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Survey and investigation of migration of monomers in toy materials

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Contents

Preface 6

Summary and conclusions 7

Abbreviations 12

1. Introduction 14
1.1 Background 14
1.2 Purpose 15
1.3 Scope of the report 15

2. Carcinogenic monomers 16
2.1 CMR substances in toys 16
2.2 The five monomers 18

3. Legislation 19
3.1 The Danish Statutory Order on Toys 19
3.1.1 Existing regulations for the five monomers in toys 20
3.2 Legislation for monomers in food contact materials 20
3.3 Proposal from ANEC for legislation on monomers in toys 21
3.3.1 TIE’s answer to ANEC’s proposal for legislation 22

4. Survey - materials 24
4.1 Contact to relevant interested parties in the toy sector 24
4.1.1 Information from TIE (Toy Industries of Europe) 24
4.1.2 Information from a Danish producer/importer of toys 25
4.2 Literature search/internet search 26
4.2.1 Information from various producers’ websites 26
4.2.2 Information from various articles 27
4.3 Information from producers/importers of toy 29
4.4 Information from UL Prospector database 30
4.5 Summary of materials used in toys 33

5. Survey - monomers 34
5.1 Theoretical considerations about residual monomers 34
5.1.1 Physical/chemical properties of monomers 34
5.1.2 Content of monomers – theoretical considerations 35
5.1.3 Migration of monomers – theoretical considerations 36
5.1.4 Summary – theoretical considerations 37
5.2 Existing data on content of residual monomers 38
5.2.1 Content of residual monomers in toys 38
5.2.2 Content of residual monomers in plastic 40
5.2.3 Summary of data regarding the content of residual monomers in plastic 42
5.3 Existing data on migration of residual monomers from plastic 45
5.3.1 Migration of residual monomers from toys 45
5.3.2 Migration of residual monomers from plastic 46

5.3.3 Summary of data regarding migration from plastic 50
5.4 Summary and discussion regarding content and migration 53

6. Selection of products for analysis 55
6.1 Description of methods 55
6.1.1 Products sent from producers 55
6.1.2 Products purchased in shops in Denmark or via the internet 56
6.2 Monomers and materials in focus 56
6.3 Types of toy products in focus 56
6.4 Complete overview of the selected products for analysis 57

7. Content analyses 59
7.1 Analysis method for the content analyses 59
7.2 Results of the content analyses 59
7.3 Discussion of the analysis results 61

8. Migration analyses 63
8.1 Background for selection of migration analyses 63
8.2 Selected products for migration analyses – stage 1 64
8.3 Analysis method for the migration analyses – stage 1 65
8.4 Results of the migration analyses – stage 1 65
8.4.1 Discussion of the results – stage 1 67
8.5 Selected products for migration analyses – stage 2 67
8.6 Analysis method for the migration analyses – stage 2 68
8.7 Results of the migration analyses – stage 2 68
8.7.1 Discussion of the results – stage 2 69
8.8 Discussion of the migration analyses 69

9. Analyses of recycled plastic 70
9.1 Analyses for content of residual monomer 71
9.1.1 Results of the content analyses for recycled plastic 71
9.2 Analyses for migration of residual monomer 71
9.2.1 Results of migration analyses for recycled plastic 71
9.3 Discussion of analysis results 72

10. Hazard assessment 74
10.1 Acrylonitrile 74
10.1.1 Identification and physical-chemical parameters 75
10.1.2 Background levels 75
10.1.3 Absorption and distribution 76
10.1.4 Acute and chronic effects 77
10.1.5 Critical effect and calculation of DNEL/DMEL 77
10.2 Butadiene 78
10.2.1 Identification and physical-chemical parameters 79
10.2.2 Background levels 79
10.2.3 Absorption and distribution 80
10.2.4 Acute and chronic effects 80
10.2.5 Critical effect and calculation of DNEL/DMEL 80
10.3 Styrene 81
10.3.1 Identification and physical-chemical parameters 82
10.3.2 Background levels 82
10.3.3 Absorption and distribution 83
10.3.4 Acute and chronic effects 84
10.3.5 Critical effect and calculation of DNEL 85

10.4 Vinyl chloride 86
10.4.1 Identification and physical-chemical parameters 86
10.4.2 Background levels 87
10.4.3 Absorption and distribution 88
10.4.4 Acute and chronic effects 88
10.4.5 Critical effect and calculation of DNEL/DMEL 88

11. Risk assessment 90
11.1 Calculation of acceptable migration 90
11.2 Discussion of the hypothetical scenarios 93
11.3 Discussion and conclusion 94

12. Discussion in relation to ANEC's proposal 96

13. Economic impact 97
13.1 Economic impact of limit values for migration 97
13.2 Economic impact of limit values for content 97

14. References 99

Preface

Migration of selected monomers in toy materials

This project has studied and describes which materials (plastic and rubber) toys consist of as well as to what extent selected monomers migrate from toys. Furthermore, an assessment of the health risk of migration of monomers from toys has been carried out. The results of the survey and the chemical analyses are presented in the report.

This project was completed in the period from May 2018 to December 2018.

The project is performed by FORCE Technology with Eurofins Product Testing A/S as the subcontractor of the chemical content analyses and migration of selected monomers in toys.

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Summary and conclusions

Survey of migration of selected monomers from toy materials

When plastic is produced a polymerisation process occurs where monomers, i.e. the ”building blocks” or the basic substance of the plastic, are linked together. However, a residue of monomers will always be present in the plastic as all substances will not have completed the reaction in the polymerisation process. This concentration of residual monomers is generally low and depends on the process conditions of the production of the plastic raw material. Typical concentrations of residual monomers are between 0 and 2 % according to Hansen et al. (2018).

Some of these monomers are hazardous to health. For instance, some monomers are classified as carcinogenic. Therefore, there is a natural wish to limit the content and/or the release of these residual carcinogenic monomers in the plastic materials which might be found in toys. This applies especially to the substances which are genotoxic carcinogens where no threshold for carcinogenic effects exists.

The five carcinogenic monomers

In the EU Expert Group on Toy Safety ‘sub group chemicals’, the below five monomers have been identified as particularly problematic as they are regarded as carcinogenic and all are found in materials used for toys. The classification of the individual monomers as well as the existing limit values for these substances in legislation for both toys and food contact materials are presented in Table 1 below.

Table 1. The five relevant carcinogenic monomers

Monomer	Present for instance in the following materials	Classification according to CLP	Restriction in toys (EU Directive 2009/48) *EN 71-9 to EN 71-11[b]*	Restriction in food content materials (EU Regulation 10/2011)
Vinyl chloride	PVC	**Carc. 1A**	Content: 1000 mg/kg	Content: 1 mg/kg Migration: LOD[c]
1,3-butadiene	ABS, SBR, SBS, NBR	**Carc 1A, Mut. 1B**	Content: 1000 mg/kg	Content: 1 mg/kg Migration: LOD[c]
Acrylonitrile	SAN, ABS, ASA, NBR	**Carc. 1B**	Content: 1000 mg/kg	Content: - Migration: LOD[c]
Acrylamide	PAM	**Carc. 1B, Mut. 1B, Rep.2**	Content: 1000 mg/kg *Migration: 0.02 mg/l[b]*	Content: - Migration: LOD[c]
Styrene	PS, ABS, SBR, SEBS, SAN	**Rep. 2[a]**	Content: 30,000 mg/kg (1000 mg/kg [a]) *Migration: 0.75 mg/l[b]*	Content: - Migration: -

a. In 2018, IARC has assessed styrene as ‘Carc. Group 2A’.
b. No limit values for migration have been set in the toys directive. On the other hand, limit values in the standards EN 71-9 to EN 71-11 have been set, but these are not harmonised.
c. LOD = ’Level of detection’, i.e. a detectable migration is not allowed. The detection limit is 0.01 mg/kg food. The standards in the EN 13130 series regarding ”Materials and articles in contact with foodstuffs – Plastics substances subject to limitation” are typically used.
- means that no limitation has been set for the content of acrylonitrile and acrylamide in food contact materials or for content and migration of styrene in food contact materials.

In 2010, the Scientific Committee on Health and Environmental Risks (SCHEER) has assessed that no genotoxic carcinogens ought to be present in toys as intentionally added substances (SCHER 2010). The EU Directive on Toys allows content concentrations in the accessible parts up to the classification limit of 1000 mg/kg – which is relatively high in comparison with the food contact material legislation (1 mg/kg).

The consumer organisation ANEC's proposal for restriction of the five monomers

The European consumer organisation ANEC (European Association for the Coordination of Consumer Representation in Standardisation) has proposed the below limit values for the five monomers (ANEC, 2018). The limit values are solely proposed to be valid for toys intended for use by children below 3 years and for toys which are intended to be placed in the mouth.

- 1 mg/kg for the content of vinyl chloride in PVC toys
- 1 mg/kg for the content of 1,3 butadiene in toys when the substance is used as a monomer
- 1 mg/kg for the content of acrylonitrile in toys when the substance is used as a monomer
- 1 mg/kg for the content of acrylamide in toys when the substance is used as a monomer
- Migration limit value of 0.077 mg/l simulant for styrene following 3 hours extraction or a third of this value if the extraction procedure as described in EN 71-10 is used (where extraction for 1 hour is used).

A restriction of monomers which are genotoxic carcinogens can in practice mean a ban on several plastic and rubber materials in toys dependent on the wording of the restriction of the monomers. A possible restriction through a very low limit value for residual monomers in plastic and rubber materials in toys will have extensive consequences. Therefore, with this project, the Danish Environmental Protection Agency wants to gain more knowledge on the migration of relevant monomers under different conditions.

Purpose and scope

Among other things, this project has had the purpose to examine which plastic and rubber materials that are used in toys. The migration of the five above monomers from plastic materials used in toys has been examined when there is a convergence between the materials used for toys and these monomers. Finally, the purpose with this project has also been to assess whether a possible migration of monomers from toys can constitute a health risk for children playing with the toy. Overall, the purpose of this project has thus been to assess if a possible regulation of monomers in toys might be relevant.

The project is limited to focus on plastic and rubber materials which are used in toys intended for children at the age of 0-3 years as well as toys which are intended to be placed in the mouth as ANEC's proposal for restriction for the five monomers includes this group of toys. However, materials in toys for older children might also be included to some extent in this project. It was decided that focus was solely to be on new toy products and not on “older” toys (reusable toys).

Survey of materials used in toys

A survey of which types of materials (based on the five above monomers) that are typically used for toys was made. The survey was carried out through a literature search, a search in a material database as well as through contact to the toy sector in Denmark and in Europe via contact to the TIE ‘Toys Industries of Europe’.

Based on information from the survey (the literature and the toy industry), it seems that far the most important materials (which contain the relevant five monomers) in toys are ABS, PVC and PS. This also applies for materials in toys intended for children at the age of 0-3 years as well as materials in toys which are intended to be placed in the mouth. Furthermore, it is indicated that TPE (thermoplastic elastomers), including for instance SEBS, seem to be used to a small extent in parts of toys.

Chemical analyses – content and migrations of four monomers from toy materials
Based on the survey of materials used in toys, it was decided to focus on the four monomers vinyl chloride, butadiene, acrylonitrile and styrene which according to the survey seem to be used for the production of the most frequently used toy materials. The number of analyses of toy materials containing the different monomers was distributed based an estimate of which materials that most often seem to be used for toys. Therefore, it was decided to make chemical analyses for content of residual monomers in the following toy materials:

- 10 products of ABS (analysed for content of acrylonitrile, butadiene and styrene)
- 11 products of PVC (analysed for content of vinyl chloride)
- 5 products of PS (analysed for content of styrene)
- 2 products of SEBS (analysed for content of styrene)
- 2 products of SBC (analysed for content of butadiene and styrene)

In total, 30 different materials were analysed (of these, one toy product consisted of two different materials). The 29 different toy products came from minimum 18 different producers/importers of toys. Out of the in total 30 different toy materials which were analysed for content of residual monomers, 7 products were purchased in Denmark or at Danish websites and 4 products were ordered directly from China via a webshop. The remaining toy materials were received from European producers of toys. This procedure had the advantage that the material was identified in advance.

The results from the content analyses of the examined 30 toy materials are stated in Table 2 below together with the results from corresponding surveys of toys identified in literature. For some monomers, no results were identified from surveys of toys or only from a few surveys. For that reason, results from other products (especially food contact materials (FCM)) are also presented in the table. Data which are more than 10 years old are not included in the table.

Table 2. Content of residual monomers in different materials

Monomer	Material	Content measured in toys in this project (mg/kg)	Other measurements in toys (mg/kg)	Other measurements in other products (mg/kg)
Vinyl chloride	PVC	< 0.1	< 0.1	< 1 (raw material)
Acrylonitrile	ABS	8 - 64	< 0.01 - 55	0.15 - 50 (FCM)
Butadiene	ABS	0.23 - 1.55	< 0.01 - 5	0.06 - 1.7 (FCM)
	SBC	< 0.1 - 0.2	*No data*	*No data*
	SBS	*Not analysed*	< 0.1	*No data*
Styrene	ABS	595 - 1350	1.3 - 2600	Max. 3042 (FCM)
	PS	230 - 490	Max. 800	345 - 1000
	SBC	< 0.2 - 8	*No data*	*No data*
	SEBS	< 0.2	< 0.05 - 1.1	*No data*
	SBR/SBS	< 0.1	*No data*	*No data*

FCM = food contact materials

Based on the results of the content analyses for the four selected monomers, it was decided to perform the below migration analyses on two products of ABS and two products of PS with the highest levels of acrylonitrile, butadiene and styrene respectively. The migration analyses of the other materials were intentionally deselected due to the low content of residue monomers.

- Migration to 20 % ethanol at 40 °C for 30 minutes at stirring – to simulate toys used in bath water added oil
- Migration to artificial sweat at 37 °C for 8 hours at static migration – to simulate children holding their favourite toys for a large part of the day

- Migration to artificial saliva at 37 °C for 3 hours at stirring – to simulate a child placing the toy in the mouth (sucking on the toy without swallowing the toy material)
- Migration to water at 37 °C for 3 hours at static migration
- Migration to stomach acid (acidic liquid in the form of HCl) adjusted to a pH between 1.0 and 1.5 at 37 °C for 2 hours – to simulate toys which are swallowed and end in the stomach

These five migration analyses were performed for both ABS toy materials and both PS toy materials. The result was that no migration from any of the monomers (acrylonitrile, butadiene and styrene) were identified, either to artificial sweat, 20 % ethanol, artificial saliva, demineralised water or stomach acid from either ABS or PS in any of the in total four examined toy materials. The detection limit of the migration analyses was 0.01 mg/l migration liquid (corresponding to 10 µg/l) for acrylonitrile and butadiene and 0.02 mg/l migration liquid (corresponding to 20 µg/l) for styrene.

Chemical analyses of recycled material (industrial waste)
It was decided to examine if a possible content and migration of residual monomers from recycled material can be expected to be at the approximately same level as for a new toy product. Therefore, corresponding content and migration analyses were made on recycled plastic of ABS and PS. The recycled material which was analysed is the ‘purest’ kind of recycled plastic – namely industrial waste (partly from toy production and partly from production of food contact materials). Here, ‘pure’ solely corresponds to the plastic type, i.e. that industrial waste of ABS can be expected to consist of 100 % ABS.

The content of the different residual monomers in the analysed recycled plastic was at approximately the same level as the analyses carried out in this project and in other projects on new toy materials. At the migration analyses of the recycled plastic, no migration above the detection limit for any of the monomers was identified just like for the analyses of the toy material of virgin plastic. Therefore, the examined recycled materials (in the form of industrial waste) of ABS and PS do not seem to contain or release higher concentrations of monomers than the examined virgin (new product) ABS and PS material for toys.

Discussion
A significant conclusion in this project is that no migration of any of the examined monomers (acrylonitrile, butadiene and styrene) was measured above the detection limit of 10 µg/l migration liquid (corresponding to 0.01 mg/l) in either the two examined ABS toy materials or in the two PS toy materials at any of the five performed migration analyses, including migration to stomach acid simulant.

The detection limit for migration to stomach acid has been used as an expression of the maximum amount of monomer which might hypothetically be released in the stomach if a child swallows a little piece of toy material. This is a hypothetical amount of released monomer as the detection limit has been used as the level of migration even though it is unknown whether a migration actually occurs. This exposure calculation of intake of toy material showed that the migration (or the content in the situations where migration to stomach acid was not analysed) of residual monomers from the examined toy materials will not constitute a health risk for any of the examined monomers or any of the examined toy materials (ABS, PS, PVC, SEBS and SBC).

Regarding the assessment of the risk by oral exposure when small children have the toy in their mouth (i.e. sucking on the toy without swallowing the toy material), an ‘acceptable’ migration from the toy material was estimated. ‘Acceptable’ migration means the migration which based on the acceptable levels as to health (the so-called DMEL values (Derived Minimum Effect Level) for the individual monomers can be assumed to constitute a minimum health effect for children. The detection limit for the migration analyses for both butadiene and styrene is somewhat lower than the estimated ‘acceptable’ migration from toy materials for these two monomers. Therefore, these two monomers are not considered to constitute a risk for children who play with toy materials based on these monomers.

For acrylonitrile, the used detection limit at the migration analyses is, however, too high to be able to give an opinion of a possible risk. Thus, a lower detection limit at migration analyses is needed in order to be able to determine whether a possible risk occurs. However, the same detection limit has been used for migration of acrylonitrile from food contact materials which might indicate that at present it is not possible to reach a lower detection limit unless the method for analyses is further developed or non-standardised analysis methods are used. It must, however, be emphasised that there is a disagreement about the approach for estimating the DMEL value for which reason it is necessary with an updated assessment of the DMEL value for children. This assessment has been outside the scope of this project.

Reflections on ANEC’s proposal for restrictions
The analyses performed in this project as well as results identified in the survey show that toy materials in PVC have a content of vinyl chloride below the suggested content limit value for vinyl chloride of 1 mg/kg. Similarly, it seems that migration of the monomer styrene from relevant toy materials like ABS, PS, SEBS and SBC will not be above the suggested limit value for migration of styrene of 0.077 mg/l. For butadiene, it seems that the suggested content limit value of 1 mg/kg can be met for the major part of the examined toys, but some analysis results from both this and earlier surveys show that some products have a content above this value (values up to 5 mg/kg have been identified). Acrylamide has not been examined in this project.

However, for acrylonitrile it applies that the content limit value proposed by ANEC of 1 mg/kg cannot be complied with for ABS materials. All the 10 examined ABS products in this project had a content of acrylonitrile above this value and data from literature also indicate that the content of acrylonitrile typically is above the proposed limit value. In practice, an implementation of this proposed limit value might actually mean a ban on the use of ABS as a material in toys intended for children below 3 years or for toys intended to be placed in the mouth. ABS is a material which is widely used and especially for toys for children below 3 years which is partly due to its mechanical physical properties. Therefore, a ban on the use of ABS will have extensive economic consequences and affect the whole toy sector widely as new toy products must be developed in different materials. It must be noted that for food contact materials, no corresponding limit value for content of acrylonitrile is set, but only a limit value for migration of the monomer corresponding to the detection limit which is used in this project. The migration analyses performed in this project as well as earlier performed migration analyses for acrylonitrile in toy materials of ABS show that there is no migration of acrylonitrile from toy materials of ABS above this set migration limit value for food contact materials.

However, it must be noted that these proposed content limit values of 1 mg/kg for four of the monomers are based on the assumption that the entire amount of residual monomer in 8 mg toy material which is swallowed will be released in the body. The migration analyses performed in this project show that this is not the case as no migration above the detection limit at migration analyses to stomach acid has been measured.

