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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

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Foreword

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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.

- Morphology: representative pictures showing clearly the structure and formation, such as shape and agglomeration state of clay nanoplates taken by microscopy. The measurement method used shall be indicated as AFM, TEM or SEM. The magnification scale shall be shown on each picture. The appropriate number of pictures may be agreed between buyer and seller.
- The pH value of a clay nanoplate sample when it is provided in aqueous suspension form. The pH of an aqueous suspension is measured by the glass electrode method and the results are expressed as dimensionless. The measurement temperature is also reported.
- The International Standard used (including its year of publication).
- Name of characteristics measured or identified that are listed in Table 1. When any characteristics listed in Table 2 are measured, the results can be reported in this test report.
- Measurement methods used for individual characteristics determination.
- Date of measurement and name of organization that made the measurements for individual characteristics.
- Quantitative and/or qualitative results of measurements for individual characteristics, including a reference to the clause which explains how the results were calculated.
- Information on the uncertainty of measurement results. Repeatability and reproducibility are recommended.
- Any unusual features observed.
- Additional information, if any, supporting the measurement results.
- If there are deviations from this document, give the name of and detailed information on the measurement methods used and their justification.

Annex A
(informative)

Measurement protocols

A.1 General

Sample preparations, measurement procedures and data analyses generally used for characterizing clay nanoplate samples in powder and suspension forms are informatively provided in this annex for individual characteristics.

A.2 Mineral composition

The powder X-ray diffraction method is most often used for the determination of mineral compositions and their contents of clay nanoplate samples. The obtained pattern is compared with each mineral pattern file and the minerals are identified. The d spacing is calculated from the peak value of the obtained pattern. It is common to use internal standards.[12]

The d spacing is calculated from Bragg's law:

$$d = n\lambda/(2 \sin \theta)$$

where

n is an integer;

θ is the angle of incidence (or reflection) of the X-ray beam;

λ is the X-ray wavelength.

Most X-ray machines use Cu-Kα1 radiation with λ = 0,154 056 2 nm. For the principal reflection, n = 1.

Typical measurement conditions are as follows: Cu X-ray, tube voltage of 40kV, tube current of 40 mA, measurement angle from 2 degrees to 60 degrees.

The mineral composition is calculated from the peak intensity ratio of minerals.

A.3 Chemical composition

The chemical composition contents are most frequently measured by XRF or SEM-EDX for powder samples. Usually, instruction manuals of instrument manufacturers can be used for the measurement procedures.

A.4 Cation exchange capacity

The measurement procedure of cation exchange capacity is as follows[16]:

The equipment used is a leachate container, a leaching pipe and a receiver. A small amount of absorbent cotton is placed on the lower part of the leaching pipe so that the upper surface is flat, and an emulsified paper is laid on the leaching pipe to a thickness of 2 mm to 3 mm as the supporting layer of the sample. A sample of 0,4 g to 0,5 g and 10 times the mass of the quartz powder is uniformly mixed. Weigh the sample to a precision of 0,1mg.

Quartz powder having a particle size of about 40 mesh to 60 mesh is boiled with dilute hydrochloric acid then thoroughly washed with water and dried.

The reagents used in the test method are as follows. Use special grade reagent.

A.4.1 pH 7 - 1 N ammonium acetate solution. 2 N Ammonia water and 2 N acetic acid are mixed in equal amounts and prepared with concentrated ammonia water or glacial acetic acid to give a pH of 7. The pH is measured using a glass electrode pH meter.

A.4.2 pH 7-80 % ethyl alcohol. 20 volumes of purified water and 80 volumes of ethyl alcohol are mixed and prepared with a sodium hydroxide solution to give a pH of 7 while being examined with a BTB test paper.

A.4.3 10 % potassium chloride solution. Dissolve 100 g of potassium chloride in 900 ml of purified water.

The leaching operation in the test method is as follows:

a) Pour 100 ml of ammonium acetate solution into the dropping funnel. Next, drop the ammonium acetate solution into the leaching tube containing the sample so the sample is sufficiently impregnated with the solution. Next, attach the dripping funnel and the leaching tube to the leaching solution receiver. Adjust the cock of the dropping funnel and finish dropping the remaining ammonium acetate solution in 4 h to 24 h.

b) Wash the dropping funnel thoroughly, then wash the sample by adding 50 ml of 80 % ethyl alcohol and allowing it to flow down.

c) After thoroughly rinsing the dropping funnel and the receiver, pour 100 ml 10 % potassium chloride solution into the dropping funnel and let it flow down to exchange ammonium ion in the sample with potassium ion.

d) Transfer the potassium chloride solution of the receiver to the distillation apparatus and distil ammonia according to the Kjeldahl method. The distillate is added to 0,1 N sulfuric acid and excess sulfuric acid is titrated with 0,1 N sodium hydroxide solution. At the same time, carry out a blank test, calculated from Formula (A.1), and display the first decimal place as milliequivalent number per 100 g of dry sample (meq/100 g).

$$C = [(A - B) \times f \times 10]/[S \times (100 - M)/100] \quad \text{(A.1)}$$

where

A is the volume in ml of 0,1 N · NaOH required for the blank test;

B is the volume of 0,1 N · NaOH required;

C is the cation exchange capacity (meq/100 g);

f is the factor of 0,1 N · NaOH;

S is the sample mass (g);

M is the moisture content of the sample (%).

