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Safety assessment of the substance, montmorillonite clay modified with hexadecyltrimethylammonium bromide, for use in food contact materials

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Abstract

The EFSA Panel on Food Contact Materials, Enzymes and Processing Aids (CEP) assessed the safety of montmorillonite clay modified with hexadecyltrimethylammonium bromide (HDTA) when used as an additive at up to [REDACTED] in polylactic acid (PLA) bottles intended for contact with water for long-term storage at ambient temperature or below. The modified clay, which 90% w/w of the particles have a dimension of 33.1 µm or less and the average size is 9 µm, has a layered structure with layers of a thickness below 100 nm. When incorporated in PLA, nanosized layers can be dispersed in the matrix, but are not expected to migrate. Thermal degradation is not expected at the maximum manufacturing temperature. No loss of integrity of the PLA surface due to interaction with bottled water was observed. The overall migration was very low. No migration of HDTA was detected at the limit of detection [REDACTED]. Migration of aluminium was below or at the limit of detection [REDACTED], which would conservatively correspond to approximately [REDACTED]. Comparative analysis of bottled water with and without the modified clay did not reveal additional peaks corresponding to impurities identified in the modifier and/or in the modified clay. Moreover, [REDACTED], and the modifier HDTA have been evaluated and authorised. Therefore, the CEP Panel concluded that the substance montmorillonite clay modified with HDTA bromide is not of safety concern for the consumer if the substance is used as an additive at up to [REDACTED] in PLA plastic bottles and other containers intended for long-term storage of water at ambient temperature or below, as requested by the applicant.

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Note: The full opinion will be published in accordance with Article 10(6) of Regulation (EC) No 1935/2004 once the decision on confidentiality, in line with Article 20(3) of the Regulation, will be received from the European Commission. The following information has been provided under confidentiality and it is redacted awaiting the decision of the Commission: the manufacturing process, the composition and the maximum use percentage of the substance; part of the manufacturing process of the material and article manufactured with the substance; part of the characterisation of the substance in the manufactured material and article; some of the migration testing conditions and method of analysis; some of the migration results and limits of detection.

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1. Introduction

1.1. Background and Terms of Reference as provided by the requestor

Before a substance is authorised to be used in food contact materials (FCM) and is included in a positive list EFSA's opinion on its safety is required. This procedure has been established in Articles 8, 9 and 10 of Regulation (EC) No 1935/2004¹ of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food.

According to this procedure, the industry submits applications to the Member States competent authorities which transmit the applications to the European Food Safety Authority (EFSA) for their evaluation.

In this case, EFSA received an application from the Food Safety and Nutrition Agency, Spain, requesting the evaluation of the substance "nano-hexadecyltrimethylammonium bromide modified montmorillonite organoclay" with the FCM substance No 1075. The dossier was submitted by Packaging, Transport and Logistics Research Centre, Itene.

According to Regulation (EC) No 1935/2004 of the European Parliament and of the Council on materials and articles intended to come into contact with food, EFSA is asked to carry out an assessment of the risks related to the intended use of the substance and to deliver a scientific opinion.

2. Data and methodologies

2.1. Data

The applicant has submitted a dossier in support of its application for the authorisation of the substance nano-hexadecyltrimethylammonium bromide modified montmorillonite organoclay, to be used in plastic food contact materials.

Additional information was provided by the applicant during the assessment process in response to requests from EFSA sent on 12 June 2015, 24 May 2018 and 3 October 2018 (see 'Documentation provided to EFSA').

Data submitted and used for the evaluation are:

Non-toxicological data

- Data on identity
- Data on physical and chemical properties
- Data on intended use and authorisation
- Data on residual content of the substance and its components
- Data on migration of the substance and its components
- Data on identification, quantification and migration of impurities and reaction products.

Toxicological data

None (see Section 3.2).

2.2. Methodologies

The assessment was conducted in line with the principles laid down in Regulation (EC) No 1935/2004 on materials and articles intended to come into contact with food. This Regulation underlines that applicants may consult the Guidelines of the Scientific Committee on Food (SCF) for the presentation of an application for safety assessment of a substance to be used in FCM prior to its authorisation (European Commission, 2001), including the corresponding data requirements. The dossier that the applicant submitted for evaluation was in line with the SCF guidelines (European Commission, 2001).