Abbreviations

List of abbreviations used in the report

ABS	Acrylonitrile Butadiene Styrene
ANEC	European Association for the Coordination of Consumer Representation in Standardisation
ASA	Acrylonitrile Styrene Acrylate
BfR	Bundesinstitut für Risikobewertung (German Federal Institute for Risk Assessment)
CA	Cellulose Acetate
CAB	Cellulose Acetate Butyrate
CAP	Cellulose Acetate Propionate
CMR	Carcinogenic, mutagenic or reprotoxic
EVA	Ethylene Vinyl Acetate Copolymer
EPS	Expanded polystyrene
HDPE	High Density Polyethylene
HMWPE	High Molecular Weight Polyethylene
IARC	International Agency for Research on Cancer
LDPE	Low Density Polyethylene
LEG	The Danish trade organisation for toys
LLDPE	Linear Low Density Polyethylene
LMDPE	Linear Medium Density Polyethylene
MABS	Methyl Methacrylate / ABS
MDPE	Medium Density Polyethylene
MIPS	Medium Impact Polystyrene
MMBS	Methyl Methacrylate Butadiene Styrene
mMDPE	Metallocene Medium Density Polyethylene
NBR	Acrylonitrile Butadiene Rubber
OBC	Olefin Block Copolymer
PAM	Polyacrylamide
PEHD	Polyethylene High Density
PELD	Polyethylene Low Density
PBR, Low Cis	Low Cis Polybutadiene Rubber
PBS	Polybutylene Succinate
PC	Polycarbonate
PETG	Polyethylene Terephthalate Glycol Comonomer
PLA	Polylactic Acid
PMMA	Polymethyl methacrylate
Polyester, TP	Thermoplastic Polyester
POM	Polyoxymethylene
PP	Polypropylene
PP+EPDM	PP+Ethylene Propylene Diene Rubber
PS (GPPS)	Polystyrene (General Purpose Polystyrene)
PS (HIPS)	Polystyrene (High Impact Polystyrene)
PS (MIPS)	Polystyrene (Medium Impact Polystyrene)
PUR	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride

SAN	Styrene Acrylonitrile Copolymer
SBC	Styrene Butadiene Block Copolymer
SBR	Styrene Butadiene Rubber (the same as SBS)
SBS	Styrene Butadiene Styrene Block Copolymer
SCHEER	Scientific Committee on Health and Environmental and Emerging Risks, formerly known as SCHEER (Scientific Committee on Health and Environmental Risks)
SCCS	Scientific Committee on Consumer Safety
SEBS	Styrene Ethylene Butylene Styrene Block Copolymer
SML	Specific Migration Limit used in EU Regulation no. 10/2011 on plastic materials and articles intended to come into contact with food
SMMA	Styrene Methyl Methacrylate Acrylic
TDI	Tolerable Daily Intake
TIE	Toy Industries of Europe
TP	Thermoplastic (unspecified)
TPE	Thermoplastic Elastomer, can be e.g. SEBS, SBS, SBC
TPO (POE)	Thermoplastic Polyolefin Elastomer
TPS+PP	Thermoplastic Starch + PP
TPU	Thermoplastic Polyurethane Elastomer
XPS	Extruded polystyrene

1. Introduction

When plastic is produced a polymerisation process occurs where monomers, i.e. the ”building blocks” or the basic substance of the plastic, are linked together. However, a residue of monomers will always be present in the plastic as all substances will not have completed the reaction in the polymerisation process. This concentration of residual monomers is generally low and depends on the process conditions of the production of the plastic raw material. Typical concentrations of residual monomers are according to Hansen et al. (2018) between 0 and 2 %.

Some of these monomers have effects hazardous to health. For instance, vinyl chloride (monomer in PVC) and 1,3-Butadiene (monomer in ABS) are classified as carcinogenic Carc. 1A. Naturally, it is desired to limit the content and/or the release of these and other carcinogenic residual monomers in plastic which might be found in toys. This applies especially to the substances which are genotoxic carcinogens and thus do not have any lower limitation for carcinogenic effects.

1.1 Background

In 2010, the Scientific Committee on Health and Environmental Risks (SCHER) assessed that no genotoxic carcinogens ought to be present in toys as intentionally added substances (SCHER, 2010). Residues of certain monomers from certain types of plastic are examples of genotoxic carcinogens. In Commission Regulation (EU) no. 10/2011 on plastic materials and articles for contact with food, the term “non-intentionally added substance” is used and is defined among other things as an impurity in the applied substances or a reaction intermediate. Thus, monomers which are basis for the reaction of plastic polymers do not belong to the definition of “non-intentionally added”. There is no doubt that monomers are intentionally added as they form the basic material of plastic polymers, but it is a grey area in relation to the question if the residues of non-reacted monomers are considered as being “intentionally added” in polymer materials.

In practice, a restriction of monomers which are genotoxic carcinogens would mean a ban on a large number of plastic and rubber materials in toys depending on the actual restrictions made. A possible restriction through a very low limit value for residual monomers in plastic and rubber materials in toys would have extensive consequences. Therefore, with this project, the Danish Environmental Protection Agency (Danish EPA) wants to gain knowledge about the migration of relevant monomers under different conditions.

In the EU Expert Group on Toy Safety ”Sub-group Chemicals”, the following monomers have been identified as particularly problematic:

- Vinyl chloride, which is found in PVC.
- 1,3-Butadiene, which is found in e.g. acrylonitrile butadiene styrene (ABS) styrene-butadiene rubber (SBR/SBS), and other synthetic rubber materials like acrylonitril-butadiene (NBR).
- Acrylonitrile, which is found in styrene-acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS), acrylonitrile-styrene-acrylate (ASA), and other synthetic rubber materials like acrylonitrile-butadiene (NBR).
- Acrylamide, which is found in polyacrylamide (PAM).
- Styrene, which is found in e.g. polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), styrene-butadiene rubber (SBR), styrene-ethylene-buthylene-styrene rubber (SEBS), styrene

butadiene block co-polymer (SBC), styrene-acrylonitrile resin (SAN) and unsaturated polyesters.

Based on the toxic properties of these monomers and the assessment from SCHER (2010), ANEC[1], which is an European consumer organisation, has prepared a proposal for limit values for the above five monomers as a content in plastic or as a migration from plastic in toys. The details of the proposal are described further in chapter 3 ”Legislation”.

Thus, there is an ongoing discussion within the European framework regarding establishing possible limit values for these five residual monomers either in plastic or as migration from plastic.

1.2 Purpose

First, this project has the purpose to examine which plastic and rubber materials that are used in toys. Furthermore, the project has the purpose to examine the conditions under which the identified relevant carcinogenic monomers migrate from plastic materials used in toys when there is a convergence between the materials used for toys and the above-mentioned carcinogenic monomers. The examination focuses on the most used plastic types in toys. Additionally, the purpose is to identify the migration of the monomers under different conditions. Finally, the purpose of this project is to assess whether a possible migration of monomers from toys constitutes a health risk for children who have played with the toys.

Thus, the overall purpose of this project is to assess whether a possible regulation of monomers in toys might be relevant.

1.3 Scope of the report

ANEC has suggested that a limitation of monomers in toys is inserted in Appendix C of the Danish Statutory Order on Toys which is a list of “*specific limit values for chemicals used in toys intended for use by children under 36 months or in other toys intended to be placed in the mouth*”.

Therefore, the focus in this project is on plastic and rubber materials which are used in toys for children at the age 0-3 years as well as toys which are intended to be placed in the mouth. However, materials in toys for older children will also to some extent be included in the project

In relation to the exposure situation, it is important to distinguish between the exposure of children at the age 0-3 years who tend to place toys in their mouth (i.e. both oral and dermal exposure) and older children where the primary exposure of monomers will be dermal exposure when they hold the toy in their hands. Exposure by inhalation has not been examined in this report but is assumed to be negligible as this type of exposure will be considerably diluted by the surrounding air.

It was decided that focus was solely to be on new toy products and not on “older” toys (reusable toys). Reusable toys might give information about for instance change in migration in aged toys (compared to new toys) but as it is uncertain whether for instance a large migration from old toys might be due to aging of the material or the content of residual monomer was higher years back when the toys were produced, it was decided solely to assess new toy products. It might be possible to perform ageing tests on new toys, but ageing tests take a long time compared to the set time frame of this project and thus they have not been included in the project.

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[1] European Association for the Coordination of Consumer Representation in Standardisation

2. Carcinogenic monomers

This chapter describes which monomers that can be found in toy materials and are carcinogenic. The description is primarily based on the assessment which the German Federal Institute for risk assessment, BfR, (Bundesinstitut für Risikobewertung), has made on CMR substances (carcinogenic substances, mutagenic substances or substances harmful to reproduction) – thus including carcinogenic substances (Lenzner et al., 2018).

2.1 CMR substances in toys

BfR has carried out an evaluation of which monomers that have a harmonised classification as CMR and that can be found in toys. This evaluation is based on Annex I of the Commission Regulation (EU) no. 10/2011 on plastic materials and articles for contact with food. Annex I is a "Union list of authorised monomers, other starting substances, macromolecules obtained from microbial fermentation, additives and polymer production aids". These substances have individually been assessed by EFSA (European Food Safety Authority) before they were approved and included in Annex I. BfR has afterwards gone through the harmonised classification of the monomers and their use in the production of toys.

The result is a list of 20 relevant substances (monomers) classified as CMR and regarded as relevant for toys, i.e. some toys are produced in plastic/rubber material with the stated monomer as the basic substance. Their results are stated in Table 3 below and are identical with "Table 1" in Lenzner et al. (2018) with the exception that below the relevant plastic/rubber materials for the relevant monomers in this project are added and a new assessment from IARC regarding styrene has been published. In April 2018, IARC has made a reassessment of styrene and now classifies styrene as "*Group 2A Probably carcinogenic to humans*" which in the long term may result in a classification according to CLP as Carc. 1B (IARC, 2018).

As also illustrated in Table 3, a migration limit value for bisphenol A and phenol exists in the Danish Statutory Order on Toys and the migration limit values for formaldehyde are about to enter Appendix C in the Danish Statutory Order on Toys. Furthermore, non-harmonised limit values in EN71-9 and EN71-11 for acrylamide and styrene are established. For the remaining substances, specific migration limits for food contact materials are established.

The Scientific Committee on Health and Environmental and Emerging Risks (SCHEER) has assessed that no genotoxic carcinogens ought to be present in toys as intentionally added substances, i.e. substances classified as carcinogenic and genotoxic (SCHER, 2010). The regulations in the Danish Statutory Order on Toys (see chapter 3.1 "The Danish Statutory Order on Toys") permit here values of 0.1 % (or 1000 ppm) – which is proportionally high compared to the food contact material legislation (1 ppm) and considering it is genotoxic carcinogens which have no lower limit for effects.

Table 3. Monomers with CMR properties, which are used in toys (Source: Lenzner et al., 2018). The five monomers marked with bold are the monomers which are defined as the relevant carcinogenic monomers in this project.

CAS No.	Chemical name	Material (examples)	EU Regulation 10/2011 (Plastic materials in contact with food)		EU Regulation 1272/2008 (CLP)	The Danish Statutory Order on Toys 2009/48/EC or EN 71-9 to EN 71-11	
			SML [a] (migration) (mg/kg food)	Other limitations (content) (mg/kg product)	Classification	Content limit (mg/kg)	Migration limit (mg/l)
80-05-7	Bisphenol A		0.6		Rep. 1B	3000	0.1 (0.04 [e])
108-95-2	Phenol		3		Mut. 2	10,000 (10 [d])	15 (5 [e])
50-00-0	Formaldehyde		15		Carc. 1B, Skin Sens. 1	1000 (500 [d])	1.5 (like monomers)
75-01-4	**Vinyl chloride**	**PVC**	**Non-detectable**	**1**	**Carc. 1A**	**1000**	
106-99-0	**1,3-Butadiene**	**ABS, SBR, NBR, SBS**	**Non-detectable**	**1**	**Carc 1A, Mut. 1B**	**1000**	
75-21-8	Ethylene oxide		Non-detectable	1	Carc 1A, Mut. 1B	1000	
75-56-9	Propylene oxide		Non-detectable	1	Carc 1A, Mut. 1B	1000	
78-79-5	2-Methyl-1,3-Butadiene		Non-detectable	1	Carc 1A, Mut. 2	1000	
106-89-8	Epichlorhydrine		Non-detectable	1	Carc. 1B	1000	
107-13-1	**Acrylonitrile**	**ABS, SAN, ASA, NBR**	**Non-detectable**		**Carc. 1B**	1000	
79-06-1	**Acrylamide**	**PAM**	**Non-detectable**		**Carc. 1B, Mut. 1B, Rep.2**	1000	**0.02**
151-56-4	Ethylenimine		Non-detectable		Carc. 1B, Mut. 1B	1000	
584-84-9	2,4-Toluene-diisocyanate		Non-detectable	1 [b]	Carc. 2, Skin Sens. 1	10,000	
5873-54-1	2,4′-Methylene-diphenyl diisocyanate		Non-detectable	1 [b]	Carc. 2, Skin Sens. 1	10,000	
123-31-9	Hydroquinone		0.6		Carc. 2, Mut. 2, Skin Sens. 1	10,000	
108-05-4	Vinyl acetate		12		Carc. 2	10,000	
75-35-4	Vinylidene chloride		Non-detectable		Carc. 2	10,000	
108-45-2	1,3-Phenylenediamine		Non-detectable		Mut. 2	10,000	
110-88-3	1,3,5-Trioxane		5		Rep. 2	30,000	
100-42-5	**Styrene**	**ABS, PS, SAN, SBR, SBS, SEBS**	**-**		**Rep. 2 (Carc. 1B [c])**	**30,000 (1000 [c])**	**0.75**

a. SML = Specific Migration Limit according to EU Regulation 10/2011 on plastic materials for food contact materials; b. Is calculated as isocyanide; c. In 2018, IARC has reassessed styrene as ‘Group 2A’, i.e. new CLP classification may be Carc. 1B; d. Limit value as preservative; e. New limit value is valid from November 2018.

Therefore, BfR carried out a risk assessment of selected monomers and found that the permitted limit values were too high in toys from a risk assessment point of view. Monomers like ethylene oxide and propylene oxide were prioritised low in the sub-group ”Chemicals” in the EU Expert Group on Toy Safety (ANEC, 2018). It is unknown why ethylene oxide and propylene oxides were prioritised low, but the reason might be that the corresponding polymer materials are not applied so often in toys compared to the four monomers which BfR found problematic:
- Vinyl chloride (in PVC)
- 1,3-Butadiene (i ABS, SBR/SBS)
- Acrylonitrile (in SAN, ABS, ASA, NBR)
- Acrylamide (in PAM)

Furthermore, styrene is also assessed as problematic by the EU Export Group on Toy Safety – the sub-group ”Chemicals” (Source: The Danish EPA). Styrene is used as monomer in several plastic types, including ABS which is used in many toys.

2.2 The five monomers

In this project, the relevant carcinogenic monomers are thus defined as the following five monomers:
- Vinyl chloride (in PVC)
- 1,3-Butadiene (in ABS, SBR/SBS, NBR) (is stated as ”butadiene” in this report)
- Acrylonitrile (in SAN, ABS, ASA, NBR)
- Acrylamide (in PAM)
- Styrene (in among other things ABS, PS, SBR/SBS, SAN, SEBS)

As stated by BfR (Lenzner et al., 2018), other monomers than the above-mentioned, are also classified as carcinogenic, but the above-mentioned five monomers are the monomers which BfR, the EU Export Group on Toy Safety – the sub-group ”Chemicals”, as well as ANEC consider as being the most important in relation to toys (which materials that are used in toys) and in relation to harmful health effects.

In this report, these five relevant carcinogenic monomers are generally mentioned as the “five monomers”.

3. Legislation

In this chapter, the existing legislative rules of the Danish Statutory Order on Toys concerning plastic/rubber materials in toys are described. Furthermore, the regulations which are valid today for the five monomers in food contact materials are described as among other things, these limit values form the basis of the proposal for limit values for selected monomers in toys which ANEC, a European Consumer Organisation, has proposed. The proposal for legislation for the five specific monomers is also presented and discussed in this chapter.

3.1 The Danish Statutory Order on Toys

The Danish Statutory Order on safety requirements for toys (Stat. Ord. no. 309, 2017) implements the EU directive on the safety of toys no. 48/2009 (EU Directive no. 48, 2009). According to the Danish Statutory Order on safety requirements for toys, the toy must be designed and manufactured in such a way that there is no risk of adverse effects on human health due to the physical and mechanical properties but also due to exposure to the chemical substances and mixtures which the toy consists of or which the toy contains. This applies when the toy is used as intended or in a foreseeable way, bearing in mind the behavior of children (§28 and Appendix II, section III, item. 1).

According to the Appendix II of the Danish Statutory Order (section III on “Chemical properties”, item 3, 4 and 5), no substances classified as CMR category 1A, 1B or 2 must be used in toys, in components of toys or in micro-structurally distinct parts of toys. The term “micro-structurally distinct parts of toys” means the same as the term “homogeneous materials”[2], which is used in the RoHS Statutory Order (Stat. Ord. no. 327, 2018).

However, CMR substances are allowed in concentrations below the classification limits for the individual substances, which are specified in the CLP regulation on classification, labelling and packaging of substances and mixtures. Furthermore, CMR substances may be used if these substances and mixtures are inaccessible for children (including inhalation) when the toy is used in a way which children can be expected to use it. If no specific classification limit for the individual substances is available (there is none for the five monomers) the following general classification limits apply:

- Carc. and Mut. category 1A and 1B: 0.1 % (1000 ppm)
- Repr. category 1A and 1B: 0.3 % (3000 ppm)
- Carc. and Mut. category 2: 1.0 % (10,000 ppm)
- Repr. category 2: 3.0 % (30,000 ppm)

However, CMR substances can be excepted from this rule if they are assessed to be safe use in toys by the EU Scientific Committee on Consumer Safety (SCCS) and are adopted in Appendix A of the Statutory Order. At present (May 2018), Appendix A only includes the substance nickel which has a classification as Carc. 2. Nickel is allowed for use in stainless steel in toys and in toy parts which are to carry electrical current.

Previously, the CMR requirement was, however, excepted from this rules for materials which were approved according to the food contact material regulation (EU regulation no. 1935, 2004

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[2] In the RoHS directive, a homogeneous material is defined as “either one material of uniform composition throughout or a material, consisting of a combination of materials, that cannot be disjointed or separated into different materials by mechanical actions such as unscrewing, cutting, crushing, grinding and abrasive processes” (https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011L0065&from=en)

and corresponding regulations for specific materials). I.e. previously, plastic materials used in toys but at the same time approved for food contact was excepted from this CMR requirement for toys. However, this exception was only valid until 20 July 2017.

3.1.1 Existing regulations for the five monomers in toys

As described above, there is a content limit value for the five monomers in toys due to the classification as carcinogenic. Furthermore, limit values for migration of a few of the five monomers are specified in the existing standards. This is described in detail below.

3.1.1.1 Content limit value for the five monomers in toys

As described above, the five monomers have a content limit value of 0.1 % (or 1000 ppm) because of their harmonised classification as carcinogenic Carc. 1A or Carc. 1B. The exception is, however, styrene which has a harmonised classification as Rep. 2 and not as carcinogenic. Today the current content limit value for styrene is thus 3 % (or 30,000 ppm) due to the classification as Rep. 2. Due to IARC's reassessment of styrene in April 2018 as probably carcinogenic (IARC, 2018), this can result in a harmonised classification as Carc. 1B and thus a future content limit value of 0.1 % (or 1000 ppm) like the other carcinogenic monomers according to CLP. However, this requires that first of all a proposal for a classification as carcinogenic for styrene is made and then that RAC (ECHA's Committee for Risk Assessment) also interprets data as IARC (which might not necessarily be the case) before a possible harmonised classification as carcinogenic becomes effective.

3.1.1.2 Migration limit value for selected monomers of the five monomers in toys

As described in Table 3, today limit values for migration of some monomers from toys are specified in the standard EN 71-9. This applies for bisphenol A, phenol, formaldehyde, acrylamide and styrene. The existing regulations for the two last-mentioned monomers are described in detail below as they are among the five monomers which are in focus in this project. The standards EN71-10 and EN 71-11 describe the associated procedures for sample preparation and chemical analyses.

However, it must be noted that the standards EN 71-9, EN 71-10 and EN 71-11 are not referenced in the Official Journal of the European Union and thus do not demonstrate compliances with the regulations of the directive. Normally, producers who meet the requirements in the referenced harmonised standards are presumed to demonstrate compliance with the corresponding requirements in the associated directives. This presumption is not the case when complying with EN 71-9 to EN 71-11 which are not referenced in the Official Journal.

Acrylamide is limited through a migration limit value for acrylamide as a monomer. A so-called "action limit value" is listed for acrylamide in EN 71-9 "Organic chemical compounds – requirements" which means that reference is made to the actual detection limit value as stated in EN 71-11 "Organic chemical compounds – methods of analysis", i.e. 0.02 mg/l simulant.

Styrene is listed with a limit value for migration as monomer in EN 71-9 "Organic chemical compounds – requirements" and EN 71-11 "Organic chemical compounds – methods of analysis" of 0.75 mg/l simulant.

3.2 Legislation for monomers in food contact materials

The legislation for materials in contact with food (food contact materials) is described in the EU Regulation no. 1935/2004. Based on this, specific regulations for different materials can be specified as is the case for plastic in EU Regulation no. 10/2011.

According to the EU Regulation no. 10/2011 on plastic materials intended to come into contact with food, it is only allowed to use approved substances for production of plastic which is to be in contact with food. Substances to be authorised are among other things monomers and other basic substances, additives (except from colourants) and aids to polymerisation. Furthermore, specific migration limits (SML) have been defined for specific substances (including monomers) as well as a total migration limit for the total amount of chemical substances which are allowed to migrate from the plastic material. In addition to this, there might be other restrictions and specifications for specific substances, for instance a limit value for the content of monomers in the plastic material itself used for food contact.

The five monomers which are in focus in this project are all authorised for use as monomers for production of plastic for food contact but with the following specific limit values:

- For vinyl chloride and butadiene
    - Must not migrate in detectable amounts into food, i.e. up to 10 µg/kg food
    - May only be found in the plastic material in amounts up to 1 mg/kg plastic (1 ppm)

- For acrylonitrile and acrylamide
    - Must not migrate in detectable amounts into food, i.e. up to 10 µg/kg food

- Styrene
    - The migration must comply with the total migration limit of 10 mg/dm^2 plastic or 60 mg/kg food which applies for the sum of all substances which release/migrate from plastic food contact materials. According to the Danish Veterinary and Food Administration, this limit is set as a quality requirement for plastic and is non-toxicologically based.

