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Safety assessment of the substance (butadiene, styrene, methyl methacrylate, butyl acrylate) copolymer cross-linked with divinylbenzene or 1,3-butanediol dimethacrylate for use in food contact materials

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Abstract

This scientific opinion of the EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF) deals with the safety re-assessment of (butadiene, styrene, methyl methacrylate, butyl acrylate) copolymer cross-linked with divinylbenzene or 1,3-butanediol dimethacrylate for use at up to 40% w/w in blends of styrene acrylonitrile copolymer (SAN)/poly (methyl methacrylate) (PMMA). Finished articles are intended for repeated contact at room temperature or below with aqueous, acidic and/or low alcoholic foodstuffs for less than 1 day and with dry foodstuffs for more than 1 day. The substance has a low molecular weight fraction (LMWF) below 1,000 Da up to 3.3%. It starts to thermally degrade at ca 230°C, below the maximum temperature of processing finished articles, 250°C. Among the substances released from the heated polymeric additive, four were detected to be released from the finished food contact material (FCM). Migration of oligomers and reaction products into 3% acetic acid and 20% ethanol from a SAN/PMMA material was found to decrease with repeated uses. After the third contact, cyclo-octatetraene, toluene and a hexanedioic acid related substance were detected by GC–MS analysis of the simulant samples, at approximately 5 µg/kg food. From analysis with headspace-GC–MS of heated plastic samples with and without the substance, four volatiles were (semi)quantified at ca 1 µg/6 dm² or less. Considering that the substance is a polymeric additive without structural alert for genotoxicity, manufactured using authorised monomers and with limited potential migration of the LMWF, no toxicological data were requested. The CEF Panel concluded that the substance is not of safety concern for the consumer if it is used at up to 40% w/w in blends of SAN/PMMA repeat-use articles intended for contact at room temperature with aqueous, acidic and/or low alcoholic foodstuffs for less than 1 day and with dry foodstuffs without a time limit.

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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 Ministry of Health, Welfare and Sport, the Netherlands, requesting the evaluation of the substance (butadiene, styrene, methyl methacrylate, butyl acrylate) copolymer cross-linked with divinylbenzene or 1,3-butanediol dimethacrylate, with the CAS number 25101-28-4, the PM Ref. No 40563 and the FCM substance No 856. The dossier was submitted on behalf of Kaneka Belgium NV.

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 (butadiene, styrene, methyl methacrylate, butyl acrylate) copolymer cross-linked with divinylbenzene or 1,3-butanediol dimethacrylate, to be used in FCM. Data submitted and used for the evaluation are:

Non-toxicological data and information

- Data on intended use and authorisation
- Data on thermal stability
- Data on the release of substances on heating
- Data on overall migration
- Data on migrating substances including oligomers

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(s) 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 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:

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.

- 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, 2009) and considering the relevant existing Guidance from the EFSA Scientific Committee.

3. Assessment

The substance (butadiene, styrene, methyl methacrylate, butyl acrylate) copolymer cross-linked with divinylbenzene or 1,3-butanediol dimethacrylate has been evaluated for its use as impact modifier in rigid poly(vinyl chloride) (PVC) by the CEF Panel in 2011 (EFSA CEF Panel, 2011). The CEF Panel concluded that there is no safety concern for the consumer if the substance is used at up to 12% w/w in rigid PVC materials at room temperature or below. It has then been authorised with the corresponding restriction and the substance is listed in the amendment Commission Regulation (EU) No 1282/2011².

Now, the applicant is requesting an extension of use of the substance as an impact modifier at up to 40% w/w in blends of styrene acrylonitrile copolymer (SAN)/poly(methyl methacrylate) (PMMA). Finished articles are intended for repeated contact at room temperature or below with aqueous, acidic and/or low alcoholic (< 20%) foodstuffs for less than 1 day and with dry foodstuffs for more than 1 day up to and including long-term storage conditions. Typical examples of food contact articles are water jugs and storage boxes for cereals or pasta.

3.1. Non-toxicological data

The substance is a polymeric additive made using the authorised monomers butadiene (BD; FCM Substance No 223), styrene (FCM Substance No 193), methyl methacrylate (MMA; FCM Substance No 156) and butyl acrylate (BA; FCM Substance No 325). It is cross-linked with divinylbenzene (DVB; FCM Substance No 405) or 1,3-butanediol dimethacrylate (made with the monomers 1,3-butanediol and methacrylic acid, FCM substances No 228 and 150, respectively) (Commission Regulation (EU) No 10/2011³). Styrene and 1,3-butanediol are authorised without specific restriction. Methacrylic acid, MMA and BA are authorised with a group specific migration limit, SML(T) = 6 mg/kg food. BD is authorised with a restriction of maximum residual quantity, QM = 1 mg/kg final product, and it shall not migrate, which means that its migration shall not be detectable with a detection limit of 0.01 mg/kg food. DVB is authorised and shall not be detectable with a detection limit of 0.01 mg/kg food expressed as the sum of divinylbenzene and ethylvinylbenzene and may contain up to 45% (m/m) of ethylvinylbenzene.

The substance is insoluble in most solvents and 95% by mass has a high molecular weight of more than 750 kDa. Nonetheless, the low molecular weight fraction (LMWF) below 1,000 Da is quite substantial at up to 3.3% of the substance.

Based on thermogravimetric analysis (TGA), the substance starts to thermally degrade at ca 230°C which is below the maximum applied temperature of processing finished articles, which according to the applicant is 250°C. Thermal degradation studies were conducted by heating the substance to 250°C and to 260°C in a stream of air or nitrogen. Gas chromatography–mass spectrometry (GC–MS) analysis of the released substances revealed that at both temperatures and under both gases, the additive released a large number of volatile substances as a result of both thermal desorption and thermal decomposition.