The methodology is based on the characterisation of the substance that is the subject of the request for safety assessment prior to authorisation, its impurities and reaction and degradation products, the evaluation of the exposure to those substances through migration and the definition of minimum sets of toxicity data required for safety assessment.

To establish the safety from ingestion of migrating substances, the toxicological data indicating the potential hazard and the likely human exposure data need to be combined. Exposure is estimated from

¹ Regulation (EC) No 1935/2004 of the European parliament and of the council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC. OJ L 338, 13.11.2004, p. 4–17.

studies on migration into food or food simulants and considering that a person may consume daily up to 1 kg of food in contact with the relevant FCM.

As a general rule, the greater the exposure through migration, the more toxicological data is required for the safety assessment of a substance. Currently, there are three tiers with different thresholds triggering the need for more toxicological information as follows:

- a) In case of high migration (i.e. 5–60 mg/kg food), an extensive data set is needed.
- b) In case of migration between 0.05 and 5 mg/kg food, a reduced data set may suffice.
- c) In case of low migration (i.e. < 0.05 mg/kg food), only a limited data set is needed.

More detailed information on the required data is available in the SCF guidelines (European Commission, 2001).

The assessment was conducted in line with the principles described in the EFSA 'Guidance on transparency in the scientific aspects of risk assessment' (EFSA Scientific Committee, 2009) and considering the relevant guidance from the EFSA Scientific Committee such as the 'Guidance on risk assessment of the application of nanoscience and nanotechnologies in the food and feed chain: Part 1, human and animal health' (EFSA Scientific Committee, 2018).

3. Assessment

According to the applicant, the substance named 'nano-hexadecyltrimethylammonium bromide modified montmorillonite organoclay', renamed by the CEP Panel as 'montmorillonite clay modified with hexadecyltrimethylammonium bromide', is intended to be used as an additive at up to [REDACTED] in polylactic acid (PLA) to improve thermal, barrier and mechanical properties. Final articles are bottles intended for contact with water for long-term storage at ambient temperature or below.

The substance montmorillonite clay modified with hexadecyltrimethylammonium bromide (HDTA) has not been evaluated by SCF or EFSA. However, [REDACTED], [REDACTED], a minor component/impurity), and the modifier HDTA (CAS No. 57-09-0), are each listed in the Regulation (EU) 10/2011² under the FCM Substance No. [REDACTED], the FCM substance No. [REDACTED], and the FCM Substance No. 104 with a specific migration limit (SML) of 6 mg/kg food, respectively.

3.1. Non-toxicological data

[REDACTED] is modified with a quaternary ammonium salt, HDTA by means [REDACTED] and the quaternary ammonium. [REDACTED]
[REDACTED]
[REDACTED] The clay modification is needed in order to make the clay hydrophobic and compatible with the polymer, PLA.

² Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. OJ L 12, 15.1.2011, p. 1.

Hexadecyltrimethylammonium bromide:

- Chemical formula: $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$
- Molecular weight: 364.45 Da
- Chemical structure:



- Physical and chemical properties of the modified montmorillonite clay

The modified montmorillonite clay is composed of [REDACTED] HDTA and [REDACTED], the remaining being water. [REDACTED]

The modified montmorillonite clay [REDACTED] used to produce PLA bottles by injection stretch blow moulding at a maximum temperature of 230°C. Thermogravimetric analysis (TGA) under nitrogen of the modified clay showed a 10% mass loss when heated up to 299°C, which is attributed to the evaporation of water. Thermal degradation is therefore not expected at the maximum manufacturing temperature of 230°C.

Of the particles, 90% w/w are of a diameter of 33.1 µm or less and the average size is 9 µm. The substance has a layered structure with a layer (platelet) thickness below 100 nm. When added to the PLA matrix, these platelets can be dispersed in the matrix. Distribution and particle size of the modified clay particles in PLA bottles with the maximum intended load was characterised by transmission electron microscopy (TEM). It confirmed the presence of [REDACTED] platelets and [REDACTED] sheets of thickness below 100 nm ([REDACTED]). However, examination of the TEM data showed that the [REDACTED] platelets retained width and/or length in the order of hundreds of nanometers. In addition, they are oriented parallel to the plastic surface and completely embedded. Consequently, in agreement with Bott et al. (2014a,b,c), the CEP Panel does not anticipate migration of the nano- platelets and sheets.