3.3 Proposal from ANEC for legislation on monomers in toys

Based on an assessment from the German organisation BfR (Bundesinstitut für Risikobewertung) regarding residues of carcinogenic monomers in plastic materials, the European consumer organisation ANEC has proposed the following limit values for five selected monomers (ANEC, 2018):

- A content limit of 1 mg/kg for vinyl chloride in toys of PVC
- A content limit of 1 mg/kg for 1,3 butadiene when the substance is used as a monomer in toy materials
- A content limit of 1 mg/kg for acrylonitrile when the substance is used as a monomer in toy materials
- A content limit of 1 mg/kg for acrylamide when the substance is used as a monomer in toy materials
- A migration limit value of 0.077 mg/l simulant for styrene following 3 hours extraction of the toy material or one third of this value if the extraction procedure as described in EN 71-10 is used (where extraction for 1 hour is used).

ANEC argues for using a content limit value for the four first monomers which are genotoxic carcinogens and thus do not have any lower limit for health effects, based on that the Scientific Committee on Health and Environmental and Emerging Risks (SCHEER) has assessed that no genotoxic carcinogens ought to be present in toys as intentionally added substances (SCHER, 2010; ANEC, 2018). On the contrary, a migration limit value is calculated for styrene based on the TDI (Tolerable Daily Intake) value set by WHO as the method which ought to be used for CMR category 2 substances as stated in SCHER (2010). In 2018, styrene has by IARC been re-classified to a more severe CMR category – a category 1 substance (IARC, 2018).

The limit values are suggested to be inserted into Appendix C of the Statutory Order on Toys or the supplement which is called Appendix C to Enclosure II in the Danish Statutory Order on safety requirements on toys (Stat. Ord. no. 309, 2017). Appendix C contains specific limit values for chemicals used in toys which are intended for use by children below 36 months or in other toys which are intended to be placed in the mouth. This means that it is suggested that the limit values are solely meant to be valid for toys for children below 3 years and for toys which are intended to be placed into the mouth.

3.3.1 TIE's answer to ANEC's proposal for legislation

TIE (Toy Industries of Europe) has published an answer to ANEC's proposal for legislation regarding monomers in toys (TIE, 2018a). TIE suggests that more studies regarding the total content and migration of these five residual monomers are initiated before these substances are restricted in toys. Furthermore, TIE suggests that the EU Commission gives SCHEER a mandate to prepare an independent assessment which takes the exposure into consideration based on new studies regarding content and migration.

Of comments to the specific limit values for the individual monomers, TIE has the following (selected) comments:

- Vinyl chloride
    - There is a limited amount of data on both the residual monomer content of vinyl chloride in PVC and migration of vinyl chloride from PVC but the available data indicate that it is levels in the ppb area.
    - PVC pipes with residual monomer content of vinyl chloride of less than 1 mg/kg gave no detectable migration.
    - Provided that the residual monomer content in toys is proportional, there should be no reason to set a limit value of 1 mg/kg for vinyl chloride.
    - If data show that the residual monomer content of vinyl chloride in toys exceeds 1 mg/kg TIE will support that the limit value is set at 1 mg/kg.

- 1,3-butadiene
    - Studies show that on average the residual monomer content of butadiene in toys is below the suggested value of 1 mg/kg. A few values above 1 mg/kg are identified. The migration of butadiene is generally very low (not detected) in the few available studies.
    - As the migration seems to be low and the residual monomer content on average lies below 1 mg/kg TIE does not support that a limit value of 1 mg/kg is set.

- Acrylonitrile
    - There are both studies which show that the residual monomer content of acrylonitrile in toys is above 1 mg/kg and studies which show that in most cases the migration is not detectable.
    - In practise, a limit value of 1 mg/kg will mean that ABS no longer can be used and a usually safe polymer which is used widely has to be replaced by less suitable materials.

- Acrylamide
    - Acrylamide is primarily used for production of PAM which is a material type that is not used especially often in toys (is primarily used for so-called “grow-in-water toys”, i.e. for instance a dinosaur which “grows” out of an egg when it is placed in water) and primarily for toys for children above 3 years.
    - Data regarding the residual monomer content of acrylamide in PAM are lacking.

- Styrene
    - Styrene is a monomer for many materials which are used in toys. The residual monomer content of styrene might be much higher than the content of the other four monomers. On the other hand, studies show that the potential of styrene to migrate into water is low even at high content values.
    - The existing limit value in EN 71-9 is 0.75 mg/l and ANEC suggests lowering the limit value by a factor of 10. TIE suggests that SCHEER ought to assess this more closely before a final limit value is established.

4. Survey - materials

Which plastic materials are used in toys?

In this chapter, the survey of which plastic and rubber materials that are used in toys is described. The information has been provided through:
- Contact to the toy sector
- Literature search/internet search
- Search in material database

4.1 Contact to relevant interested parties in the toy sector

Contact has been made to relevant interested parties in the toy sector, such as sector associations, distributors and producers of toys. Among other things, the following has been contacted to get more information about which plastic materials that are used in toys on the Danish market:
- LEG – the Danish sector association for toys
- TIE (Toy Industries of Europe) – the European sector association for toys
- The Danish Plastics Federation
- The PVC Information Council (*In Danish: PVC Informationsrådet)*
- The LEGO Group
- Top Toy
- Malte Haaning Plastic A/S
- VN Legetøj
- Hasbro
- Amo toys
- Maki
- COOP
- Dansk Supermarked Group
- Legekæden
- AV form

An inquiry was sent to the members of both the Danish sector association for toys (LEG) and the European sector association for toys (TIE). The inquiry dealt with which materials the members' toys typically contain but also the possibility that the members could make toys available for the analyses in the project.

Contact to the Danish toy importers resulted in the general picture, that the importers do not necessary have information about of which materials the toys consist of. The importers generally refer to the producers of toys. The primary information source in this project has thus been producers of toys and TIE – the European sector association for toys.

4.1.1 Information from TIE (Toy Industries of Europe)

TIE accepted to send a number of questions to their members regarding which materials toys typically consist of as well as their knowledge on content and/or migration of monomers from selected materials. Information regarding the project as well as a number of questions was sent to the members of TIE and they had approx. 3 weeks to answer. TIE collected and anonymised the answers which were then sent to FORCE Technology. The answers from the members of TIE are described below.

4.1.1.1 Types of materials used for toys

When questioned regarding the distribution in percentages of plastic/rubber materials used in toys, in total seven producers/distributors answered and stated the below distributions in percentages (see Table 4). From the table it can be seen that there is a big difference in the use of materials for toys among the individual toy producers and of course, it depends on which types of toys they sell. However, the general picture is that the materials which are interesting for this project are (in prioritised order): ABS, PVC, PS/HIPS, TPE (thermoplastic elastomers which can consist of for instance SEBS).

Table 4. Information from TIE: Seven toy producers' use of materials in toys for all ages, i.e. 0-14 years

Producer 1	Producer 2	Producer 3	Producer 4	Producer 5	Producer 6	Producer 7
ABS: 45 %	**ABS: 60 %**	PP: 60 %	PP: 80 %	**ABS: 45 %**	PP: 74 %	**ABS: 80 %**
PP: 25 %	PP: 30 %	PE: 30 %	PE: 10 %	**PVC: 40 %**	**PS: 19 %**	**HIPS: 10 %**
PVC: 15 %	**MMBS: 5 %**	**ABS: 2 %**	**ABS: 4 %**	PP: 10 %	PE: 6 %	**SEBS: 3 %**
PE: 5 %	PE: 2 %	**PVC: 2 %**	**PVC: 4 %**	PE: 2.5 %		
HIPS: 3 %	**TPE: 1.5 %**	**TPE: 2 %**	EVA: 0.5 %	**TPE: 2 %**		
TPE: 1 %	**PVC: 1 %**		**TPE: 0.5 %**			
			PS: 0.5 %			

Materials marked with bold are materials which contain the five monomers in focus in this project. Please note, that TPE is a collective name for thermoplastic elastomers which might cover rubber materials which contain one or several of the five monomers (like e.g. SEBS, SBS).

Furthermore, based on the information from their members, TIE states that especially the materials ABS, PVC and PS are used in toys targeted children at the age of 0-3 years and toys which are intended to be placed in the mouth. Generally, it is approx. 20 % of the toy (of plastic/rubber) and for some producers up to between 50 and 100 % of the toy (of plastic/rubber) for the children of the age 0-3 years (and toys intended to be placed in the mouth) that contains one or several of these materials interesting for this project.

4.1.1.2 Quality of material used for toys

From the information which TIE collected from their members, it is seen that some of TIE's members use plastic and/or rubber materials of toy quality, i.e. that the materials are assessed to be in conformity with the toy regulations. Other members state that they use materials of food quality (i.e. they comply with the regulations for food contact materials). Finally, some of the members state that they use a standard quality of materials where it is proved that this quality can comply with the chemical requirements for their specific toy.

Furthermore, TIE states that residual monomers are expected to evaporate at the injection moulding process as most of the monomers are volatile organic compounds (VOCs).

4.1.2 Information from a Danish producer/importer of toys

A Danish producer/importer of toys has delivered the information listed in Table 5 regarding which materials that are used in their toys. It must be noted that the document is an internal report which they prepared in 2012 and which does not necessarily show a representative extract of toys on the market. The document does not say anything about amounts either but solely illustrate how often a material was registered in their database at the time in question. The document is not based on quality assured data. For instance, several types of polystyrene (PS) and several types of polyethylene (PE) are listed as these for historic reasons have been registered separately – among other things, PS is stated as both "PS" and "polystyrene".

Furthermore, the company has pointed out that a piece of toy can consist of several different materials and that the list is sorted with the most used material listed first. Polyester and nylon are found at the top of the list as polyester is found in teddy bears, doll's clothes etc. and nylon in strings, buckles etc. Therefore, these materials are in a lot of toys but not necessarily in large amounts and can thus appear over-represented in the list (compared to amounts).

Despite these reservations, the list can still give knowledge on which materials that are used in toys.

Table 5. Materials used in toys sold by a Danish producer/importer in 2012

Materials in toys – in prioritised order
Polyester
ABS (acrylonitrile butadiene styrene)
PVC (polyvinyl chloride)
PP (polypropylene)
Nylon
PE (polyethylene)
EVA (ethylene vinyl acetate copolymer)
PU (polyurethane)
TPR (thermoplastic rubber)
PA (polyamide)
HIPS (high impact polystyrene)
PC (polycarbonate)
HDPE (high density polyethylene)
POM (polyoxymethylene)
Polystyrene (PS)
Natural rubber
PS (polystyrene)
LDPE (low density polyethylene)
PET (polyethylene terephthalate)

4.2 Literature search/internet search

To identify which plastic/rubber materials that are typically used in toys, a literature search and an internet search were carried out. A search on a few producers' websites was undertaken but also a general search for literature which has earlier examined the use of plastic and rubber materials in toys.

4.2.1 Information from various producers' websites

4.2.1.1 The LEGO Group

According to the LEGO Group's website[3], the major part of the LEGO Group's LEGO elements is produced of high-quality ABS. Wheels for their LEGO elements are produced of SBS or SEBS

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[3] https://www.lego.com/en-us/service/help/bricks-building/brick-facts/what-lego-bricks-are-made-from-408100000007855

4.2.1.2 Dantoy

According to Dantoy's own website[4], Dantoy's plastic toys are mainly produced of polyethylene (PE) and polypropylene (PP). Furthermore, it is specified that their plastic toys are neither produced of PVC nor contain bisphenol A. In addition, Dantoy states that their plastic kitchen toys all are produced in food approved raw materials, i.e. that the plastic fulfils the requirements which are specified in the EU Regulation no. 11/2010 on plastic materials intended to come into contact with food.

4.2.1.3 Hasbro

According to Hasbro's website[5], Hasbro has removed PVC from their packaging and they examine the possibilities for alternatives to PVC in their products. This statement indicates that Hasbro still uses PVC in some of their toy products.

4.2.1.4 Geobra Brandstätter GmbH & Co. KG

According to several websites[6], toys from the German company Geobra Brandstätter GmbH & Co. KG (Playmobil) are produced in ABS but no information on the type of material could be found on their own website.

4.2.1.5 Fisher Price and Mattel

According to several websites of an earlier date[7], both Fisher Price and Mattel are using PVC in their toys. However, no information on the type of materials could be found on the companies' own websites.

4.2.2 Information from various articles

An internet search has also been performed for articles describing which materials toys are typically made of.

4.2.2.1 Dutch screening of plastic toys (VWA, 2005)

In a Dutch survey from 2005 (VWA, 2005), they purchased and analysed in total 113 pieces of plastic toys on the Dutch marked. They made FTIR[8] examinations of the toy products to identify which materials the toy consisted of. The results are reproduced in Table 6. If a toy product consisted of several materials all the materials were identified (i.e. 186 materials in total in 113 products). No analysis for content of residual monomer was carried out in this survey.

In the survey, it is stated that:
- PVC was mainly found in toys of soft plastic and primarily in bath toys
- ABS was mainly found in toys of hard plastic, for instance in teething rings and rattles

This survey shows – like the information from the Danish producer/importer and the smaller survey from TIE – that primarily ABS and PVC are the most used materials for toys when looking at the materials which contain the five relevant monomers for this project. However, PS also seems to be used to a less extent together with other co-polymers with styrene (which are not specified).

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[4] https://dantoy.dk/faq/

[5] https://csr.hasbro.com/safety/material-usage

[6] http://www.momgogreen.com/2007/08/toy-origins.html; https://playmobilvslego.tumblr.com/post/104608206855/final-article-the-cbbe-pyramid-and-how-lego-and; http://onelittlewordsheknew.blogspot.com/2011/11/toxic-toys-fisher-price-little-people.html

[7] https://www.change.org/p/fisher-price-and-mattel-please-stop-using-pvc-in-your-toys; http://livingsafe.com.au/toxic-pvc-in-plastic-toys-how-to-avoid-them/

[8] FTIR means "Fourier Transform Infrared Spectroscopy" and is a spectroscopic measurement method for identification of materials.

Table 6. Materials used in toys. Dutch survey from 2005 (VWA, 2005)

Material	Number	Percentage
PVC	48	25 %
ABS	42	23 %
PP	25	13 %
EVA (ethylene vinyl acetate)	18	10 %
PE	14	8 %
Co-polymers with styrene	10	5 %
PUR	7	4 %
NR (natural rubber)	6	3 %
PC (polycarbonate)	5	3 %
PS	5	3 %
Other	6	3 %
Total	**186**	**100 %**

4.2.2.2 Literature search on toys (KEMI, 2012)

The Swedish Chemicals Agency (KEMI) examined which materials toys consisted of as well as which chemical substances that were contained in toys through a comprehensive literature search in various published articles in 2011-2012. The literature search was a general search for English-language articles. In the report (KEMI, 2012), there is a list with the results, i.e. how many articles mentioning a specific material (plastic/rubber material) used in toys. This list is reproduced in Table 7 below. Only plastic and rubber materials are repeated and not other types of materials which they identified in the survey.

Table 7. Materials used in toys. Swedish survey from 2012 (KEMI, 2012)

Material	Number*	Percentage
PE	221	19 %
PVC	211	18 %
PP	164	14 %
EVA	105	9 %
PET	99	8 %
Unknown synthetic rubber material	81	7 %
PVA	79	7 %
SBS – synthetic rubber material?	73	6 %
SBR	72	6 %
ABS	69	6 %
Total	**1174**	**100 %**

* Number = number of articles identified with the material in question

For the materials of interest for this project, i.e. materials containing the five monomers, this Swedish survey shows that it is primarily PVC and different rubber materials which are mentioned in the literature. ABS is the material which is mentioned least in the literature. However, it must be emphasised that the table shows the number of results of articles which mention the materials and it does not necessarily give a representative picture of which materials that are used most frequently.

4.2.2.3 Polymer toys based on butadiene and styrene (Abe et al., 2013)

Abe et al. (2013) has examined and analysed a number of toy products from the Japanese market. In the survey, focus is on ABS and rubber materials of thermoplastic elastomers such as SEBS and SBS/SBR. Here it is described that:

- ABS is a hard plastic which is used as the main ingredient in toy cars or other vehicles, in the handle of baby rattles and teething rings for babies and similar products.
- Thermoplastic elastomers such as SEBS and SBS/SBR are used as the soft material in for instance teething rings and rattles for babies.

4.2.2.4 CMR substances in consumer products (Lenzner et al., 2018)

In 2017, the German Federal Institute for Risk Assessment (BfR) has prepared Germany's statement (in German) to the EU Commission's Expert Group on Toy Safety and its sub-group "Chemicals" on the exception for food contact materials from the CMR requirement in the toy directive. This document has been processed and published as an article in English in 2010 (Lenzner et al., 2018).

In this document, it is described that the following plastic types are used in toys (with monomers stated in brackets):

- PVC for among other things inflatable toys, dolls and balls (vinyl chloride)
- Acrylamide vinyl acetate copolymer for so-called "grow-in-water" toys like for instance a dinosaur in an eggshell which grows out of the eggshell when the egg is put into water (acrylamide)
- ABS for different types of activity toys (acrylonitrile, butadiene and styrene)
- EVA for puzzle mats (vinyl acetate)

However, in relation to this project, only the first three mentioned materials are relevant in relation to content of the five monomers.

4.3 Information from producers/importers of toy

A number of producers and/or importers of toys have been contacted in connection with this project, including TIE. Through these contacts, the below information (see Table 8) was received and it is considered as being generally representative for toys. However, it must be emphasised that it is a general picture and there might be specific examples of toys which are produced of other materials. Detailed material from TIE is described in Appendix 1.

Table 8. Materials which different toys are typically made of (Source: Contacted toys producers/importers and TIE)

PVC
Dolls – the head will typically consist of PVC (also in dolls for small children)
Dolls – arms and legs can also be produced of PVC but only if these are soft, flexible and can be squeezed together
Mannequin dolls
Balls
Inflatable products, such as pools, inflatable water toys
Action figures (if they are semi-soft)
Farm animals, smurf figurers etc.
Cables and figures on for instance baby activity toys
Bath toys for instance suction cups
Scooter or other toys to ride on – for instance wheels and handles
ABS

Is used for a lot of toys

Is also used for a lot of toys for small children

Is a hard clear and normally opaque (coloured) plastic with round forms

Is found in for instance LEGO elements, Playmobil etc.

Can be used for dolls and accessories for dolls

Teething rings

Rattles (for non-opaque parts)

Sand toys

SEBS / SBS

Is typically used for tyres on cars but this can also be normal rubber (latex)

Rubber parts in “happy” colours like for instance bright blue will typically be a synthetic rubber

Suction cup for bath toys

The rubber material on teething rings

PS

A hard/stiff plastic type which both can be transparent and coloured

Is not used so often as ABS

Is found for instance in rails for Flexitrack

Hard plastic parts for instance button on plush animals/plush toys

Hinges on stimulating toys

Music instruments

Puzzles

MMBS

Is primarily used for clear plastic material on for instance rattles

Clear plastic on for instance push/pull-along toys, walkers, activity toys for babies, pushcarts and similar

PAM

Is used in so-called ”grow-in-water” toys, i.e. products which are submerged into water where for instance a figure grows out of an egg

4.4 Information from UL Prospector database

UL is a global independent company which among other things works with certification, validation and testing with the safety area and the scientific area. The Prospector® database from UL contains information about raw materials and ingredients and is used by product developers and engineers. The database contains technical information from more than 10,000 products from global suppliers and searches can be made for materials or ingredients. Some of the industrial areas which the database covers are plastic, plastic additives, additives for food and household products. According to the website, more than half a million of formulators around the world use the database to search for and analyse technical product information.

In the database, it is possible to search for different search words including toys. A search for toys and commercially active raw materials gives in total 1,956 results. No limitation of the search on availability has been made as it is assumed that not only raw materials in Europe are interesting but raw materials on the global market as a lot of toys is produced in the East. The search gives a long list of different raw materials from different suppliers which all are stated as applicable for toys. These raw materials are listed in the table below. However, raw materials which are stated as “unspecified”, “fragrance”, “blowing agent” etc. are not described in the table but solely the specific plastic/rubber materials and therefore the sum does not amount to 1,956 in total.

It must be noted that the result of the search for e.g. ABS of 53 hits only shows that there are 53 named ABS raw materials in the database for which it is stated that they can be used for toys. Of these 53 different names of ABS raw materials, several of them might come from the same supplier. The database does not contain information about amounts. Each hit is a unique search for a specific raw material stated with the name and the company which sells it. Thus, the search in the UL Prospector database does not state anything about the amounts on the market but about which materials in the database that are listed as suited for production of toys.

Table 9. Result of the extract of materials from the UL Prospector database on the search word “toys”.