A.5 Particle size

A.5.1 General

Particle sizes of the clays in the suspensions are measured using a DLS or a laser diffraction particle size-analyser. Examples of the measurement protocol are as follows.

A.5.2 Measurement protocol

Clay samples in powder form are initially dried at 110 °C for one night. When the dry matter content is too high, the proportion of associated particles increases. This is because agglomeration proceeds as the concentration increases. On the other hand, if it is too diluted, sufficient peak intensity of article size distribution spectrum cannot be obtained. Therefore, a dilute clay dispersion is prepared using distilled water within a concentration range where sufficient peak strength is obtained. Clay dispersions of 0,2 wt % are prepared by mixing the clays and distilled water. The data are obtained as water dispersion particle size.

A.5.3 Suspension liquid

If the clay is not water-dispersible and organic solvent dispersible, an appropriate organic solvent is used. Adopt the appropriate concentration and report the type of organic solvent. Suspension is prepared with a stirrer or similar.

A.6 Loss on ignition

The procedure of loss on ignition measurement is as follows.

a) Place a sample in suspension or powder form of 1 g to 2 g in a dried crucible and dry it to constant mass in an oven at 110 °C. Then cool in a desiccator and weigh to 0,1 mg.

b) Place the crucible with the dried sample in an electric furnace and heat at 1000 ± 25 °C for 60 min.

c) After heating, cool in a desiccator and weigh to 0,1 mg.

The loss on ignition is calculated to the first decimal place as expressed in wt % by Formula (A.2).

$$L = (W_1 - W_2)/(W_1 - W_3) \times 100 \qquad \text{(A.2)}$$

where

L is the loss on ignition (wt%);

W_1 is the mass of the crucible with sample before the heat treatment (g);

W_2 is the mass of the crucible with sample after the heat treatment (g);

W_3 is the mass of the dried crucible (g).

A.7 Methylene blue adsorption capacity

There are two methods, the filter paper method and the colorimetric method. The filter paper method is described here. For the colorimetric method, see Reference [16].

A clay nanoplate powder (0,500 grams) is placed in a conical beaker with tetrasodium pyrophosphate (TSPP) solution (2 %, 50 ml). The suspension is dispersed by ultrasonic treatment for 20 minutes or boiling for 10 minutes. Methylene blue (MB) solution (0,01 M) is added to the solution step-by-step with an increment of 1 ml. At every addition, the solution is stirred using magnetic stirrers and a drop of the solution is placed on a filter paper to make a spot. The end point is indicated by the presence of a halo of

1,5 mm width around the spot after stirring for 2.5 minutes. The MB adsorption capacity is determined from the amount of added MB at the end point.

MB adsorption capacity [mmol/100g] = (amount of added MB at the end point [mmol])/(mass of dried sample [g]) × 100

Filter papers satisfying the following characteristics are recommended.

Mass: about 140 g/m^2.

Thickness: about 0.25 mm.

Pore size: about 3 µm.

Filtration time (i.e. the time for filtering 100 cm^3 distilled water through 10 cm^2 of filter paper by pressure of 0,98 kPa at 20 °C): about 240 s or less.

A.8 Aspect ratio

The aspect ratio of clay nanoplates in a sample is often measured by AFM. A 0,1 wt % suspension sample is first prepared and is further diluted to 5 × 10^{-5} wt %. Finally, the dilution is cast and dried on a highly flat substrate before the observations. Measure a statistically significant number of lateral sizes of individual planer objects and calculate the circle equivalent diameter. The circle equivalent diameter is divided by the average thickness of the planer objects to obtain the aspect ratio. For measurement of the aspect ratio using TEM, SEM and AFM, see References [15], [19], [20] and [18], respectively.

A.9 Film formability

A.9.1 General

An aqueous clay nanoplate suspension sample is first prepared.[1,12] The dry matter content is around 2 wt % to 3 wt %. The aqueous suspension of 110 cm^3 is stirred vigorously to finely disperse it, then it is degassed in a vacuum chamber. The suspension is poured into a polypropylene tray (200 mm × 140 mm × 25 mm) and dried at 60 °C for 1 day. The evaluation of film formability is carried out under normal air condition as detailed in A.9.2.[10]

A.9.2 Film formability

Visually observe the presence or absence of shrinkage of the resulted specimen and take photos. Carefully peel the resulting specimen from the casting substrate. Observation on the form retention of the specimen is made and the film formability of the sample is classified into four ranks. The judgment criteria are shown in Table A.1.