- Migration of the modified montmorillonite clay and of the quaternary ammonium modifier

The inner surface of a PLA bottle loaded with the maximum intended percentage of the modified clay was analysed by Scanning Electron Microscopy before and after contact with water for 40 days at 45°C, which covers the requested intended uses. No loss of integrity of the PLA surface due to interaction with bottled water was observed. This is supported by the low overall migration result that was determined for the bottles ([REDACTED]).

Migration of aluminium from PLA bottles loaded with the maximum intended percentage of the modified clay into water [REDACTED] was measured by inductively coupled plasma mass spectrometry (ICP-MS) as a marker of the potential migration of the modified clay. Migration was below or at the limit of detection (LoD) [REDACTED]. Assuming that all the aluminium comes from the clay, this LoD would correspond to approximately [REDACTED]. Additionally, migration of aluminium complies with the SML of 1 mg/kg food.

Migration of free HDTA (i.e. not linked with the clay) into water for 40 days at 45°C was analysed by liquid chromatography coupled to mass spectrometry (LC-MS). Tests were performed with samples of PLA made with the maximum intended percentage of the modified clay. Migration was not detected at the LoD of [REDACTED].

Those results support the previous consideration that release of nanoparticles from the PLA bottles into water is not expected.

- Migration of reaction products and impurities

The modifier and the modified clay were analysed by [REDACTED] for the identification of potentially migrating impurities. Detected substances included alkanes, bromo- and chloro-alkanes, alcohols, esters, ketones, amides and amines.

The impurities were compared in PLA bottles made with- and without the modified clay additive, using [REDACTED]. Their migration was compared in water after 40 days contact at 45°C, using [REDACTED].

Of the halogenated alkanes identified in the modifier and/or in the modified clay, none was detected in the PLA with the maximum intended load, nor in the water samples after contact, at a limit of detection below 1 µg/kg both for PLA and water.

With regard to the other impurities identified in the modifier and/or in the modified clay, the comparative analysis of the water samples did not reveal any additional peaks, with a limit of detection in the region of 1 µg/kg water.

3.2. Toxicological data

[REDACTED], [REDACTED] (a minor component/impurity), the modifier HDTA and aluminium have been evaluated and authorised to be used in the manufacture of plastic (cf. Regulation (EU) 10/2011). Moreover, based on the above data, the modified montmorillonite clay and specifically the platelets and sheets are not expected to migrate from the PLA under the intended conditions of uses. Migration of the modifier was not detected. Migration of aluminium was, at most, at the limit of detection. And migration of the impurities was not detected.

4. Conclusions

The CEP Panel, based the above-mentioned data, concluded that the substance montmorillonite clay modified with HDTA is not of safety concern for the consumer if the substance is used as an additive at up to [REDACTED] in PLA plastic bottles and other containers intended for long-term storage of water at ambient temperature or below, as requested by the applicant.

Documentation provided to EFSA

- 1) Technical dossier. July 2013. Submitted by Packaging, Transport and Logistics Research Centre, Itene.
- 2) Additional information. April 2018. Submitted by Packaging, Transport and Logistics Research Centre, Itene.
- 3) Additional information. July 2018. Submitted by Packaging, Transport and Logistics Research Centre, Itene.
- 4) Additional information. October 2018. Submitted by Packaging, Transport and Logistics Research Centre, Itene.

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Abbreviations

CAS	Chemical Abstracts Service
CEP	Scientific Panel on Food Contact Materials, Enzymes and Processing Aids

FCM	food contact materials
[REDACTED]	[REDACTED]
HDTA	hexadecyltrimethylammonium bromide
[REDACTED]	[REDACTED]
ICP-MS	inductively coupled plasma mass spectrometry
[REDACTED]	[REDACTED]
LC-MS	liquid chromatography coupled to mass spectrometry
LoD	limit of detection
PLA	poly(lactic acid)
SCF	Scientific Committee on Food
SML	specific migration limit
[REDACTED]	[REDACTED]
TEM	transmission Electron Microscopy
TGA	thermogravimetric analysis
w/w	weight per weight