Material	Explanation	Number
TPE	Thermoplastic Elastomer, might be based on SEBS, SBS, SBC	464
PP Impact Copolymer		166
HDPE	High Density Polyethylene	137
PP Homopolymer		121
LDPE	Low Density Polyethylene	97
SEBS	Styrene Ethylene Butylene Styrene Block Copolymer	75
PP, Unspecified		67
PVC, Flexible		59
CAB	Cellulose Acetate Butyrate	58
LLDPE	Linear Low Density Polyethylene	57
PS (HIPS)	Polystyrene (High Impact Polystyrene)	56
PP Copolymer	Polypropylene	54
ABS	Acrylonitrile butadiene styrene	53
PS (GPPS)	Polystyrene (General Purpose Polystyrene)	50
SBS	Styrene Butadiene Styrene Block Copolymer	41
TP, Unspecified	Thermoplastic	39
Plasticizer		38
PP Random Copolymer		34
EVA	Ethylene Vinyl Acetate Copolymer	27
TPO (POE)	Thermoplastic Polyolefin Elastomer	24
MDPE	Medium Density Polyethylene	17
CA	Cellulose Acetate	14
HDPE Copolymer		13
PC	Polycarbonate	12
SBC	Styrene Butadiene Block Copolymer	12
PUR, Unspecified	Polyurethane	11
PVC Homopolymer	Polyvinyl Chloride	10
Acrylic, Unspecified		9

Material	Explanation	Number
MMBS	Methyl Methacrylate Butadiene Styrene	9
PVC, Unspecified		9
CAP	Cellulose Acetate Propionate	8
Copolyester, Bio-based		8
Acrylic (PMMA)	Polymethyl methacrylate	7
Copolyester		7
LMDPE	Linear Medium Density Polyethylene	7
Polyester, TP	Thermoplastic Polyester	7
PP+EPDM	PP+Ethylene Propylene Diene Rubber	7
Acrylic (SMMA)	Styrene Methyl Methacrylat Acrylic	6
Polyolefin, Unspecified		6
PS (MIPS)	Polystyrene (Medium Impact Polystyrene)	6
Acetal (POM) Copolymer	Polyoxymethylene	5
Biodeg Polymers		5
MABS	Methyl Methacrylate / ABS	5
Nylon 6		4
PBS	Polybutylene Succinate	4
PE, Unspecified		4
Nylon 66		3
SAN	Styrene Acrylonitrile Copolymer	3
ASA	Acrylonitrile styrene acrylate	2
HMWPE	High Molecular Weight Polyethylene	2
PBR, Low Cis	Low Cis Polybutadiene Rubber	2
PC+Acrylic		2
LDPE+Nylon		1
mMDPE	Metallocene Medium Density Polyethylene	1
OBC	Olefin Block Copolymer	1
PETG	Polyethylene Terephthalate Glycol Comonomer	1
PLA	Polylactic Acid	1
Plasticizer, Bio-based		1
PS (Specialty)		1
Rubber		1
SBR, Emulsion	Styrene Butadiene Rubber	1
TPS+PP	Thermoplastic Starch + PP	1
TPU, Unspecified	Thermoplastic Polyurethane Elastomer	1

Figure 1 below is an overview of the top 10 materials with the highest number of raw materials found in the UL Prospector database. The remaining materials are compiled under the category “Other”. As illustrated in Table 9 and in Figure 1, it is the below materials for which most raw materials are found in the UL Prospector database and which are based on the carcinogenic raw materials that are in focus in this project:

- TPE (is a broad term which includes several different rubber materials which can be based on e.g. styrene and possibly butadiene such as for instance SEBS, SBS, SBC, but can also contain irrelevant rubber materials (seen from the point of view of this report))
- PS
- PVC
- SEBS
- ABS
- SBS

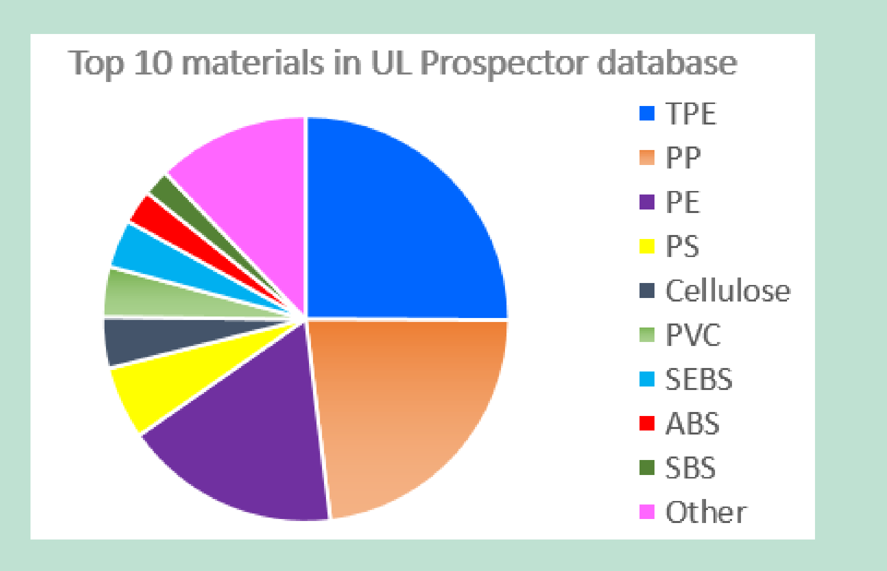


Figure 1. The number of results of raw materials at a search for ”toys” in the UL Prospector database

Similarly, to the information from the literature and from the toy sector, it is primarily ABS, PVC and PS which are relevant as plastic materials and for instance SEBS and SBS which are relevant rubber materials.

Another interesting aspect which can be read from the UL Prospector database is that out of the 1,956 results of different raw materials which are stated as usable for toys, 868 of them (i.e. 44 %) are also stated as usable for food contact. Whether this overlap corresponds to what is actually used is unknown. However, the food contact material quality is not stated in the database, i.e. if for instance it is for the European market or the American market where the requirements for the qualities are different.

4.5 Summary of materials used in toys

Based on both information from literature and information received from toy producers (including TIE), it is indicated that the vast majority of the most important materials (which contain the relevant monomers) in toys – and also in materials in toys for children at the age 0-3 years as well as materials in toys which are intended to be placed in the mouth - is ABS, PVC and PS (including HIPS). Additionally, it seems that TPE, including for instance SEBS, appears to be used to a lesser extent for smaller parts of toys. Furthermore, the survey from TIE shows that the plastic type MMBS seems to be used to a lesser extent in toys where there is a need for a clear plastic.

5. Survey - monomers

Existing knowledge about content and migration of the five monomers from polymers

In this chapter, the results of a literature search for content of residual monomers in toys (and polymers in general) are described as well as results from surveys of migration of residual monomers from polymers. Focus is on the five monomers which are selected in the project (see chapter 2). At first, the theoretical considerations about residual monomers and possible migration of these from polymers are described.

5.1 Theoretical considerations about residual monomers

Initially, the theoretical considerations about content in and migration of residual monomers from polymer materials are explained.

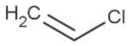
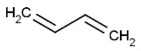
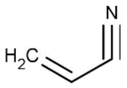
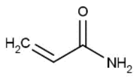
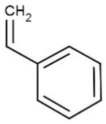
5.1.1 Physical/chemical properties of monomers

Physical/chemical parameters, such as boiling point and solubility for the five monomers which are in focus in this project, are listed in Table 10 below. All data are gathered from ECHA's database of registered substances unless otherwise stated.

It is worth noting that acrylonitrile and styrene are liquids at room temperature and acrylamide a solid substance while vinyl chloride and butadiene are gases at room temperature. According to the EU definition of volatile organic compounds (VOC), all the five monomers are defined as VOC as all have a boiling point below 250 °C (EU Directive no. 42, 2004).

There is a substantial difference between the water solubility of the five monomers. The water solubility of acrylonitrile and acrylamide is very high whereas the water solubility of styrene and butadiene is low. Theoretically, it might therefore be expected that migration to aqueous agents will be low for styrene and butadiene. On the other hand, all the five monomers are soluble in ethanol (which among other things is used as food simulant for fatty foods in migration tests of food contact materials). Theoretically, this means that the migration of the some of the five monomers can be higher to fatty liquids such as bath water added bath oil or child sweat added sunscreen lotion. For acrylamide, the solubility in aqueous agents is, however, higher than in ethanol (corresponding to fatty agents). For acrylonitrile and vinyl chloride which have a very high solubility in water, data are, however, lacking and it is therefore not possible to determine in which media the solubility will be highest. Some observations of an older date (Lickly et al., 1991) illustrate that migration of acrylonitrile to fatty food simulants like heptane is lower than migration to water under the same conditions. Vice versa, data have been identified showing a high solubility of acrylonitrile in methanol (see Table 10). In general, data are lacking in this area.

Table 10. Physical/chemical properties for the five monomers

Monomer	Vinyl chloride	Butadiene	Acrylonitrile	Acrylamide	Styrene
CAS No.	75-01-4	106-99-0	107-13-1	79-06-1	100-42-5
Chemical name	Chloroethylene	Buta-1,3-diene	Acrylonitrile	Acrylamide	Styrene
Structure					
Molecular formula	C_2H_3Cl	C_4H_6	C_3H_3N	C_3H_5NO	C_8H_8
State (at 20 °C)	Colourless gas	Colourless gas	Colourless liquid	Solid white crystalline substance	Colourless to yellowish liquid
Boiling point (at 1013 hPa)	- 13.4 °C	- 4.4 °C	77. °C	192.6 °C[9]	145 °C
Steam pressure (at 20 °C)	3330 hPa[10]	2440 hPa[11]	115 hPa	2.3 hPa sublimes at 85 °C	6.67 hPa
Water solubility (at 20 °C)	9.15 g/l High	0.735 g/l Low	73 g/l Very high	2155 g/l (at 30 °C) Very high	0,32 g/l (at 25 °C) Low
Solubility in ethanol (at 30 °C)	No data Is soluble [12]	No data Is soluble [13]	No data Is soluble [14] Possibly a very high solubility as the solubility in methanol is 100 g/l[15]	862 g/l Very high solubility	No data Soluble[16][17]

5.1.2 Content of monomers – theoretical considerations

Plastic materials (or synthetic rubber materials) consist of macromolecules which constitute the plastic material. The plastic material is formed through a chemical reaction of the respective monomers – the so-called building stones – which form the polymer (macromolecule), (Hahladakis et al., 2018). It is expected that residual monomers in plastic will always be present to a certain extent.

Several techniques exist for reduction of the content of residual monomers and several of the techniques have been patented. Araujo et al. (2002) divides the techniques into the following categories:

- Chemical methods where the residual monomer reacts or forms new chemical compounds, for instance:
    - Chemical removal with suitable chemical compounds or ion exchange resin

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[9] Not found in ECHA's database of registered substances. Found here: TOXNET https://chem.nlm.nih.gov/chemidplus/rn/79-06-1

[10] According to OECD SIDS report on vinyl chloride (https://hpvchemicals.oecd.org/ui/handler.axd?id=c39b3fef-21c9-4d3d-a685-4698e7280ebc)

[11] According to EU RAR report on 1,3-butadiene (https://echa.europa.eu/documents/10162/1f512549-5bf8-49a8-ba51-1cf67dc07b72)

[12] https://pubchem.ncbi.nlm.nih.gov/compound/vinyl_chloride#section=Solubility

[13] https://pubchem.ncbi.nlm.nih.gov/compound/1_3-butadiene#section=Top

[14] http://www.chemicalbook.com/ChemicalProductProperty_EN_CB8764818.htm

[15] https://sitem.herts.ac.uk/aeru/ppdb/en/Reports/2545.htm

[16] https://pubchem.ncbi.nlm.nih.gov/compound/styrene#section=Flash-Point

[17] https://pubchem.ncbi.nlm.nih.gov/compound/styrene#section=Flash-Point

    - Use of correct initiator or catalyst
- Physical methods where the residual monomer is removed from the polymer through for instance:
    - Volatilisation (increased temperature)
    - Extraction with a solvent
    - Electromagnetic radiation

Some of the above techniques are applied directly in the same reactor as termination of the polymerisation process while other techniques – typically the physical methods – are completed after the polymerisation process and require additional equipment and are thus also more expensive. Often it is a combination of several techniques which are used to reduce the residual monomer content in the polymer. Which techniques that might or can be used will depend on the polymer as not all polymers tolerate for instance heat or pressure. Thus, it is a combination of several parameters (the properties of the polymer, the durability of the polymer, the application of the polymer etc.) that are significant for which techniques that are used to reduce the residual monomer content. Finally, the economic considerations are of course an important issue as the use of several techniques gives higher production costs which must be compared with the wanted physical/chemical properties of the polymer. It is unknown if or which of these techniques that are used in connection with the production of plastic for toys, but the techniques are generally described as used in the plastic production.

In general, it is desirable to reduce the residual monomer content as the presence of residual monomers can result in for instance shrinkage of the polymer in boiling water, potential discolorations caused by oxidation of the monomer, objectionable odour etc. (Araujo et al., 2002).

For vinyl chloride and butadiene which have a low boiling (below 0 °C) and thus are gases at room temperature, it can be expected based on theoretical considerations that possible residues of these monomers will easily evaporate from the polymer or during the high moulding process temperatures unless the residues are encapsulated in the polymer. This is partly correct but also other factors come into play. Heating of the plastic, for instance at injection moulding, might be expected to lower the content of residual monomers but not necessarily to a very large extent. Through heating, the solubility of most substances increases which will counteract a possible degassing of monomers with low boiling point and/or high vapour pressure. At the same time, the degassing requires that there is volume to degas to and an outlet, so a possible degassing does not just create a balance which counteract the release of residual monomers. From theoretical considerations based on reaction kinetics it can be expected that there will be a correlation between process type and removal of residual monomers. Injection moulding can be expected to have more difficulties in removing residual monomers due to the closed tools for the design while an inflated film (for instance for the use of inflatable toys made of plasticized PVC) with a large surface compared to the mass, low thickness of the material and a process where much air is blown by the surface can be expected to be relatively better to remove residual monomers.

5.1.3 Migration of monomers – theoretical considerations

The solubility of monomers in the polymer and the affinity of the monomers (i.e. tendency to bond by electrostatic forces) for the polymer are in general so high that as a rule, the monomers are difficult to force out. The rule of thumb is that the monomer is the best solvent for a given polymer. Therefore, it cannot be expected that the residual monomers disappear completely with time. However, this does not mean that the content of the residual monomers increases over time. Like for all chemical processes, a phase equilibrium will occur. It is known among other things from composites where it is possible to smell styrene monomers if a person saws in glass fibre composites from boats and wind turbines, even after 20 years of operation. For instance, for food contact materials, it is recommended that the additives which are used in the plastic are soluble in this but insoluble in the liquid/food with which the plastic is in contact. Thus, the migration is minimised (Hahladakis et al., 2018; Hansen et al., 2013).

The rate of migration for organic chemical substances is dependent on among other things the size and structure of the molecules. Small molecules such as monomers will typically migrate faster than large molecules as they also have a low boiling point (Hansen et al., 2013). According to Hansen et al. (2013), some of the monomers such as vinyl chloride and butadiene will have a high tendency to migrate quickly, even at room temperature.

Parameters like initial concentration of the monomer in the plastic, the thickness of the plastic material, the crystallinity of the plastic and the surface structure of the plastic have all a complex influence on the rate of migration (Hansen et al., 2013). Residual monomers in plastic will be in a phase equilibrium with the atmosphere and the plastic in which they are dissolved. At the beginning where the concentration of the residual monomers is highest, the diffusion to the surface will be expected to follow Fick's Law (mathematical description of the migration). This means, as described above, there is a dependence of the plastic type (the concentration of the monomer in the plastic), the temperature and the thickness of the material. With time, it can be expected that an equilibrium (between the plastic and the medium) will occur with an approximately constant concentration of residual monomers – of course, if the medium is the same.

The presence of a mobile phase, i.e. small molecules which are liquids at the use temperature, will help the diffusion of residual monomers towards the surface if the atmosphere is not saturated with the residual monomers. The mobile phase can consist of plasticizers, dissolved colourants, perfume and much more. This means that addition of additives to plastic will influence the diffusion coefficient and thus the amount which migrates from the plastic as well as the migration rate (Genualdi et al., 2014). From a purely theoretical point of view, it must therefore be expected that the migration from soft plastic such as for instance PVC will be faster than for solid plastic products, such as for instance ABS.

5.1.4 Summary – theoretical considerations

Seen from a theoretical point of view, the following conditions regarding residual monomers in plastic and migration of residual monomers from plastic apply:

- The actual production process of the polymer is significant for the content of residual monomers. It is possible to reduce the content of residual monomers in the polymer by controlling the process conditions and use subsequent processes which may reduce the monomer content but there will always be a certain amount of residual monomer left in the polymer.
- The production method of toys (for instance injection moulding versus blown film) may be important for the content of residual monomers in the polymer.
- The migration of residual monomers from the polymer follows in theory Fick's Law, i.e. the migration depends on among other things the type of plastic (initial concentration), time, temperature, thickness of material and exposure for example for liquids.
- The migration will decrease with time as the concentration of the monomer in the plastic decreases and as an equilibrium between monomer content in the plastic and monomer content in the migration medium will occur.
- The migration may be expected to be largest to the medium/liquid in which the monomer is easily soluble.

For the five monomers which are in focus in this project, the following theoretical conditions ought to be valid based on the physical/chemical properties of the five monomers:

- Vinyl chloride and butadiene have a low boiling point and therefore they can be expected to be found in the lowest concentrations as residual monomers in their respective polymer material, but also other factors may influence the migration, for instance conditions such as material thickness (the difference of thin PVC film in inflatable toys to a massive ABS toy brick).

- Butadiene and styrene have a low water solubility and in theory, migration to aqueous media ought to be low.
- On the other hand, the water solubility for acrylonitrile and acrylamide is very high and here the migration to aqueous media is expected to be higher.
- For all monomers applies that they are soluble in ethanol (fatty liquids). As some monomers are more soluble in ethanol compared to water, it may in theory be possible that a migration will take place under conditions like bath water added baby oil or in situations where sunscreen lotion is involved.

5.2 Existing data on content of residual monomers

This paragraph presents the existing data on content of residual monomers in both toys and in plastics in general which have been identified in the literature search carried out in this project. Data are presented collectively in Table 11.

5.2.1 Content of residual monomers in toys

There are very few surveys of the content of residual monomers in toys. Abe et al. (2013) states that through a search for information on the content of residual monomers in ABS, they only identified two previous surveys (Ohno & Kawamura, 2010; Ohno et al., 2008) which describe this condition. Abe et al. (2013) also writes that through their search they did not identify any surveys on the content of residual monomers in thermoplastic elastomers like SEBS and SBS.

A previous Danish EPA project (Heckmann et al., 2015), which has studied the content of CMR substances in toys, identified a content of 23 mg/kg (ppm) styrene in a dinosaur plastic figure for children at the age 1-3 years. However, it is not stated which plastic type the figure is made of.

However, the literature search for residual monomers in plastic in connection with toys shows that there is awareness of the residual monomers in the plastic, for instance as described by Naturskydssföreningen (year is missing). It is assumed that especially the large producers of plastic toys perform continuous analyses for residual monomers and that knowledge about the content of residual monomers in plastic for toys is available but most likely as confidential information.

As the products are produced in bulk, the raw materials might also be available as bulk goods and as the raw material prices also are important, it can be expected that the plastic is either of a quality which is approved for food contact or of a technical quality. A raw material search in the UL Prospector database showed that about the half of the raw materials which were stated for use in toys were also stated for use for food contact material.

Below the results of the few surveys which are identified for toys are described after which the more general surveys of plastic for other purposes such as food contact are described.

Through the contact to TIE, a few of the toy producers also delivered information about the content of residual monomers in their own toy material. This information is also stated below.

5.2.1.1 ABS

Abe et al. (2013) examined 59 toy products of ABS on the Japanese market in 2011. In the survey they identified styrene in all 59 toy products of ABS, butadiene in 52 of the 59 products and acrylonitrile in 56 of the 59 products. Styrene was identified in by far the highest amounts with concentrations between 71 and 2600 mg/kg and an average of 928 mg/kg. Butadiene was identified in amounts between 0.04 and 5.3 mg/kg with an average of 0.78 mg/kg and in amounts < 0.025 mg/kg (corresponding to the quantification limit) for the 7 products where butadiene was not identified. Acrylonitrile was identified in amounts between 0.42 and 55 mg/kg with an average of 14 mg/kg and in amounts < 0.025 mg/kg (corresponding to the quantification limit) for the 3 products where butadiene was not identified.

Ohno & Kawamura (2010) and Ohno et al. (2008) examined 9 toy products of ABS on the Japanese market in 2004 to 2006. Butadiene was identified in all 9 pieces of toys with a content between 0.06 and 1.03 mg/kg. Acrylonitrile was identified in all 9 pieces of toys with a content between 5.4 and 43.6 mg/kg. Styrene was identified in all toys with a content between 160 and 3570 mg/kg. Both the residual monomer content of butadiene and acrylonitrile in toys was at level with the 13 products of ABS for food contact which were analysed in the same survey (butadiene: 0.06 – 1.58 mg/kg; acrylonitrile: 0.3 – 50.4 mg/kg).