A.9.3 Flexibility test

The flexibility of the specimen is evaluated by the cylindrical mandrel bend test (ISO 1519).[12,13]

Table A.1 — Criteria of the film formability

Film formability rank	Appearance of precipitation	Deformation	Shape retention	Additional evaluation
A	Freestanding film	No	Excellent	Flexibility
B	Freestanding film	Yes	Good	Flexibility
C	Fragile film	Yes	Poor	—
D	No film is obtained	—	Poor	—

A.10 Viscosity

A variety of viscometers are commercially available. Follow instruction manuals provided by the instrument manufacturers for measurements. A rotational viscometer is most often used to measure the viscosity of clay dispersions. A suitable rotor shall be selected depending on the viscosity. Care must be taken because viscosity is sensitive to clay concentration, rotation speed and temperature.

Measurement method and measurement conditions can be adopted as agreed between buyer and seller.

Annex B
(informative)

Principles of a gas barrier using clay nanoplates

B.1 General

The polymer clay nanocomposite has been found to have improved gas barrier properties, and related patents and articles are numerous. For that reason, food packaging films and the like have been studied and commercialized. It is effective to improve the gas barrier property of films by arranging the nanoplates in high-loading parallel to the film.[15] There are two kinds of nanocomposite gas barrier film: plastic matrix type and coating type. In the case of the plastic matrix type, uniform mixing of plastic and clay nanoplate must be secured. In the case of coating type, a thin nanocomposite layer adhered to the plastic film is provided. In either case, gas barrier properties are manifested because the clay nanoplate crystal is impermeable to gas molecules. Typical clays used in nanocomposites include purified bentonite, synthetic smectite and organoclay. In order to prepare a transparent gas barrier film, a synthetic smectite free from coloured impurities is used. The content of clay nanoplates in the gas barrier layer is from a few to 90 wt %. The coating film can be obtained by coating and drying a mixed solution on a substrate film such as PET, and if a roll to roll coating machine is used, a long film can be obtained.

When kneading clay nanoplates into plastics to form films, the affinity between plastics and clay nanoplates is important, and organoclays are often used. Various organoclays are prepared to be suitable for plastics of different affinities. Organoclay preparation includes a method of introducing a surfactant into clay by ion exchange and a method of introducing a covalent bond with an organic molecule at the crystal edges by a silylating agent.

In a suspension casting method, clay and plastics can be mixed in a wide range of mixing ratio. In this case, a liquid or mixed liquid that disperses the clay well and simultaneously dissolves the plastic is necessary. Because clay crystals move easily in liquid media, it is easy to obtain a film with high crystal orientation using the method. For hydrophilic plastics, water-based liquid and hydrophilic clay can be used. The barrier layer made of hydrophilic plastic and clay has dry gas barrier properties but low water vapour barrier properties. In order to deal with that problem, use of clay which is resistant to water by heating has been studied.[1,14,15] Water resistance by heating utilizes the phenomenon that exchangeable cations having small ion diameters such as lithium, ammonium, and protons migrate to an octahedral vacant by heating. Water resistance is realized by heating even after the film formation. The gas barrier layer using these clays exhibits water vapour barrier properties after heating. A self-standing film with a suspension casting method can be obtained by coating the suspension on a substrate film such as PET, followed by a peeling the coating film from the substrate, and if a roll to roll coater is used, a long film can be obtained.

The polymer clay nanocomposite layer is used alone as a barrier film and also as a gas barrier component layer together with other barrier layers such as a vapour deposition barrier layer.

B.2 Basic approach

According to Nielsen's tortuous model on gas barriers in composite materials of plastics and plate crystals,[25] it is anticipated that when clay with high aspect ratio is used to make a film with high clay mixing ratio, it will become a film with high gas-barrier properties.[26] According to the model, the higher the clay content is, the better the gas barrier properties. In order to raise the loading of clay, the film forming property of the clay is an important factor. This is because if the film-forming property of clay is high, it is possible to make a film mainly composed of clay. The film formability of smectite clay depends on, among other things, the aspect ratio of clay crystals, interlayer ion species and excessive ion amount.[6,12,13,18,19]

On the other hand, problems such as occurrence of pinholes and cracks, deterioration of flexibility of the gas barrier layer and lowering of lamination strength occur. For that reason, high loading of clay is not always optimal, and the optimum clay loading is determined taking into consideration the balance of the overall characteristic values.

In order to obtain a transparent gas barrier film, the clay must be uniformly mixed with the resin at the nano level. If the surface of the film is rough, it becomes opaque, so the surface must be flat.