Overall migration into 3% acetic acid and into 20% ethanol was tested from SAN/PMMA material containing the substance at the maximum content of 40% w/w. Three successive contacts were performed at 40°C for 1, 2 and 7 days (i.e. 10 days in total), using fresh simulant for each time period. Overall migration was measured for all fractions and compared with a blank sample (not containing the substance) tested in the same conditions. No significant difference could be determined

² Commission Regulation (EU) No 1282/2011 of 28 November 2011 amending and correcting Commission Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food.

³ Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food.

between the sample and the blank, for either food simulants and for all three time periods, at the limit of detection of 0.1 mg/dm². These test conditions are more than adequate for the contact less than 1 day requested with aqueous, acidic and/or low alcoholic foodstuffs.

The exposed simulants from all three contacts were used for identification and semiquantification of migrating oligomers and reaction products using liquid chromatography–photodiode array–mass spectrometry (LC–PDA–MS) in positive mode and GC–MS. LC–PDA–MS analyses showed that all migrating components detected in 3% acetic acid originated from the SAN/PMMA material and not from the substance under evaluation. In 20% ethanol, a few peaks including a MMA oligomer were detected to be originating from the substance under evaluation. After the third contact, those peaks were below the limit of detection, which was estimated to be 0.6 µg/kg food simulant based on the response factor of PMMA. Using GC–MS analysis of the two simulants, a total of six chemicals originating from the substance were detected after the first contact and these were in the range of 3–20 µg/kg food simulant. They were tentatively identified from their mass spectra as being toluene, a substance related to hexanedioic acid, cyclo-octatetraene related to styrene, a second substance related to styrene, methyl methacrylate and nonanal. After the third contact, only the first three of these six chemicals were still detectable at concentrations (estimated using the response of a styrene standard) of approximately 5 µg/kg food.

Analysis of the same migration simulants by proton nuclear magnetic resonance spectroscopy (H-NMR) demonstrated the absence of conjugated dienes at a detection limit of 10 µg/kg food.

The same plastic samples, with- and without the additive present, were tested for the release of substances when heated for 30 min at 100°C using headspace (HS)-GC–MS analysis. The Panel considered that this test was acceptable in this case considering the intended repeated uses in contact with dry foods and the nature of the final plastic. Comparing the two samples, with- and without the additive, only styrene and methyl methacrylate were detected, at concentrations estimated to be ca 0.5–1 µg/6 dm². Two other substances, toluene and acetophenone, were also suggested in the GC–MS data but their concentrations (< 0.05 µg/6 dm²) were too low to allow proper identification and quantification. The GC–MS data was further examined for the most prominent volatiles detected in the thermal degradation GC–MS studies. No other substances than the four already described (styrene, methyl methacrylate, toluene and acetophenone) were detected.

Overall, the Panel considered that using the two liquid food simulants under conditions of 1 day plus 2 days plus 7 days repeated use contacts, along with the heating tests by HS-GC–MS, adequately covers the food contact situations envisaged for the finished articles made using the substance. It is very unlikely that important substances were missed, when considering the analytical methods used.

3.2. Toxicological data

The substance is a polymeric additive without structural alert for genotoxicity and it is manufactured using evaluated and authorised monomers. There is no detectable migration of oligomers below 1,000 Da with a detection limit of 0.6 µg/kg food simulant. Therefore, no toxicological data on oligomers were requested. The detection of trace levels of volatiles released from the FCM, including toluene, acetophenone, a substance related to hexanedioic acid, a cyclo-octatetraene related to styrene, styrene itself and methyl methacrylate, does not give rise to concern considering the low levels and the fact that migration would fall further on repeated uses of the FCM.

4. Conclusions

Having considered the above-mentioned data, the CEF Panel concluded that the substance (butadiene, styrene, methyl methacrylate, butyl acrylate) copolymer cross-linked with divinylbenzene or 1,3-butanediol dimethacrylate is not of safety concern for the consumer if used, as requested, as a polymeric additive at up to 40% w/w in blends of styrene acrylonitrile copolymer (SAN)/poly(methyl methacrylate) (PMMA) repeat-use articles intended for contact at room temperature with aqueous, acidic and/or low alcoholic (< 20%) foodstuffs for less than 1 day and with dry foodstuffs for any duration of contact including long-term storage.

Documentation provided to EFSA

- 1) Initial dossier. January 2015. Submitted by Kaneka Belgium NV.
- 2) Additional data. November 2015. Submitted by Kaneka Belgium NV.
- 3) Additional data. July 2016. Submitted by Kaneka Belgium NV.

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Abbreviations

BA	butyl acrylate
BD	butadiene
CAS	Chemical Abstracts Service
CEF	Panel on food Contact Materials, Enzymes, Flavourings and Processing Aids
DVB	divinylbenzene
FCM	food contact materials
GC-MS	gas chromatography-mass spectrometry
H-NMR	proton nuclear magnetic resonance spectroscopy
HS-GC-MS	headspace-gas chromatography-mass spectrometry
LC-PDA-MS	liquid chromatography-photodiode array-mass spectrometry
LMWF	low molecular weight fraction
m/m	mass per mass
MMA	methyl methacrylate
PM	packaging material
PMMA	poly(methyl methacrylate)
PVC	poly(vinyl chloride)
QM	maximum residual quantity
SAN	styrene acrylonitrile copolymer
SCF	Scientific Committee on Food
SML(T)	total specific migration limit
TGA	thermogravimetric analysis
w/w	weight per weight