Lv et al. (2015) examined in total 18 pieces of toys of ABS plastic purchased in China. A residual monomer content of styrene of up to 1378 mg/kg was measured.

According to TIE (2018b), during the years 2012 to 2017, a toy producer has made analyses of the content of residual monomers in their ABS material for toys (examined via the standards in the EN 13130[18] series). The content of styrene was measured to:

- 8 samples contained between 1.3 and 91 mg styrene/kg (average value 68.9 mg/kg)
- 12 samples contained between 110 to 270 mg/kg (average value 148 mg/kg)
- 12 samples contained between 430 to 640 mg/kg (average value 522.7 mg/kg)
- 10 samples contained between 830 to 1900 mg/kg (average value 1301.5 mg/kg)

Some of the same samples as listed above were also analysed for butadiene (TIE, 2018b). The results were:

- 9 samples did not contain butadiene (detection limit 0.01 mg/kg)
- 7 samples contained between 0.06 and 0.76 mg butadiene/kg (average value 0.29 mg/kg)
- 5 samples contained between 1 and 5 mg/kg

Some of the same samples as listed above were also analysed for acrylonitrile (TIE, 2018b). The results were:

- 16 samples did not contain acrylonitrile (detection limit 0.01 mg/kg)
- 3 samples contained between 0.1 and 0.11 mg acrylonitrile/kg (average value 0.1 mg/kg)
- 10 samples contained between 1.8 and 14 mg/kg (average value 7.7 mg/kg).

In all, 20 of the above ABS-samples were also analysed for migration of acrylonitril, butadiene and styrene respectively (is described later in section 5.3.1.1).

5.2.1.2 PVC

TIE (2018b) states that a toy producer has examined the content of vinyl chloride in their PVC material and that the content of vinyl chloride in all tests (number not stated) is below the detection limit of 0.1 mg/kg. No data for migration are available.

5.2.1.3 PS

TIE (2018b) states that a toy producer has examined the content of styrene in their HIPS material and that the content of styrene in all tests (number not stated) is between 50 and 500 mg/kg. No data for migration are available.

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[18] EN 13130 series: ”Materials and articles in contact with foodstuffs – Plastics substances subject to limitation”

5.2.1.4 Thermoplastic elastomers (SEBS, SBS)

Abe et al. (2013) examined in 2011 12 toy products of thermoplastic elastomers (stated as consisting of SEBS and SBS) on the Japanese market. The survey concluded that the level of residual monomers from the toy products of thermoplastic elastomers was much lower than the level of residual monomers from the toys of ABS which were also analysed in the same survey. Styrene was identified in 5 of 12 toy products at levels of 0.2 to 0.5 mg/kg and with an average of 0.3 mg/kg (the detection limit was 0.2 mg/kg). Butadiene was not identified in any of the 12 toy products (the detection limit was 0.1 mg/kg).

TIE (2018b) states that a toy producer has examined the content of styrene in the years 2012 to 2015 in their SEBS material. In total, 13 different products/analyses were made, and styrene was only identified in one of them with a content of 1.1 mg/kg. The remaining values were under the detection limit of 0.05 mg/kg.

Abe et al. (2013) examined in 2011 two toy products of rubber (stated as consisting of SBR, i.e. SBS) on the Japanese market. The survey concluded that the level of residual monomers from the toy products of rubber was much lower than the level of residual monomers from the toys of ABS which were also analysed in the same survey. Neither styrene nor butadiene were identified in any of the 2 toy products of SBR rubber which were analysed. The detection limit was 0.1 mg/kg.

5.2.2 Content of residual monomers in plastic

Below data are presented where a content of residual monomers in plastic for other purposes than toys was identified. Data are mostly available for food contact materials or for water pipes of PVC.

5.2.2.1 ABS

A survey of residual monomers in kitchen appliances in ABS in Japan (Abe et al., 2014) showed a content of residual monomers of max. 2,000 mg/kg for styrene, 0.06 to 1.7 mg/kg for butadiene and 0.15 - 20 mg/kg for acrylonitrile. The approximate content of acrylonitrile is supported by another survey (Poustkova et al., 2007).

Genualdi et al. (2014) has measured the content of styrene in 24 different products for food contact. The value of ABS was 3042 mg/kg (1 product). The remaining 23 products were made of PS (this is described in section 5.2.2.3 below).

Lickly et al. (1991) has examined the content of residual monomers and migration from ABS to food simulating liquids (i.e. water and 8 % ethanol solution). Customized small round plates of ABS were used for the tests. The content of residual monomers of acrylonitrile was between 3 and 49 mg/kg for the 7 examined products.

5.2.2.2 PVC

ECVM (the European Council of Vinyl Manufactures) was contacted via the PVC Information Council in Denmark. Back in 1995, ECVM made some general standards for their production of PVC, including standards for the amount of the residue of the monomer vinyl chloride in the final PVC material. The requirements made at that time were:

- 5 g/ton vinyl chloride as residue in PVC for general purposes, corresponding to 5 mg/kg or 5 ppm
- 1 g/ton vinyl chloride as residue in PVC for food or medical applicatons, corresponding to 1 mg/kg or 1 ppm.

ECVM informs that today the content of residual monomer in PVC produced in Europe is below 1 ppm (1 mg/kg) as all European producers produce according to the strictest standard today. Furthermore, ECVM informs that the content of residual monomer of vinyl chloride is further reduced – typically by a factor of 5-10 when PVC raw material is used for production of PVC products. At these levels of the residual monomer content, the migration of vinyl chloride might not be measurable according to ECVM. However, this apply to PVC produced in Europe and not necessarily for PVC toys produced in China.

Berens & Daniels (1976) have analysed both content and migration of vinyl chloride from old PVC pipes which were between 6 and 12 months old. Four different samples of old PVC pipes contained 22, 29, 177 and 292 mg vinyl chloride/kg PVC pipes respectively. The levels of the residual monomer vinyl chloride are somewhat higher in this old survey compared to the standard of today according to the industry. The reason might be that it is an old survey from the period before knowledge and focus on vinyl chloride as a carcinogenic substance became available.

This is confirmed by Borrelli et al. (2005) who describes the historical development of the residual monomer content in PVC in the USA. In 1977, due to the newly discovered carcinogenic properties of vinyl chloride, a limit value of 10 ppm vinyl chloride was just set for the residual monomer content in PVC for pipes. In the 1980'ies, residual monomer content was below 8.5 ppm for all types of PVC according to the producers, and in year 2000 the residual monomer content of vinyl chloride was between 0.09 and 3 ppm with an average below 1 ppm for most of the PVC types. Furthermore, Borrelli et al. (2005) refers to a survey on food contact materials from 2003 where the residual monomer content typically was below 5 ppb (i.e. 0.005 ppm).

5.2.2.3 PS

A safety data sheet (SDS) on plastic material received from a producer of toys states that the content of styrene in polystyrene (HIPS) is < 0.08 % or 800 mg/kg as a maximum.

Correspondingly, an SDS from a producer of expanded PS (EPS) has been identified and this SDS states a maximum residual monomer content of styrene of 0.2 % or 2000 ppm. However, this EPS is not specifically stated as used for toys but for insulation or packaging (Dyplast, 2018). It must be assumed that the residual monomer content in foamed PS, i.e. EPS, will be different than in solid PS. Lin et al. (2016) has made a few measurements on EPS containers for food contact and states a residual monomer content of styrene of 178 mg/kg. In the same survey, EPS containers of recycled EPS (also for food contact) were examined and the concentration of styrene was a little bit higher (189 mg/kg) in the recycled EPS compared to virgin EPS – but there are no significant differences.

Amirshaghaghi et al. (2011) examined the content and migration of styrene from PS plates in an aqueous 10 % ethanol solution which is used as food simulant for oil/water emulsions. The basic concentration of styrene monomer was measured to 224 mg/kg on average and with a maximum content of 625 mg/kg. The authors state that this content concentration of residual monomers is relatively low.

Genualdi et al. (2014) has measured the styrene content in 24 different products for food contact. The content of styrene monomers was measured in several types of PS: XPS (extruded PS foam), EPS foam, HIPS (High Impact PolyStyrene) and GPPS (General-Purpose PolyStyrene). The values of XPS were between 222 and 350 mg/kg (3 products), the values of EPS were between 34 and 48 mg/kg (2 products), the values of HIPS were between 9.3 and 2866 mg/kg (17 products) and the value for GPPS was 771 mg/kg (1 product). Average content of styrene was 340 mg/kg in the 24 products (1 product was of ABS).

The Danish EPA LOUS project on styrene (Kjølholt et al., 2014) refers among other things to Gelbke et al. (2014) in which several international chemical companies state that the amount of styrene monomer may be up to 500 mg/kg PS.

In 2011 and 2012, FDA (2015) performed a survey of the residual monomer content of different types of PS on the American market: GPPS, HIPS, PS foam and EPS foam which all were used for food contact materials. The survey was carried out through anonymous questionnaire surveys to producers of PS and not via analyses. The styrene content in PS for food contact on the American market was between 71 and 1219 ppm but with small differences between the different PS types: GPPS (153 – 1079 ppm), HIPS (207 – 1219 ppm), PS foam (345 – 718 ppm) and EPS foam (71 – 586 ppm). There is thus no visible difference in the residual monomer content of styrene in foamed PS compared to non-foamed PS.

ILSI (2017) collected a number of surveys of styrene monomers in PS for food contact and stated that the migration to the food is relatively low, i.e. in the order of magnitude of 10 ppb with maximum values of 200 ppb (µg/kg) even if the residual content of styrene monomer might be relatively high – approximately 500 ppm and in some case as high as 1,000 ppm.

5.2.2.4 NBR

An article – probably written by the company Bayer itself – lists a number of measurements of the content of residual monomer of acrylonitrile in NBR rubber produced by Bayer. The content values for acrylonitrile are between 0.4 and 2.9 mg/kg in five different NBR qualities (Coster et al., 2003).

5.2.3 Summary of data regarding the content of residual monomers in plastic

Table 11 below is a summary of the data described in the text above.

It is worth noticing that it was not possible to identify data for the content of the residual monomer acrylamide. It might be due to the circumstance that it is not easy to analyse for acrylamide in solid materials. Thus, it has not been possible in this project to perform chemical content analyses of acrylamide, as this is an analysis which Eurofins does not perform because the chemical analysis is challenging due to interference issues. Therefore, it is not possible to ensure a correct quantification of the content of acrylamide at the analysis.

Table 11. Summary regarding content of residual monomers in the related polymer

Monomer	Polymer	Residual content of monomer mg/kg (ppm)	Comment / reference
Vinyl chloride	PVC	< 0.1	Analyses on toy material TIE, 2018b
Vinyl chloride	PVC	Max. 1	Content in PVC raw material produced in Europe. ECVM, 1995.
Vinyl chloride	PVC	22 - 292	Berens & Daniels, 1976 REMARK: Old data
Vinyl chloride	PVC	< 0.005	Food contact materials Borrelli et al., 2005
Butadiene	ABS	< 0.01 – 5	Analyses on toy material TIE, 2018b
Butadiene	ABS	0.06 – 1.7	Food contact materials Abe et al., 2014
Butadiene	ABS	< 0.025 – 5.3 Average 0.78	Analyses on toy products Abe et al., 2013
Butadiene	ABS	0.06 – 1.03	Analyses on toy products Ohno & Kawamura, 2010

Monomer	Polymer	Residual content of monomer mg/kg (ppm)	Comment / reference
Butadiene	ABS	0.06 – 1.58	Food contact materials Ohno & Kawamura, 2010
Butadiene	SBS	< 0.1 Not identified	Analyses on toy products Abe et al., 2013
Butadiene	SBR/SBS	< 0.1 Not identified	Analyses on toy products Abe et al., 2013
Acrylonitrile	ABS	< 0.01 – 14	Analyses on toy material TIE, 2018b
Acrylonitrile	ABS	0.15 – 20	Food contact materials Abe et al., 2014
Acrylonitrile	ABS	< 0.025 – 55 Average 14	Analyses on toy products Abe et al., 2013
Acrylonitrile	ABS	5.4 – 43.6	Analyses on toy products Ohno & Kawamura, 2010
Acrylonitrile	ABS	0.3 – 50.4	Food contact materials Ohno & Kawamura, 2010
Acrylonitrile	ABS	3 – 49	Lickly et al., 1991
Acrylonitrile	NBR	0.4 – 2.9	Coster et al., 2003 (industrial article)
Styrene	Unknown	35	Analysis om toy figure of plastic in Denmark Heckmann et al., 2015
Styrene	ABS	1.3 - 1900 Average 69 – 1302	Analyses of different series of toy material TIE, 2018b
Styrene	ABS	2000	Food contact materials Abe et al., 2014
Styrene	ABS	71 – 2600 Average 928	Analyses on toy products Abe et al., 2013
Styrene	ABS	160 and 3570	Analyses on toy products Ohno et al., 2008
Styrene	ABS	3042	Food contact materials Genualdi et al., 2014
Styrene	ABS	Max. 1378	Analyses on toy products Lv et al., 2015
Styrene	SEBS	< 0.05 – 1.1	Analyses on toy material TIE, 2018b
Styrene	SEBS/SBS	< 0.2 – 0.5	Analyses on toy products (5 out of 12) Abe et al., 2013
Styrene	SBR/SBS	< 0.1 Not identified	Analyses on toy products Abe et al., 2013
Styrene	PS	Max. 800	Safety data sheet from producer of PS for toys
Styrene	PS	Max. 625 Average 224	Food contact materials Amirshaghaghi et al., 2011
Styrene	PS	Max. 500	Information from producers Gelbke et al. (2014) i Kjølholt et al., 2014

Monomer	**Polymer**	**Residual content of monomer** **mg/kg (ppm)**	**Comment / reference**
Styrene	PS	Approx. 500 to max. 1000	Summary of food contact materials ILSI, 2017
Styrene	PS-foam	345 – 718	Food contact materials FDA, 2015
Styrene	HIPS	50 – 500	Analyses on toy material TIE, 2018b
Styrene	HIPS	9.3 - 2866	Food contact materials Genualdi et al., 2014
Styrene	HIPS	207 – 1219	Food contact materials FDA, 2015
Styrene	EPS	Max. 2000	Safety data sheet for foamed PS for use for insulation and packaging. Dyplast, 2018.
Styrene	EPS	33.7 – 47.8	Food contact materials Genualdi et al., 2014
Styrene	EPS	71 – 586	Food contact materials FDA, 2015
Styrene	EPS	178 (virgin material) 189 (recycled)	Food contact materials Lin et al., 2016
Styrene	XPS	221.8 – 349.5	Food contact materials Genualdi et al., 2014
Styrene	GPPS	771	Food contact materials Genualdi et al., 2014
Styrene	GPPS	153 - 1079	Food contact materials FDA, 2015

The levels of the content of the four other residual monomers are identified at:

- Vinyl chloride in PVC: < 0.005 to 1 mg/kg, if the old data from 1970'ies are excluded

- Butadiene:
  - In ABS: < 0.01 to 5.3 mg/kg
  - In SBS: < 0.1 (not identified)

- Acrylonitrile:
  - In ABS: < 0.01 to 55 mg/kg

- Styrene:
  - In ABS: 71 to 3042 mg/kg
  - In SEBS/SBS: < 0.2 to 1.1 mg/kg
  - In PS/HIPS: 9.3 to 2866 mg/kg

This means that the levels of the three monomers vinyl chloride, butadiene and acrylonitrile are generally low and at ppm level whereas the residual monomer content of styrene is generally substantially higher and might be up to 100 to 1,000 times higher. Maximum values of styrene might be up to approx. 0.3 % (3,000 ppm) but is at approx. 0.05 to 0.1 % (500 to 1,000 ppm) on average.

Furthermore, it is worth noticing that the residual monomer content in the rubber materials SEBS and SBS are generally very low and in most cases, not detectable compared to corresponding residual monomer content in the other plastic types (ABS, PS).

Generally, there are many data available for the residual content of styrene in different materials (ABS, different kinds of PS and rubber materials such as SEBS and SBS/SBR). However, most data are for the content of styrene in ABS and PS and not that many data for the rubber materials SEBS and SBS/SBR. A few surveys of the residual monomer content of butadiene and acrylonitrile are identified – again primarily for ABS and only a few data for the rubber materials (SBS/SBR and NBR). Only a few data are identified for the residual monomer content of vinyl chloride in PVC.

The levels of the residual monomer content in toys do not seem to be much different than the other levels of residual monomer content which are identified through the literature search for the different monomers.

If a comparison with the content limit value of 1 mg/kg, which ANEC suggests for vinyl chloride, butadiene and acrylonitrile respectively, is made, it is seen that the limit value for vinyl chloride seems to be complied with (but there are only a few data) whereas existing measurements for both butadiene and acrylonitrile exceed the suggested limit value – also for toys. For styrene, ANEC has not suggested a content limit but on the contrary, a migration limit value which is discussed in section 5.3.

Whether it makes sense to establish a limit value for the content of the residual monomer acrylamide in toys, if at present there are problems with a reliable analysis method for the content of acrylamide in solid materials, ought to be discussed and examined in detail – but this has not been a part of this project.

5.3 Existing data on migration of residual monomers from plastic

In this section, the existing data identified in the literature search carried out in this project on migration of residual monomers from both toys and from plastics in general are presented. A summary of these data is presented collectively in Table 12.

5.3.1 Migration of residual monomers from toys

Even fewer surveys are identified measuring the migration of residual monomers from toys compared to the few surveys identified on the content of residual monomers in toys. The few identified surveys are presented below.

5.3.1.1 ABS

Abe et al. (2013) examined 59 toy products of ABS on the Japanese market. They measured a residual monomer content (acrylonitrile, butadiene and styrene) in all of the 59 products and selected the 10 products with the highest content of residual monomers for migration analyses. The migration was carried out under the following conditions: 40 °C for 30 minutes in water. Of the three residual monomers from ABS, only analyses for styrene and acrylonitrile were carried out as the content of butadiene was low (max. 5.3 mg/kg). Styrene was identified in the migration liquid for 9 out of the 10 products in a concentration between 6 and 40 µg/l whereas acrylonitrile was only identified in the migration liquid for 1 out of 10 products in a concentration of 3 µg/l. The quantification limit was 1 µg/l for styrene and 3 µg/l for acrylonitrile. For acrylonitrile, it was the product with the highest content of acrylonitrile (55 mg/kg) where a migration of the detection limit (3 µg/l) was measured. Abe et al. (2013) emphasises that the migration to children's saliva from ABS toys might in fact be lower in real life than the migration they measured at the analyses, as they had added small amounts of methanol as solvent for the applied internal standard. This could have the consequence that styrene and acrylonitrile have migrated out into the water by means of the added methanol and thus have contributed to an increased migration of the monomers.

Lv et al. (2015) examined in total 18 pieces of toy of ABS plastic bought in China. For one of the toy products, the migration of styrene was examined for both sweat and saliva at 37 °C. The migration was measured at many times and increased until after 120 hours of migration where it seemed an equilibrium was reached. The migration to saliva was a touch higher than the migration to sweat at all exposure times. All in all, there was not any large difference between migration to saliva and migration to sweat. The residual monomer content of styrene in ABS was measured to 1378 mg/kg and migration to saliva was 2.87 mg/kg after 120 hours whereas the migration to sweat was 2.78 mg/kg. The values at shorter exposure time are not stated in the article but only illustrated graphically. Migration to both saliva and sweat seems to be below 0.250 mg/kg for a couple of hours of exposure.

The same toy producer, who according to TIE (2018b) in the years 2012 to 2017 made content analyses of residual monomers in their ABS material for toys, did also examine migration (via the standards in EN 13130 series, i.e. migration to 10 % ethanol solution and 3 % acetic acid solution – in both cases for 24 hours at 40 °C).

- For four samples with a content of styrene between 51 and 160 mg/kg, a migration of styrene to 10 % ethanol was analysed. The result was that no migration of styrene above the detection limit of 0.01 mg/l was measured.
- For 20 samples, migration of styrene, butadiene and acrylonitrile to 3 % acetic acid was analysed. The content of styrene in the 20 samples was between 1.3 and 1100 mg/kg, the content of butadiene was between 0.07 and 3.1 mg/kg, and the content of acrylonitrile was between 1.8 and 9 mg/kg. The result was that no migration of any of the monomers in any of the samples was identified (the detection limit was 0.01 mg/l).

5.3.1.2 SEBS

The same toy producer, who according to TIE (2018b) in the years 2012 to 2015 made a content analyse of the residual monomer styrene in their SEBS material for toys, did also examine migration (via the standards in EN 13130 series, i.e. migration to 3 % acetic acid solution for 24 hours at 40 °C). Only one migration analysis was made on that product where a content of styrene (of 1.1 mg/kg) was identified. No migration above the detection limit of 0.01 mg/l was identified.

