B.1](#)). The lamellar structure remains analogous to the parent phyllosilicate. Separation of the layers due to ion exchange as well as the change of chemical character of the clay surface, allows the *in situ* polymerization or mixing with certain polymers to obtain what is known as nanocomposite. When ordered alumina silicate or other metal silicate sheets are lying parallel to each other, separated with polymer chains of certain type, the system is classified as intercalated nanocomposite. If separation of the layers is so significant that they are no longer lying opposite to one another, but randomly ordered, then one gets the exfoliated clay nanocomposite.^{[12][13]}

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