B.3 Gas barrier film preparation

The following are examples of gas barrier film preparation. A flexible transparent clay-based film was prepared using synthetic smectite and water-soluble polymer. It was confirmed from the X-ray diffraction chart that clay crystals were highly oriented. The clay-based film was extremely heat durable, with high gas-barrier properties.[26] The film showed very low permeability of dry oxygen.

The effect of a crystal-enlargement of smectite clays on the gas-barrier property of the polymer-clay nanocomposite film was studied.[15] The smectite clay was treated under hydrothermal condition leads to its larger crystal size. The treated smectite possessed a particle size of 71 nm, approximately twice that of the original one (36 nm). The treated smectite was subsequently used to prepare nanocomposites with carboxymethylcellulose sodium salt (CMC Na) to evaluate the effect of the crystal-enlargement. The nanocomposite films, which had a CMC Na ratio ranging from 40 wt % to 90 wt %, showed improved oxygen barrier properties when compared with those of original smectite. The tortuous model revealed that this improvement is mainly due to the increase of the particle size. A several micrometre thick film with 10 wt % of CMC Na and 90 wt % of smectite was applied on a PET film to elucidate the gas barrier property.

A Li^+-exchanged purified bentonite (BentLi) was used for a gas-barrier film preparation.[29] Most exchangeable ions were Li^+ and the cation exchange capacity was 101,8 meq/100g. Glycol lignin (GL) was obtained by acid-catalysed solvolysis of the ceder with polyethylene glycol. GL was used as a binder. The film was heated to 300 °C. It was confirmed from the X-ray diffraction chart that clay crystals were highly oriented. It had a water vapour transmission rate of 1,64 g m^{-2} day^{-1}, at 40 °C, 90 % relative humidity and the higher water vapour barrier property originated from not only the water-resistant bentonite but also the GL.

B.4 Relationship between clay nanoplate characteristics and high gas-barrier film properties

Mineral composition is an important characteristic in making gas-barrier films. Bentonite contains minerals other than smectites, such as quartz, feldspar, cristobalite and mica. Minerals other than smectite do not disperse up to a single layer in water, so cannot be said to be clay nanoplates. Smectite is purified by elutriation and the purity can be known from the mineral composition. This characteristic relates to dispersibility and film formability of the powder and also to the crystal orientation property in films.

Methylene blue adsorption capacity is an important characteristic in making gas-barrier films. It is an index for evaluating the smectite content in the sample. The larger the methylene blue adsorption capacity, the higher the smectite content.[23] This characteristic is related to dispersibility and film formability of the powder and also relates to the crystal orientation property in films.

Cation exchange capacity is an important characteristic in making gas-barrier films. It is an index for evaluating the smectite content in the sample as well as methylene blue adsorption capacity. Generally, the larger the cation exchange capacity, the higher the smectite content. This characteristic is related to dispersibility and film formability of the powder, and also relates to crystal orientation property in films. This is also related to water-resistance property by heating.

Particle size distribution in suspension is an important characteristic in making gas-barrier films. It is an index on how well the clay can be dispersed in the liquid. Clay which disperses well in liquid can mix with plastics having similar affinity to the liquid. Clay particles monodispersed in liquid are easy to orient during film formation. Conversely, in a sample having a large particle diameter in the dispersion, there is a high possibility that the primary particles are agglomerated. This characteristic is related to dispersibility and film formability of the powder, and also relates to crystal orientation property in films.

Mineral composition is an important characteristic in making gas-barrier films. In the case of natural smectite, it is possible to know the smectite species from the chemical composition. The concentration of coloured element is also known. In the case of synthetic smectite, it is possible to know from the chemical composition whether or not smectite, which is a target substance, is obtained. It is also possible to know the charge ratios of the tetrahedral layer and the octahedral layer, which are important for water resistance by heating.

Aspect ratio is an important characteristic in making barrier films. According to Nielsen's tortuous model on gas barriers in composite materials of plastics and plate crystals, it is anticipated that when clay with a high aspect ratio is used this leads to high-barrier films. This characteristic is related to film formability of the powder and also to crystal orientation property in films.

Film formability is an important characteristic in making barrier films. If the clay itself has film formability, it means that films can be made without adding a lot of organic binder. According to Nielsen's tortuous model on gas barriers in composite materials of plastics and plate crystals, it is anticipated that when clay loading is high this leads to high-barrier films. From the viewpoint of heat resistance as well, it is advantageous that the clay ratio is high. For these reasons, it is readily inferred that clay which forms the film itself has advantages for preparation of high-performance films.

Loss on ignition is an important characteristic in making barrier films. Clay products can contain additives and surfactants, but it is the clay crystals that contribute to the gas barrier property. Loss on ignition indicates the ratio of clay crystals present in clay products.

Figure B.1 illustrates the relationship between characteristics of clay nanoplate products and gas barrier properties of films using the products.