5.3.2 Migration of residual monomers from plastic

Below data are presented. They are identified on migration of residual monomers from plastic to other purposes than toys. Data are mostly available for food contact materials or for PVC water pipes. The results are summarised in Table 12.

5.3.2.1 ABS

Lickly et al. (1991) has examined residual monomer content and migration from ABS to food simulating liquids (i.e. water and 8 % ethanol solution). Customized small round plates of ABS were used for the tests. The content of residual monomers of acrylonitrile was between 3 and 49 mg/kg for the 7 examined products. The migration of acrylonitrile was highest from the products with the largest content of residual monomer. No significant difference of the migration to water and 8 % ethanol solution was seen – the migration was here at approximately the same level. The migration of acrylonitrile increased by increasing exposure time and increasing temperature. The migration of acrylonitrile varied from < 25 µg/l (49 °C, 24 hours) to 2594 µg/l (49 °C, 10 days). Furthermore, Lickly et al. (1991) describes that observations suggest that migration of acrylonitrile from ABS material to fatty food simulants like heptane was lower than migration to water under the same conditions.

5.3.2.2 PVC

A survey of the migration of vinyl chloride from PVC (Benfenati et al., 1991) showed a migration of 13 to 83 ppt with an average of 48 ppt (0.048 ppb) to bottle water. This survey also showed that there was a clear connection between the concentration of vinyl chloride in the bottle water and the number of days which the water has been in the bottle: the longer time, the higher concentration of vinyl chloride in the water.

A survey of migration of vinyl chloride from PVC (Al-Malack et al., 2000) from PVC pipes (without plasticiser) showed a migration of vinyl chloride to water of maximum 2.5 ppb (corresponding to 0.11 µg to 44 ml water). The migration was examined at different temperatures (5, 22, 35 and 45 °C), at different pH (4, 5, 6, 7 and 9) and at different levels of dissolved solids (TDS – Total Dissolved Solids: 2, 160 and 2670 mg/l). The migration was measured after various number of days from 0 to 30 days. The result was that no measurable migration of vinyl chloride at temperatures below 45 °C was found. Only at 45 °C, a migration of vinyl chloride was identified, and it increased over time and reached its highest level after 30 days. The increase in the migration of vinyl chloride from 15 days to 30 days was insignificant. The surveys showed that the migration of vinyl chloride was higher at lower pH (pH=5) and indicated that an acidic pH value made the water more corrosive which might have resulted in a higher migration of vinyl chloride. Furthermore, the survey showed that migration of vinyl chloride increased with an increased content of dissolved solids (TDS) in the water.

A later survey from Al-Malack (2004) also on PVC pipes showed that the migration of vinyl chloride increased significantly when PVC pipes were exposed to a relatively high intensity of UV light. After 14 days of exposure (at 35 °C) at high intensity of UV light, the migration increased to 2.3 µg/l of water (2.3 ppb). Compared to the earlier survey (Al-Malack et al., 2000), no measurable migration at 35 °C was found. PVC exposed to UV light increases thus the migration. Al-Malack (2004) states that the used UV light did not simulate sun light.

Berens & Daniels (1976) have analysed both content and migration of vinyl chloride from old PVC pipes which were between 6 and 12 months old. Four different samples of old PVC pipes were filled with water and they stood for 3, 7 or 14 days respectively at 23 °C after which the water sample was analysed for content of vinyl chloride. Even if there were only a few samples, the tendency was clear: The higher monomer content in the PVC as starting point, the higher migration. Furthermore, the migration increased with increasing exposure time. Migration values were measured to between 0.006 and 0.113 mg/kg in the water, corresponding to between 6 and 113 ppb. These levels of the residual monomer vinyl chloride are somewhat higher in this older survey compared to what other new surveys show. It might be due to the fact that it is an old survey from before the time where knowledge and focus on vinyl chloride as a carcinogenic substance became available.

Another survey (Walter et al., 2011) on migration of vinyl chloride to drinking water from PVC pipes examined the difference in migration between new and old PCV pipes. The migration of vinyl chloride from PVC pipes, 25 years old and 2 years old respectively, was about the same when the authors looked at the short-time exposure (i.e. a couple of days) but after 2 months the migration was far larger from the new PVC pipes compared with the old PVC pipes. However, one single pipe of the old PVC pipes showed quite another tendency (> 200 ng/l after 7 days) but the authors attribute this either as being a producer-specific result or that corrosion on this PVC pipe had influenced the migration. The migration from PVC pipes was between < 6 – 20 ng/l after a few hours of migration to water (5 – 8 hours) whereas the migration reached a maximum level of approximately 300 ng vinyl chloride per litre after long-term exposure of above 700 days.

Another survey shows that the migration of vinyl chloride is reduced if the PVC contains plasticiser (Demertzis & Kontominas, 1986). These results are, however, in contrast to the theoretical considerations presented by Genualdi et al. (2014) saying that content of additives such as plasticisers potentially can increase the migration. Tests with extraction of vinyl chloride on a technical quality of PVC after 30 days of exposure to sun light showed 2.5 µg/l vinyl chloride in the extraction liquid (Al-Malack & Sheikheldin, 2001).

ECVM (the European Council of Vinyl Manufactures) has stated that there will be no measurable migration of vinyl chloride from the products with that amount of residual monomer (vinyl chloride) which is in PVC products on the European market – of course products produced with European-produced PVC. However, ECVM emphasises that toys today are primarily imported from outside Europe and therefore they will presumably be produced of non-European PVC.

5.3.2.3 PS

A survey (Saim et al., 2012) of migration of styrene from cups of polystyrene (PS) states that migration of styrene from PS cups has earlier been observed as high as 0.025 % of the total styrene content at only one single use of the cup for cold or hot drinks. In the survey, it is stated that fat content, temperature and contact time are the most common parameters which have earlier been mentioned when consumers' exposure for styrene was to be examined. Saim et al. (2012) suggested a number of analyses at different temperatures of the liquid in the PS cup (13, 30, 55, 80 and 97 °C) in combination with different pH values (4, 5, 6, 7 and 8) and for different contact times (6, 35, 78, 120 and 149 minutes), i.e. the period where that liquid is in the PS cup. In total 20 tests with random combinations of the above temperature, pH value and contact time were performed. The liquid – in total 100 ml which was used in the PS cup – was deionised water, and acetic acid or ammonia solution was used to adjust to the correct pH value. The measured amount of styrene in the water varied from 0.3 to 4.2 µg/l (ppb). The results were analysed in proportion to significance and the survey concluded that the migration of styrene was strongly dependent on the temperature of the liquid in the cup which according to the authors' conclusion corresponds to the result of earlier surveys. A higher basic temperature of the liquid resulted in a higher concentration of styrene in the liquid and thus in a higher migration. There was not the same strong correlation between migration and contact time. However, the survey also concludes that in an acid liquid (pH 5), the migration of styrene increases significantly with the temperature, i.e. that the combination of an acid liquid and a high temperature gave the highest migration of styrene.

The same conditions, i.e. that a higher temperature of the liquid gives a higher migration, can be seen in an older survey (Tawfik & Huyghebaert, 1998) which has examined migration of styrene from PS cups and containers for a number of foods and food liquids under different conditions. Furthermore, a higher migration to fatty foods and to pure ethanol is seen, compared with migration to water. The migration of styrene varied from < 1 µg/kg (at maximum 72 hours of exposure at 4 °C or maximum 2 hours of exposure at 40 °C) to 343 µg/kg (to pure ethanol at 100 °C for 1 hour).

The same conditions are confirmed by a later survey by El-Ziney & Tawfik (2016) where the highest migration of styrene from PS food contact materials is seen at high temperatures, longer exposure times and at migration to fatty foods. The highest migration was measured to 102 µg/kg to butter (kept at 4 °C for 60 days).

Hahladakis et al. (2018) refers to a number of surveys of migration of different additives in plastic. Migration of styrene monomer from PS is also mentioned. Here it is stated that migration of styrene from PS cups was dependent on the fat content in the liquid as well as the temperature of the liquid in the cup. The migration of styrene was highest for warm liquids compared with cold liquids and highest at a high fat content in the liquid compared with a low fat content. The same picture can be seen from Khaksar & Ghazi-Khansari (2009) where the migration of styrene from PS cups is highest at a high temperature and to liquids with higher fat content. Here levels up to 8.65 µg styrene/l of food liquid at a temperature of 100 °C and the longest contact time of 60 minutes are stated. At a colder temperature (20 °C) and a shorter contact time (30 minutes), the migration of styrene was between 0.48 and 0.72 µg/l.

Amirshaghaghi et al. (2011) examined content and migration of styrene from PS plates in an aqueous 10 % ethanol solution which is used as food simulant for oil/water emulsions. The migration of styrene was measured at different temperatures (5, 20 and 40 °C) and at different days (1, 7, 15, 24 and 35 days). The authors found that the migration of styrene followed Fick's Law. The measured migration was very slow at all temperatures. Higher temperature gave a higher migration rate just as longer time of exposure gave a higher migration rate.

Genualdi et al. (2014) has measured the styrene content in 24 different PS products for food contact. The content of styrene monomer was measured in several types of PS: XPS (extruded PS foam), EPS foam, HIPS (High Impact PolyStyrene) and GPPS (General-Purpose PolyStyrene). It was found that the migration was higher from XPS and EPS to the food compared with the less porous types of PS (HIPS and GPPS) which was in accordance with the expectations. The content of styrene was measured in for instance yoghurt, chicken, cakes and noodle soup. The concentration of styrene measured in the food varied from 2.6 to 163 µg/kg and was on level with other earlier surveys with which they compared results. The content of styrene measured in the food is an expression of the amount of styrene which migrates from the PS product and into the food. It was found that the migration rate increased with increasing temperatures.

The Danish EPA LOUS project on styrene (Kjølholt et al., 2014) refers among other things to Gelbke et al. (2014) in which several international chemical companies state that the migration of styrene from HIPS and GPPS is generally below 100 µg/kg. However, the migration is 75 – 590 µg/kg when the migration is to a fatty medium such as olive oil (after 10 days at 40 °C).

In 2011 and 2012, FDA (2015) performed a survey of the residual monomer content of different types of PS on the American market: GPPS, HIPS, PS foam and EPS foam which all were used for food contact materials. The survey was carried out via anonymous questionnaire surveys to producers of PS and not by chemical analyses. Based on the producers' specifications of the styrene content in the PS materials, the migration was calculated based on a calculation model for food contact materials. The migration was calculated between 0.31 and 91.6 ppm. The highest values were identified for products with the longest exposure time, highest exposure temperature or content of fatty foods. The survey from FDA (2015) does not show any difference in migration of styrene from foamed PS rather than non-foamed PS. On the other hand, a survey from Paraskevopoulou et al. (2012) does that. It shows that the migration from PS and EPS respectively exposed for the same migration conditions shows a higher migration from EPS compared with PS.

ILSI (0217) collects a number of surveys of styrene monomers in PS for food contact and states that the migration to the food is relatively low, approximately 10 ppb (µg/kg), however, with maximum values up to 200 ppb even if the residual content of styrene monomer might be relatively high (approximately 500 - 1000 ppm). ILSI describes that the migration of styrene to the food depends on the following factors:
- Higher migration to fatty foods
- Higher migration at higher temperature and longer exposure time
- Higher migration at higher basic level of styrene in the PS material

Lin et al. (2016) has made a few measurements on migration of styrene from EPS containers for food contact. Analyses on both EPS containers of virgin EPS (new product) and recycled

EPS have been performed. The migration ratio of styrene (i.e. the percentage of the total content which migrates) was in general higher in the container of recycled EPS and the authors state that this might be due to possibility that the EPS is decomposed in the reutilization process. The highest migration values measured for styrene were 657.3 µg/l in virgin material (at 40 °C for 9 days to isooctane) and 384.2 µg/l in recycled EPS (at 40 °C for 12 days to isooctane) as well as 382.6 µg/l in recycled EPS (at 40 °C for 6 days to isooctane).

5.3.2.4 SBR rubber (SBS)

Genualdi et al. (2014) has measured migration of styrene from different products for food contact in the actual food. The styrene content is measured in chewing gum which has styrene-butadiene as rubber base (SBR/SBS). The concentration of styrene measured in the foods varied from 10.5 to 21.9 µg/kg.

5.3.2.5 PAM

According to Woodrow et al. (2008), polyacrylamide is used among other things like a flocculating agent in the nature, due to its ability to absorb large amounts of water (and thus close holes). The migration of acrylamide from polyacrylamide which was exposed to iron sulphate and simulated sunlight was examined to simulate a natural impact. The migration of acrylamide was strongly dependent on the Fe^{3+} concentration and the migration was largest at the highest Fe^{3+} concentration. The highest migration of acrylamide was measured to 3.97 ppb (Woodrow et al., 2008).

5.3.3 Summary of data regarding migration from plastic

Data described in the text above are gathered in Table 12 below.

It is worth noticing that only a little information about migration of the residual monomer butadiene is available. Whether this is due to the fact that the conent of the residual monomer butadiene is normally identified in small amounts (mostly < 1.7 mg/kg, maximum measurement 5.3 mg/kg) is unknown. However, this is the argument which Abe et al. (2013) states for not measuring the migration of butadiene from the toys they examined. Only data from one of the European toy producers (TIE, 2018b) show that all the measurements (20 in total) are below the detection limit.

For the four other monomers, some migration data for vinyl chloride (measurements on PVC pipes or bottles) and a large number of migration data for styrene for especially food contact materials have been identified. Only a few (two) surveys of migration of acrylonitrile and one single survey of migration of acrylamide have been identified.

Table 12. Summary regarding migration of residual monomers from the associated polymer

Monomer	Polymer	Migration µg/l (ppb)	Migration medium	Comment / reference
Vinyl chloride	PVC	0.013 – 0.083 Average 0.048	To water in bottle	Benfenati et al., 1991
Vinyl chloride	PVC	2.5	Water	Al-Malack & Sheikheldin, 2001
Vinyl chloride	PVC	2.5	Water (45 °C, 30 days)	Al-Malack et al., 2000 Only migration at > 35°
Vinyl chloride	PVC	2.3	Water (35°C, 14 days)	Al-Malack, 2004 PVC exposed to high UV lightfor 14 days
Vinyl chloride	PVC	6 – 113	Water (23 °C, up to 14 days)	Berens & Daniels, 1976 NOTE: Old data

Monomer	Polymer	Migration µg/l (ppb)	Migration medium	Comment / reference
Vinyl chloride	PVC	< 0.006 – 0.020 Max. about 0.3	Water (5-8 hours) Water (700 days)	Walter et al., 2011
Acrylonitrile	ABS	< 10	3 % acetic acid (40 °C, 24 hours)	Analyses on toys TIE, 2018b
Acrylonitrile	ABS	< 3 - 3	Water (40 °C, 30 minutes)	Analysis on toys Abe et al., 2013
Acrylonitrile	ABS	< 25 to 2594	Water (49 °C, 24 hours – 10 days)	Lickly et al., 1991
Butadiene	ABS	< 10	3 % acetic acid (40 °C, 24 hours)	Analyses on toys TIE, 2018b
Styrene	ABS	< 10	3 % acetic acid (40 °C, 24 hours)	Analyses on toys TIE, 2018b
Styrene	ABS	< 10	10 % ethanol (40 °C, 24 hours)	Analyses on toys TIE, 2018b
Styrene	ABS	10.5 – 21.9 µg/kg	Chewing gum (food)	Genualdi et al. 2014
Styrene	ABS	< 1 – 40	Water (40 °C, 30 minutes)	Analysis on toys Abe et al., 2013
Styrene	ABS	2.87 mg/kg 2.78 mg/kg	Saliva (37 °C, 120 hours) Sweat (37 °C, 120 hours)	Analyses on toys Lv et al., 2015
Styrene	SEBS	< 10	3 % acetic acid (40 °C, 24 hours)	Analyses on toys TIE, 2018b
Styrene	PS	From < 1 µg/kg To 343 µg/kg	Maximum 72 hours, 4 °C or maximum 2 hours at 40 °C To pure ethanol at 100 °C for 1 hour	Tawfik & Huyghebaert, 1998 Generally, measured on different foods
Styrene	PS	Maximum 102 µg/kg	To butter (4 °C, 60 days)	Ziney & Tawfik, 2016
Styrene	PS	Up to 8.65 0.48 – 0.72	Cocoa in a cup (100 °C for 60 minutes) Liquid in a cup (20 °C for 30 minutes)	Khakser & Ghazi-Khansari, 2009
Styrene	PS	2.6 – 163 µg/kg	Foods, as for instance yoghurt and cakes	Genualdi et al., 2014
Styrene	PS	0.31 – 91.6 ppm	Foods, both aqueous and fatty	FDA, 2015 NOTE: Theoretically calculated values
Styrene	PS	Migration is increased by increased temperature Migration is increased by increased fat content in medium/liquid		Amirshaghaghi et al., 2011 Hahladakis et al., 2018
Styrene	PS	Normally 10 Maximum 200	Foods	ILSI, 2017

Monomer	Polymer	Migration µg/l (ppb)	Migration medium	Comment / reference
Styrene	PS (HIPS and GPPS)	Normally < 100 µg/kg 75 – 590 µg/kg	Not stated in the source Olive oil	Gelbke et al., 2014 i Kjølholt et al., 2014
Styrene	EPS	657.3 (virgin material) 384.2 (recycled) 382.6 (recycled)	Isooctane (40 °C, 12 days) Isooctane (25 °C, 12 days) Isooctane (40 °C, 6 days)	Lin et al., 2016
Styrene	SBR/SBS	10.5 – 21.9 µg/kg	Chewing gum	Genualdi et al., 2014
Acrylamide	PAM	3.97	Water with Fe^{3+} content and exposed to sunlight	Woodrow et al., 2008

The levels of the migration of the five residual monomers are identified at:

- Vinyl chloride from PVC: < 0.006 to 2.5 µg/l, if the old data are disregarded

- Acrylonitrile:
  - From ABS: < 3 to 2594 µg/l

- Butadiene:
  - From ABS: < 10 µg/l (below the detection limit)

- Styrene:
  - From ABS: < 1 to 40 µg/l
  - From PS: < 1 to 343 µg/l, if theoretically calculated data are disregarded
  - From SBR/SBS: 10.5 – 21.9 µg/l

- Acrylamide:
  - From PAM: 3.97 µg/l (only one measurement)

This means that the levels of the migration of the five above-mentioned monomers are generally low, approximately a couple of µg/l. However, some values of migration are substantially higher, for instance migration of acrylonitrile from ABS of 2594 µg/l, but this value was found at 49 °C and after 10 days, i.e. migration conditions which are not relevant for toys.

It does not seem that the migration of styrene is significantly higher than the migration of the other monomers though the content level of styrene as a residual monomer is generally at a substantially higher level. This is probably due to the circumstance that styrene has the lowest water-solubility of the five monomers.

The identified data primarily originate from materials like PVC, ABS and PS. There are only few data available for rubber materials.

If a comparison with the migration limit value of 0.077 mg/l (corresponding to 77 µg/l) simulant at 3 hours of exposure is made, which ANEC suggests for styrene, it is seen that the vast majority of the identified values is below this value but there are also values which are higher. However, in these cases, it is often a migration for several days, at high temperature and/or to fatty foods – i.e. under migration conditions which are not relevant for toys.

5.4 Summary and discussion regarding content and migration

Generally, the following can be concluded from the described surveys – however, it must be emphasised that they are complicated mechanisms where many different parameters have an influence on the migration:

- Migration of monomer is increased by increased temperature of the migration liquid
- Migration of monomer (styrene in PS, vinyl chloride in PVC) is increased via a combination of acid liquid (pH 5) and increased temperature
- Migration of monomer is increased by increased exposure time
- Migration of monomer (styrene in PS) is increased via migration to fatty media rather than aqueous media
- Migration of monomer (vinyl chloride in PVC) is increased via a high intensity of UV light (however, not UV light which simulates sunlight)

Generally, it can also be concluded from the identified examinations that the levels for the content of the three monomers vinyl chloride, butadiene and acrylonitrile are in general low and are at ppm level (< 1 ppm to 50 ppm) whereas the residual monomer content of styrene is in general substantially higher – in average of approximately 500 to 1000 ppm. On the other hand, the migration of styrene is not substantially higher than the migration of the other monomers which most probably is due to the low water solubility of styrene. The levels for migration of the monomers are generally at approximately a couple of µg/l. A few significantly higher migration values have been measured but this is often due to exposure conditions which are not relevant for toys, for instance high temperatures (100 °C) and/or 10 successive days of exposure.

As described above, the general picture is that all monomers based on the physical/chemical data are soluble in ethanol. For some of the five monomers (especially for styrene and butadiene where the solubility to ethanol is higher than to water), it seems that the migration to fatty foods/media might be higher than to aqueous media. Today, ethanol is used as a simulant for fatty foods in the food contact material legislation. However, no data are identified which can illustrate whether this is applicable for all the five monomers.

Table 13. Overview of the amount of data for content and migration respectively for the five monomers

Monomer	**Content**	**Migration**
Vinyl chloride	**Few data** New data is missing	**Some data but primarily under other conditions than relevant for toys**
Butadiene	**Some data** (ABS) Few data (SBS) No data (MMBS)	**Few data** (ABS) Few data (SBS) No data (MMBS)
Acrylonitrile	**Some data** (ABS) Few data (NBR)	**Few data** (ABS) No data (NBR)
Styrene	**Many data** (ABS, PS) **Few data** (SEBS, SBS/SBR) No data (MMBS)	**Many data** (ABS, PS) **Few data** (SEBS, SBS/SBR) No data (MMBS)
Acrylamide	No data (challenges with regard to analyses)	Few data (PAM)

Suggestions of where to perform chemical analyses in this project are marked in bold. Here it has been taken into consideration which materials that are primarily used together with existing knowledge on content and migration.

In Table 13, there is a short summary of how many data which are identified on content and migration respectively for the five monomers. From the table, it is seen that there are areas with missing or few data and here it will be relevant to focus the chemical analyses which are carried out in this project. For instance, this concerns primarily the areas marked with bold in the table. With this marking, it has also been considered that the materials which are primarily used in toys according to the survey are PVC and ABS as well as to a lesser extent PS and rubber materials such as SEBS. Even if there are relatively many data for both content and migration of styrene it will still be relevant to confirm whether the relatively few available data for toys are representative.

A part of the surveys concludes that migration to fatty liquids increases the migration compared to migration to pure aqueous media. This is specifically described for styrene. For this reason, it could be imagined that the below situations will be relevant to examine in detail in the project because the migration here might possibly be higher than to pure aqueous media, such as sweat and saliva. It could for instance be:

- Migration to water added baby oil/bath oil to simulate a worst-case scenario where baby toys are in the bath tub with oil added to the water.
- Migration to water added sunscreen lotion to simulate a worst-case scenario where for instance a swim ring is used in the sun by a child smeared in sunscreen lotion. In addition, the temperature might be high which according to the identified surveys also will increase the migration in general.

Other conditions which might be interesting to examine in detail (based on the identified data on migration) are migration to artificial sweat compared with artificial saliva as the pH value is lower in artificial sweat (pH = 5.5) compared to artificial saliva (pH = 6.8) (Tønning et al., 2009). From the identified results, this might indicate that it will be the migration to artificial sweat which will be the highest as some surveys indicate a higher migration at a low pH (pH = 5).

6. Selection of products for analysis

This chapter includes a description of which toys products (or plastic materials for toys) that are selected for the first chemical analyses carried out – the analysis of the content of residual monomers. In chapter 8 ”Migration analyses”, it is described which toy products that secondly are selected for analysis of migration of residual monomers.

6.1 Description of methods

In this project, the biggest challenge of purchase and selection of products for chemical analyses has been to identify of which plastic material(s) the toy products consist as generally the plastic material is not evident from the actual products (packaging or possible enclosed package insert). The chemical analyses which are carried out in this project to determine both content of and migration of residual monomers from the plastic material are different dependent on the monomer and thus which material the toy product consists of. Therefore, in advance, it was necessary to know of which material the selected toy products consisted to be able to target the chemical analyses. Thus, in the project, two methods were used for purchase and selection of products for the chemical analyses:

1. Contact to toy producers via among others the European sector association (TIE). Toy products were received directly from the producers with specification of the type of material.
2. Purchase of specific types of toys (based on information from the survey) and additional examination/confirmation of the type of material via FTIR screening analyses.

6.1.1 Products sent from producers

Based on the results of the survey and through contact to both the Danish sector association for toys (LEG) and the European sector association for toys (TIE), an invitation was sent to both the Danish and European toy producers/importers to send toys to the project (with specification of the materials in the toys). A description of the project was sent as well as of the materials in focus in the project (materials with the selected monomers as well as materials which the survey had shown were relevant for toys).

In total, toy products from 10 different European producers/importers of toys were received. The toy producers sent between two and six different pieces of toys where the material type was specified. However, toys from one of the producers did not arrive until after the selection was made and therefore, these products have not been in the pool of toy products for the selection.

The producers/importers of toys have selected themselves which toys they preferred to send to the project, but they have not had any influence on which of the sent toy products that were selected for analysis. Thus, not all of the sent toy products have been analysed but only selected products – and these have been supplemented with own purchase of products in shops in Denmark or in internet shops. In total, 30 different toy products were selected for content analysis of residual monomers of which 19 products came from toy producers and the remaining 11 products were purchased in shops in Denmark or via the internet.

6.1.2 Products purchased in shops in Denmark or via the internet

The amount of toy products from toy producers/importers, was supplemented with purchase of toy products in shops in Denmark as well as purchase via internet shops – both Danish and foreign. In co-operation with the Danish EPA and the remaining working group of the project, it was initially decided that cheaper toys from China were to be ordered, for instance via Wish.com or via cheap shops in Denmark.

However, the common issue for the purchased products via the internet or in Danish shops was that the material was unknown. Identification of the material was therefore made by FTIR screening analyses before it was decided whether the toy was to be selected for analysis for content of residual monomers or not.

Out of the in total 30 different toy products which were analysed for content of residual monomer, 11 products were purchased in Denmark or via the internet, of which 4 products were ordered directly from China through webshops.

6.2 Monomers and materials in focus

It was decided to focus on the four of the five selected monomers (for which it was possible to analyse) and which according to the survey seem to be present in materials in toys, i.e.:

- Vinyl chloride (in PVC)
- 1,3-butadiene (in for instance ABS, SBC)
- Acrylonitrile (in for instance ABS)
- Styrene (in for instance ABS, PS, SEBS)

The number of analyses of toys containing the different monomers were distributed on the basis of which materials that most often seem to be present in toys. Therefore, it was decided to carry out chemical analyses for content of residual monomers in the following toy products:

- 10 products of ABS (analysed for content of acrylonitrile, butadiene and styrene)
- 11 products of PVC (analysed for content of vinyl chloride)
- 5 products of PS (analysed for content of styrene)
- 2 products of SEBS (analysed for content of styrene)
- 2 products of SBC (analysed for content of butadiene and styrene)

In total, 30 different materials were analysed (of these, one toy product consisted of two different materials). The 29 different toy products come from minimum 18 different producers/importers of toys. It is a minimum number as the toy ordered directly from China does not necessarily state the actual producer and this webshop is counted as one importer.

6.3 Types of toy products in focus

As described in the introduction, focus in this project has been on toys of plastic and/or rubber materials for children at the age of 0-3 years as well as toys to be placed in the mouth. However, toys for older children are to some extent also included in the project – primarily in the cases where products of a specific material were missing. For instance, it was not easy to identify toys for the age group of 0-3 years containing PS. Therefore, toys for older children were included here.

The focus has been on the following types of toy products:

- Swim rings, beach balls and other inflatable bath toys of PVC
- Non-inflatable bath toys of PVC
- Dolls of PVC
- Activity toys of ABS
- Rattles or teething rings of ABS

- Other baby toys of ABS
- Musical instruments of PS (intended to be placed in the mouth)
- Rattles or teething rings with SEBS rubber
- Wheels for vehicles of SEBS rubber

6.4 Complete overview of the selected products for analysis

The complete overview of the toy products which were selected for content analysis of residual monomers is shown in Table 14 below. The explanation of the table is as follows:

- ”Product no.” is the name which is used in this project. The product name is an anonymous name stating which material the product is made of. The naming is the material abbreviation with a continuous number.
- ”Purchased in” is here indicated as China, Europe or Denmark and indicates solely whether the product is purchased directly from China (via a webshop), whether the product comes from an European producer/importer, or whether it is purchased in a Danish shop. Still, the product can be produced in China even if it comes from a European producer/importer.
- ”Produced in” indicates in which country the product is produced. China or Europe are also primarily used here. A “?” indicates that it is not written on the product or it is unknown in which country the toy is produced.
- ”Received from” indicates whether the product is sent from a toy producer/importer (indicated as ”the producer”) or whether the project team has made the purchase in the project (indicated as “purchased”).
- ”Intended for” indicates to which age the toy is intended for. It is stated in parenthesis (mouth) if the toy is intended to be placed in the mouth, for instance a rattle or a musical instrument. It is the specification of the producer which is described.
- ”Type of toy” is an overall description of the type of toy in question.

Table 14. Overview of toy products selected for analysis. Furthermore, the table describes in which continent the toy is purchased and where the toy is produced. There are both toys purchased for analysis as well as toys received directly from producers. The toys are primarily intended for children at the age below 3 years.

Product no.	Purchased in	Produced in	Received from	Intended for	Type of toy
ABS1	Europe	Europe	The producer	> 1½ years	Activity toy
ABS2	Europe	Europe	The producer	> 1½ years	Activity toy
ABS3	China	China	Purchased	0-3 years	Activity toy
ABS4	Europe	China	The producer	> 0 year	Bath toy
ABS5	Europe	China	The producer	> 1½ years	Activity toy
ABS6	Denmark	China	Purchased	> 18 months	Activity toy
ABS7	Denmark	China	Purchased	All (mouth)	Musical instrument
ABS8	Denmark	China	Purchased	All (mouth)	Musical instrument
ABS9	Europe	China	The producer	> 18 months	Activity toy
ABS10	Europe	China	The producer	0-2 years	Teething ring/ rattle
PVC1	China	China	Purchased	0-3 years	Doll
PVC2	Europe	China	The producer	> 6 months	Bath toy
PVC3	Europe	China	The producer	> 2 years	Doll
PVC4	Europe	China	The producer	> 1 year	Bath toy

Product no.	Purchased in	Produced in	Received from	Intended for	Type of toy
PVC5	Denmark	China	Purchased	> 18 months	Bath toy, activity toy
PVC6	Denmark	?	Purchased	> 6 months	Bath toy
PVC7	Europe	Vietnam	The producer	> 0 year	Bath toy
PVC8	Europe	China	The producer	> 18 months	Doll
PVC9	China	China	Purchased	0-3 years	Doll
PVC10	Europe	China	The producer	0-2 years	Inflatable bath toy
PVC11	China	China	Purchased	0-3 years	Inflatable bath toy
PS1	Europe	Europe	Purchased	> 3 years (mouth)	Musical instrument
PS2	Europe	Europe	The producer	> 3 years	Activity toy
PS3	Europe	China	The producer	> 3 years	Activity toy
PS4	Europe	China	The producer	> 18 months	Doll
PS5	Europe	Europe	The producer	1½ -3 years	Activity toy
SEBS1	Europe	?	The producer	> 1½ years	Activity toy
SEBS2	Europe	Europe	The producer	> 18 months	Vehicle
SBC1	Europe	China	The producer	> 6 months	Teething ring/ rattle
SBC2	Denmark	?	Purchased	> 3 years (mouth)	Musical instrument

7. Content analyses

Results of content analyses of residual monomers in selected toy materials

This chapter describes analysis method and results of the content analyses of residual monomers in selected toys carried out in this project. The analyses are carried out by Eurofins Product Testing A/S, Denmark.

7.1 Analysis method for the content analyses

The five monomers are analysed quantitatively with an analysis for each monomer. The below standard methods for food contact materials have been applied dependent on the type of residual monomer. It was not possible to offer a quantitative content analysis for the residual monomer acrylamide in solid materials:

- For butadiene: DS/EN 13130-4 (2004) – ”Determination of 1,3-butadiene in plastics”
- For vinyl chloride: DS/EN 13130-6 (2004) – ”Determination of vinylidene chloride in plastics”
- For styrene and acrylonitrile: DS/EN 13130-22 (2005) – ”Determination of ethylene oxide and propylene oxide in plastics”

For the four selected monomers, the analyses were in all cases performed by headspace (HS) and gaschromatografy (GC) with mass selective (MS) detection (HS-GC-MS) but the solvent varied.

The content of residual monomer in the selected toy samples was determined by adding solvent to a known partial sample. The analysis was performed by HS-GC-MS. Standards of all substances, control solutions as well as spike for control of retrieval were made.

The analyses were performed as true duplicate determination. The detection limit is: 0.1 mg/kg for acrylonitrile, butadiene and vinyl chloride but 0.2 mg/kg for styrene. The expanded measurement uncertainty is 20 %.

7.2 Results of the content analyses

The results of the content analyses are listed in the tables below (Table 15 to Table 19). A table is available for each type of examined material. The average result of the two duplicate determinations is stated and with the analysis results from the duplicate determinations in brackets. The below 30 toy products have been analysed for content of the below monomers:

- 10 products of ABS for content of acrylonitrile, butadiene and styrene respectively (see Table 15)
- 11 products of PVC for content of vinyl chloride (see Table 16)
- 5 products of PS for content of styrene (see Table 17)
- 2 products of SEBS for content of styrene (see Table 18)
- 2 products of SBC for content of butadiene and styrene (see Table 19)

Table 15. Content of the residual monomers acrylonitrile, butadiene and styrene in 10 toy products of ABS. The average result of the two duplicate determinations is stated and with the analysis results from the duplicate determinations in brackets.

Product no.	Content of acrylonitrile (mg/kg)	Content of butadiene (mg/kg)	Content of styrene (mg/kg)
ABS1	11 (11; 11)	0.67 (0.7; 0.63)	595 (620; 570)
ABS2	10.5 (11; 10)	0.68 (0.68; 0.67)	600 (600; 600)
ABS3	33 (32; 34)	0.48 (0.49; 0.46)	1300 (1300; 1300)
ABS4	33 (33; 33)	0.35 (0.36; 0.34)	1350 (1300; 1400)
ABS5	8.2 (7.8; 8.5)	0.25 (0.25; 0.24)	590 (570; 610)
ABS6	18 (17; 19)	0.25 (0.25; 0.25)	1150 (1100; 1200)
ABS7	53.5 (54; 53)	1.05 (1.1; 0.99)	645 (660; 630)
ABS8	17 (17; 17)	0.25 (0.26; 0.24)	670 (660; 680)
ABS9	18.5 (18; 19)	0.23 (0.26; 0.19)	850 (860; 840)
ABS10	64 (64; 64)	1.55 (1.6; 1.5)	670 (690; 650)

Table 16. Content of the residual monomer vinyl chloride in 11 toy products of PVC. The average result of the two duplicate determinations is stated and with the analysis results from the duplicate determinations in brackets.

Product no.	Content of vinyl chloride (mg/kg)	Product no.	Content of vinyl chloride (mg/kg)
PVC1	< 0.1 (<0.1; <0.1)	PVC7	< 0.1 (<0.1; <0.1)
PVC2	< 0.1 (<0.1; <0.1)	PVC8	< 0.1 (<0.1; <0.1)
PVC3	< 0.1 (<0.1; <0.1)	PVC9	< 0.1 (<0.1; <0.1)
PVC4	< 0.1 (<0.1; <0.1)	PVC10	< 0.1 (<0.1; <0.1)
PVC5	< 0.1 (<0.1; <0.1)	PVC11	< 0.1 (<0.1; <0.1)
PVC6	< 0.1 (<0.1; <0.1)		

Table 17. Content of the residual monomer styrene in 5 toy products of PS. The average result of the two duplicate determinations is stated and with the analysis results from the duplicate determinations in brackets.

Product no.	Content of styrene (mg/kg)	Product no.	Content of styrene (mg/kg)
PS1	355 (360; 350)	PS4	355 (360; 350)
PS2	325 (300; 350)	PS5	230 (230; 230)
PS3	490 (510; 470)		

Table 18. Content of the residual monomer styrene in 2 toy products of SEBS. The average result of the two duplicate determinations is stated and with the analysis results from the duplicate determinations in brackets.

Product no.	Content of styrene (mg/kg)
SEBS1	< 0.2 (<0.2; <0.2)
SEBS2	< 0.2 (<0.2; <0.2)

Table 19. Content of the residual monomers butadiene and styrene in 2 toy products of SBC. The average result of the two duplicate determinations is stated and with the analysis results from the duplicate determinations in brackets.

Product no.	Content of butadiene (mg/kg)	Content of styrene (mg/kg)
SBC1	< 0.1 (<0.1; <0.1)	< 0.2 (<0.2; <0.2)
SBC2	0.2 (0.29; <0.1)	8 (6; 9.9)

7.3 Discussion of the analysis results

In general, no content of the residual monomer vinyl chloride above the detection limit (0.1 mg/kg) in any of the 11 analysed toy products of PVC has been identified. These values correspond with the few values which are identified in the literature (see chapter 5.2 ”Existing data on content of residual monomers”) and the values which are reported by TIE (2018) and by ECVM (the European Council of Vinyl Manufactures) respectively where a residual monomer content of less than 0.1 mg/kg or less than 1 mg/kg respectively is stated. The content analyses which are identified in the literature are of an earlier date (year 2000) but were about 1 mg/kg. Thus, common for all products of PVC is that the content of the residual monomer vinyl chloride is below the limit value of 1 mg/kg which ANEC proposes as a content limit value for toys of PVC.

The content of styrene in the rubber material SEBS is below the detection limit of 0.2 mg/kg and the content of butadiene and styrene in the rubber material SBC is also below the detection limit (0.1 and 0.2 mg/kg respectively) or at low levels (0.2 mg/kg for butadiene and 8 mg/kg for styrene respectively). The content of butadiene in SBC is thus below the limit value of 1 mg/kg for butadiene which ANEC proposes as a content limit value for butadiene in toys. The measured values correspond to the few data which are identified in the literature where only one survey of content of the residual monomers butadiene and styrene in this type of rubber materials (Abe et al., 2013) is identified. In this survey, no butadiene above the detection limit of 0.1 mg/kg was identified and for styrene, the content was either below the detection limit of 0.2 mg/kg or maximum of 0.5 mg/kg.

For ABS, residual monomers are identified above the detection limit in all products. The monomer butadiene is identified at the lowest levels and is generally below 1 mg/kg (which is the content limit value proposed by ANEC) but with two products with a content above 1 mg/kg (with a content of 1.05 mg/kg and 1.55 mg/kg). On average, the content of butadiene is 0.57 mg/kg in the 10 examined products. This corresponds to results from the literature which states levels from 0.06 to 1.7 mg/kg – however, with a single survey of toys with a content of up to 5.3 mg/kg.

The monomer acrylonitrile in ABS is identified at levels from 8.2 to 64 mg/kg, with an average of 26.7 mg/kg in 10 products of ABS. In all cases, the content of the monomer acrylonitrile is thus above the content limit of 1 mg/kg as proposed by ANEC. The identified values correspond with the content values identified in the literature which are between < 0.01 and 55 mg/kg.

The content of the monomer styrene in ABS is identified at higher levels from 590 to 1350 mg/kg with an average of 842 mg/kg for the 10 products of ABS. The identified values correspond to the content values identified in the literature which are between 1.3 and 3570 mg/kg with average values between 69 and 1302 mg/kg.

The content of styrene in toy products of PS is generally lower than the content of styrene in ABS. The content of styrene in the toy products is between 230 and 490 mg/kg with an average of 351 mg/kg for the 5 examined products of PS. This also corresponds with data identified in the literature of maximum up to 1000 mg/kg.

8. Migration analyses

Results of migration of residual monomers from selected toy materials

This chapter describes which toy products (and which plastic/rubber materials) that were selected for analyses for migration of residual monomers from the toy in this project. The chapter describes and furthermore gives reason for the selected migration conditions. Two stages of migration analyses (stage 1 and stage 2) were carried out with the purpose to be able to adjust the need for other migration analyses based on the results of the first stage of migration analyses. All migration analyses are performed by Eurofins Product Testing A/S, Denmark.

8.1 Background for selection of migration analyses

As described in section 5.4 ”Summary and discussion regarding content and migration”, the following can be concluded in general regarding migration of monomer:

- Migration of monomer is increased by increased temperature of the migration liquid
- Migration of monomer is increased via a combination of acid liquid (pH 5) and increased temperature (this is observed for styrene in PS and vinyl chloride in PVC)
- Migration of monomer is increased by increased exposure time
- Migration of monomer is increased via migration to fatty media rather than aqueous media (this is observed for styrene in PS but will not necessarily be in evidence for acrylonitrile which is soluble in water)

In general, the products with the highest content of residual monomer have been selected for the migration analyses. Furthermore, worst-case temperature and exposure time have been used – however, considering that small children at the age of 0-3 years are in focus in this report. Correspondingly, migration to fatty media (rather than aqueous media) has been considered, because as earlier described there will be bath situations (bath water added bath oil or a child covered with sunscreen lotion) where a more fatty migration media will be realistic.

Finally, differences in migration to artificial sweat (pH = 5.5), artificial saliva (pH = 6.8) (Tønning et al., 2009) and water (pH = 7) are also relevant for a closer view as the result of the survey indicates a higher migration at low pH value (pH = 5).

For the above reasons, in co-operation with the Danish EPA, it was therefore decided that the following migration analyses were relevant to perform:

- Migration to 20 % ethanol at 40 °C for 30 minutes at stirring – to simulate toys used in bath water added oil
- Migration to pure oil at 40 °C for 2 hours at stirring – to simulate inflatable bath toys used in the sun and with sunscreen lotion
- Migration to artificial sweat at 37 °C for 8 hours at static migration – to simulate children holding their favourite toys for a large part of the day
- Migration to artificial saliva at 37 °C for 3 hours at stirring – to simulate a child placing the toy in the mouth (sucking on the toy without swallowing the toy material)
- Migration to water at 37 °C for 3 hours at static migration – to see if there is a difference between migration to water rather than artificial saliva/sweat

The 20 % ethanol and pure oil are selected with basis in the EU Regulation no. 10/2011 on plastic materials and articles intended for contact with foods. Here, in Annex III “Food simulants” it is described that the food simulant C (with 20 % ethanol) is selected for “foods which contain a relevant amount of organic ingredients that render the food more lipophilic“. In the situation with a baby who is bathed in water added baby oil, it will be a liquid with a certain amount of organic ingredients. However, the food simulant C (20 % ethanol) is regarded as being worst-case for migration to this kind of bath water.

Correspondingly, the migration liquid pure oil is chosen on the basis of EU Regulation no. 10, 2011 where pure oil (food simulator D2 – vegetable oil containing less than 1 % of unsaponifiable matter) is used as food simulator for foods with lipophilic properties which are able to extract lipophilic substances. According to Annex III (EU Regulation no. 10, 2011), food simulator D2 must be used for foods which contain free fats at the surface. However, it is also described in Table 2 in Annex III that for fresh meat the migration result has to be divided by 4 to give the correct migration. This food simulator (D2 – fresh meat with fatty contact to plastic) is used as worst-case to simulate a child body covered with sunscreen lotion which has contact with bath toys of plastic.

Migration for three hours to artificial saliva was chosen as three hours are stated as standard exposure time for children who place toys in their mouth during a day (EU Directive no. 898, 2017). At the same time, three hours are the exposure time which is suggested in connection with ANEC’s proposal for legislation for the five monomers (ANEC, 2018).

8.2 Selected products for migration analyses – stage 1

Based on section 8.1 and the results of the content analyses, the below migration analyses were at first carried out on the two products of ABS and PS with the highest identified content of residual monomers, i.e. ABS4, ABS10, PS1 and PS4. However, PS3 which had the highest content of styrene was deselected as it is a product for older children above 3 years.

The migration analyses for toys of PVC, SEBS and SBC were at first deselected as the content of residual monomers either was below the detection limit or very low (just above the detection limit). As no content of residual monomers above the detection limit was identified in any of the products of PVC, the migration to pure oil was not selected. This migration was supposed to simulate a child covered in sunscreen lotion who uses an inflatable bath toy of PVC, such as a swim ring. These migration conditions are not relevant for other toy products.

The following migration analyses are thus performed for ABS4, ABS10, PS1 and PS4 where migration of acrylonitrile, butadiene and styrene is quantified in the migration liquid for the two ABS products and styrene is quantified in the migration liquid for the two PS products:

- Migration to 20 % ethanol at 40 °C for 30 minutes at stirring – to simulate toys used in bath water added oil
- Migration to artificial sweat at 37 °C for 8 hours at static migration – to simulate children holding their favourite toys for a large part of the day
- Migration to artificial saliva at 37 °C for 3 hours at stirring – to simulate a child placing the toy in the mouth (sucking on the toy without swallowing the toy material)
- Migration to water at 37 °C for 3 hours at static migration – to see if there is a difference between migration to water rather than artificial saliva/sweat

It must be noted that it was a deliberate choice for all the migration analyses that the toy material was immersed entirely into the migration liquid. Thus, the toy material has not been cut open or cut more than absolutely necessary to be able to carry out the migration analyses in practice.

8.3 Analysis method for the migration analyses – stage 1

The migration of residual monomers from the relevant plastic and rubber materials was determined by placing a known amount of material in the migration liquid for a certain time at a given temperature. For the first stage of migration analyses, the migration liquid was artificial sweat, artificial saliva, 20 % ethanol as well as demineralised water.

The migration liquid was analysed for the monomers vinyl chloride, 1,3-butadien, acrylonitrile as well as styrene in the following way: A known amount is added solvent and the analysis is carried out by HS-GC-MS. Standards of all substances, control solutions as well as spike for control of retrieval were made. The analysis was performed as true duplicate determination. The same standard methods were used for the content determination of the migration liquid as described in section 7.1 ”Analysis method for the content analyses”. The detection limit was 0.01 mg/l but 0.02 mg/l for styrene. The expanded measurement uncertainty was 20 %.

8.4 Results of the migration analyses – stage 1

The results of stage 1 of the migration analyses are listed in the tables below (Table 20 to Table 23). A table is listed for each piece of toy. The average result of the duplicate determination is stated. The 4 toy products (ABS4, ABS10, PS1 and PS4) have been analysed for migration under the stated conditions in section 8.2 ”Selected products for migration analyses – stage 1”.

The overall result is that no migration of either acrylonitrile, butadiene and/or styrene above the detection limit is identified. The stated values are thus the detection limit of the analyses. The detection limit of the migration in mg/l in the first column is the amount of monomer which in fact can be detected in the migration liquid. As different amounts (g) and surface area (cm^2) of the toy material have been used dependent of which migration analysis that has been made, the converted values therefore vary in the last two columns where a migration corresponding to the detection limit is converted to per kg of toy material and per cm^2 of surface area of the toy material respectively.

Table 20. Migration of the residual monomers acrylonitrile, butadiene and styrene from ABS4. The average result of the duplicate determination is stated.

Monomer	Migration conditions	Sample material used	Migration* (mg/l)	Migration* (mg/kg)	Migration* (µg/cm^2)
Acrylonitrile	20 % ethanol	100 ml simulant	< 0.01	< 0.12	< 0.008
Butadiene	30 minutes at 40°C	1.33 dm^2	< 0.01	< 0.12	< 0.008
Styrene	Stirring**	8.56 g	< 0.02	< 0.22	< 0.02
Acrylonitrile	Artificial saliva	100 ml simulant	< 0.01	< 0.17	< 0.02
Butadiene	3 hours at 37°C	0.73 dm^2	< 0.01	< 0.17	< 0.02
Styrene	Stirring**	4.70 g	< 0.02	< 0.34	< 0.03
Acrylonitrile	Artificial sweat	100 ml simulant	< 0.01	< 0.46	< 0.03
Butadiene	8 hours at 37°C	0.34 dm^2	< 0.01	< 0.46	< 0.03
Styrene	Static	2.19 g	< 0.02	< 0.91	< 0.06
Acrylonitrile	Demineralised water	100 ml simulant	< 0.01	< 0.22	< 0.02
Butadiene	3 hours at 37°C	0.93 dm^2	< 0.01	< 0.22	< 0.02
Styrene	Static	6.00 g	< 0.02	< 0.43	< 0.03

* The migration in the first column is stated in mg of monomer per litre of migration liquid, in second column in mg of monomer per kg of toy material and in third column converted to mg of monomer per cm^2 of toy material.** A magnetic stirrer has been used (500 rpm).

Table 21. Migration of the residual monomers acrylonitrile, butadiene and styrene from ABS10. The average result of the duplicate determination is stated.

Monomer	**Migration conditions**	**Sample material used**	**Migration*** (mg/l)	**Migration*** (mg/kg)	**Migration*** (µg/cm^2)
Acrylonitrile	20 % ethanol	100 ml simulant	< 0.01	< 0.07	< 0.007
Butadiene	30 minutes at 40°C	1.47 dm^2	< 0.01	< 0.07	< 0.007
Styrene	Stirring**	14.1 g	< 0.02	< 0.14	< 0.014
Acrylonitrile	Artificial saliva	100 ml simulant	< 0.01	< 0.07	< 0.007
Butadiene	3 hours at 37°C	1.47 dm^2	< 0.01	< 0.07	< 0.007
Styrene	Stirring**	14.1 g	< 0.02	< 0.14	< 0.014
Acrylonitrile	Artificial sweat	100 ml simulant	< 0.01	< 0.11	< 0.011
Butadiene	8 hours at 37°C	0.97 dm^2	< 0.01	< 0.11	< 0.011
Styrene	Static	9.34 g	< 0.02	< 0.21	< 0.021
Acrylonitrile	Demineralised water	100 ml simulant	< 0.01	< 0.11	< 0.011
Butadiene	3 hours at 37°C	0.97 dm^2	< 0.01	< 0.11	< 0.011
Styrene	Static	9.34 g	< 0.02	< 0.21	< 0.021

* The migration in the first column is stated in mg of monomer per litre of migration liquid, in second column in mg of monomer per kg of toy material and in third column converted to mg of monomer per cm2 of toy material.** A magnetic stirrer has been used (500 rpm).

Table 22. Migration of the residual monomer styrene from PS1. The average result of the duplicate determination is stated.

Monomer	**Migration conditions**	**Sample material used**	**Migration*** (mg/l)	**Migration*** (mg/kg)	**Migration*** (µg/cm^2)
Styrene	20 % ethanol 30 minutes at 40°C Stirring**	100 ml simulant 1.42 dm^2 8.40 g	< 0.02	< 0.24	< 0.02
Styrene	Artificial saliva 3 hours at 37°C Stirring**	100 ml simulant 0.90 dm^2 5.32 g	< 0.02	< 0.38	< 0.03
Styrene	Artificial sweat 8 hours at 37°C Static	100 ml simulant 0.90 dm^2 5.32 g	< 0.02	< 0.38	< 0.03
Styrene	Demineralised water 3 hours at 37°C Static	100 ml simulant 0.90 dm^2 5.32 g	< 0.02	< 0.38	< 0.03

* The migration in the first column is stated in mg of monomer per litre of migration liquid, in second column in mg of monomer per kg of toy material and in third column converted to mg of monomer per cm^2 of toy material. ** A magnetic stirrer has been used (500 rpm).

Table 23. Migration of the residual monomer styrene from PS4. The average result of the duplicate determination is stated.

Monomer	Migration conditions	Sample material used	Migration* (mg/l)	Migration* (mg/kg)	Migration* (µg/cm^2)
Styrene	20 % ethanol 30 minutes at 40°C Stirring**	100 ml simulant 0.97 dm^2 10.27 g	< 0.02	< 0.19	< 0.02
Styrene	Artificial saliva 3 hours at 37°C Stirring**	100 ml simulant 0.46 dm^2 4.87 g	< 0.02	< 0.41	< 0.05
Styrene	Artificial sweat 8 hours at 37°C Static	100 ml simulant 0.20 dm^2 2.12 g	< 0.02	< 0.94	< 0.1
Styrene	Demineralised water 3 hours at 37°C Static	100 ml simulant 0.97 dm^2 10.27 g	< 0.02	< 0.19	< 0.02

* The migration in the first column is stated in mg of monomer per litre of migration liquid, in second column in mg of monomer per kg of toy material and in third column converted to mg of monomer per cm^2 of toy material. ** A magnetic stirrer has been used (500 rpm).

8.4.1 Discussion of the results – stage 1

No migration above the detection limit of any of the examined monomers (acrylonitrile, butadiene and styrene) has been identified from either ABS or PS in any of the examined toy materials. The detection limit for the migration analyses was 0.01 mg/l of migration liquid (corresponding to 10 µg/l) for acrylonitrile and butadiene and 0.02 µg/l of migration liquid (corresponding to 20 µg/l) for styrene.

These migration limits correspond with migration limits identified in the literature (see Table 12) even if lower detection limits are also identified in the literature:

- Detection limit for acrylonitrile in ABS: Between 3 and 25 µg/l
- Detection limit for butadiene in ABS: 10 µg/l
- Detection limit for styrene in ABS: Between 1 and 10 µg/l
- Detection limit for styrene in PS: 1 µg/kg and lower levels are measured

8.5 Selected products for migration analyses – stage 2

As the results from the migration analyses from stage 1 did not show any migration above the detection limit for any of the analysed monomers in any of the analysed toy materials it was decided to perform a migration analysis to stomach acid as described in EN 71-3 for the same toy materials (i.e. ABS4, ABS10, PS1 and PS4). The purpose of this was to assess whether an oral intake of toy material actually could result in a release of residual monomer from the toy material in the stomach.

The performed migration analysis is in practice a standard migration analysis to acidic liquid (hydrochloric, HCl) which is described in EN 71-3 for metals. It is carried out at the following conditions:

- Migration to acidic liquid (HCl) adjusted to pH between 1.0 and 1.5 at 37 °C for 2 hours – to simulate toy which is swallowed and ends in the stomach

8.6 Analysis method for the migration analyses – stage 2

The migration of residual monomer from the relevant plastic and rubber materials was determined by placing a known amount of material in migration liquid for a given period, at a given temperature. For the second session of migration analyses, the migration liquid was acidic liquid (stomach acid) performed according to EN 71-3 (June 2018) where the migration liquid is 0.07 mole of hydrochloric acid (HCl).

The migration liquid was analysed for the monomers vinyl chloride, 1,3-butadiene, acrylonitrile as well as styrene in the following way: A known amount is added solvent and the analysis is performed by HS-GC-MS. Standards of all substances, control solutions as well as spike for control of retrieval were made. The analysis was performed as true duplicate determination. The same standard methods were used for the content determination in the migration liquid as described in section 7.1 ”Analysis method for the content analyses”.

The detection limit was 0.01 mg/l but 0.02 mg/l for styrene. The expanded measurement uncertainty was 20 %.

8.7 Results of the migration analyses – stage 2

The result of stage 2 for the migration analyses, i.e. the results of migration to stomach acid as described in EN 71-3 are stated in the tables below (Table 24 to Table 25). A table is listed for each piece of toy (ABS4, ABS10, PS1 and PS4). The average result of the duplicate determination is stated. The overall result for the 4 toy products is that no migration of either acrylonitrile, butadiene and/or styrene above the detection limit is identified. The stated values are thus the detection limit for the migration analyses.

Table 24. Migration of the residual monomers acrylonitrile, butadiene and styrene from ABS4 and ABS10. The average result of the duplicate determination is stated.

Monomer	Migration conditions	Sample material used	Migration* (mg/l)	Migration* (mg/kg)	Migration* (µg/cm^2)
ABS4:					
Acrylonitrile	According EN 71-3:	20 ml simulant	< 0.01	< 2.0	< 0.15
Butadiene	Migration to	0.0141 dm^2	< 0.01	< 2.0	< 0.15
Styrene	0.07 mol/L HCl	0.102 g	< 0.02	< 3.9	< 0.29
ABS10:					
Acrylonitrile	According EN 71-3:	20 ml simulant	< 0.01	< 1.8	< 0.15
Butadiene	Migration to	0.0137 dm^2	< 0.01	< 1.8	< 0.15
Styrene	0.07 mol/L HCl	0.115 g	< 0.02	< 3.6	< 0.30

* The migration in the first column is stated in mg of monomer per litre of migration liquid, in second column in mg of monomer per kg of toy material and in third column converted to mg of monomer per cm^2 of toy material.

Table 25. Migration of the residual monomer styrene from PS1 and PS4. The average result of the duplicate determination is stated.

Monomer	Migration conditions	Sample material used	Migration* (mg/l)	Migration* (mg/kg)	Migration* (µg/cm^2)
PS1: Styrene	According EN 71-3: Migration to 0.07 mol/L HCl	20 ml simulant 0.0158 dm^2 0.117 g	< 0.02	< 3.4	< 0.25
PS4: Styrene	According EN 71-3: Migration to 0.07 mol/L HCl	20 ml simulant 0.0134dm^2 0.111 g	< 0.02	< 3.6	< 0.30

* The migration in the first column is stated in mg of monomer per litre of migration liquid, in second column in mg of monomer per kg of toy material and in third column converted to mg of monomer per cm^2 of toy material.

8.7.1 Discussion of the results – stage 2

No migration of residual monomer to stomach acid above the detection limit of any of the examined monomers (acrylonitrile, butadiene and styrene) from either ABS or PS in any of the examined toy materials was identified. The detection limit of the migration analyses was 0.01 mg/l of migration liquid (corresponding to 10 µg/l) for acrylonitrile and butadiene and 0.02 mg/l of migration liquid (corresponding to 20 µg/l) for styrene. No other results of migration of residual monomer from toy materials to stomach acid were identified in this survey.

8.8 Discussion of the migration analyses

No migration of residual monomer was identified to either artificial sweat, 20 % ethanol, artificial saliva, demineralised water or stomach acid at any of the examined monomers (acrylonitrile, butadiene and styrene) from either ABS or PS in any of the in total four examined toy materials. The detection limit of the completed migration analyses was 0.01 mg/l of migration liquid (corresponding to 10 µg/l) for acrylonitrile and butadiene and 0.02 mg/l of migration liquid (corresponding to 20 µg/l) for styrene.

By comparison, in their proposal for legislation of monomers in toy materials ANEC has suggested a migration limit value of 0.077 mg/l simulant for styrene at 3 hours extraction of toys or a third of this value if the extraction procedure as described in EN 71-10 is used (where extraction for 1 hour is used). In EN 71-10 it is stated that 10 cm^2 of surface area of toy material has to be used for 100 ml simulant. At the migration analyses in this project, migration to simulant for minimum 3 hours is performed (with the exception of the migration to 20 % ethanol) and up to 8 hours for migration to artificial sweat. The proportion between surface area of the toy material and volume of simulant was different dependent on the shape of the toy material but at best it was up to 147 cm^2 per 100 ml simulant. The four examined toy materials in this project (ABS4, ABS10, PS1 and PS4) will thus comply with the suggested limit value for migration of styrene.

9. Analyses of recycled plastic

Results of analyses for content and migration of residual monomers from selected recycled materials

As far as it is known, toys are today solely produced of new virgin plastic material. With the increased demands for recycling of plastic materials which are discussed under the auspices of both Denmark and the EU, it might be a possibility that production of toys in recycled plastic could be a possibility in the future. Therefore, it was decided to perform the corresponding content and migration analyses of recycled plastic of ABS and PS.

Various companies (producers of recycled plastic) were contacted and recycled material of both ABS and PS was provided from two different Danish companies. Both companies stated that the recycled plastic originates from industrial waste from various companies. This was the type of recycled plastic which it was possible to provide in these two materials. The recycled plastic of ABS originated most probably from production of toy products, but it was not possible to get a clear identification of the received recycled material. The recycled plastic of PS originated from food contact material.

Both granulate, i.e. recycled plastic in the form of pellets, and recycled plastic in the form of sample plates, where pellets have been moulded to plastic plates, were received. Thus, the sample plates have in fact been through all the manufacturing processes which toys produced of recycled plastic also are: shredding, washing, heating/pelletising as well as heating/moulding whereas the granulate in the form of pellets has not been exposed to the last finishing process (heating and moulding).

It must be noticed that content and migration analyses for the relevant residual monomers are only performed on one single recycled material of ABS and one single recycled material of PS. It is essential to be aware of the fact that large variations in content (and migration) of the relevant residual monomers can be expected dependent on from where the plastic material originates. As the sources for recycled plastic not necessarily remain the same, variations in recycled material from the same source can be expected with time. Thus, these analyses solely give a small snapshot of content and migration of residual monomer from the specific recycled materials.

The recycled materials which are analysed in this project are named as follows:
- ABS-G1, which is recycled material no. 1 consisting of ABS
- ABS-G1-Pr, which is sample plates moulded from the recycled material no. 1 (ABS)
- PS-G1, which is recycled material no. 1 consisting of PS
- PS-G1-Pr, which is sample plates moulded from the recycled material no. 1 (PS)

The following analyses of the recycled materials are performed, corresponding to (some of) the analyses which are carried out on the toy materials:
1. Content analysis of residual monomer – on pellets of recycled plastic (i.e. on ABS-G1 and PS-G1)
2. Migration to stomach acid – on pellets (i.e. on ABS-G1 and PS-G1)
3. Migration to 20 % ethanol (for 30 minutes at 40 °C) – on sample plates (i.e. on ABS-G1-Pr and PS-G1-Pr)

9.1 Analyses for content of residual monomer

The analyses for content of residual monomers in the recycled plastic were analysed by the same method as the content analyses of the toy described in section 7.1 ”Analysis method for the content analyses”.

9.1.1 Results of the content analyses for recycled plastic

The results of the content analyses of the recycled plastic are stated in the tables below (Table 26 to Table 27). A table for each type of examined material is listed. The average result of the two duplicate determinations is stated.

Table 26. Content of the residual monomers acrylonitrile, butadiene and styrene in one material of recycled ABS. The average result of the two duplicate determinations is stated.

Product no.	Content acrylonitrile (mg/kg)	Content butadiene (mg/kg)	Content styrene (mg/kg)
ABS-G1	10	2.1	330

Table 27. Content of the residual monomer styrene in one material of recycled PS. The average result of the two duplicate determinations is stated.

Product no.	Content styrene (mg/kg)
PS-G1	270

9.2 Analyses for migration of residual monomer

The analyses for migration of residual monomers from the recycled plastic were analysed by the same method as the migration analyses for the toys described in section 8.6 ”Analysis method for the migration analyses – stage 2”.

9.2.1 Results of migration analyses for recycled plastic

The results of the content analyses of the recycled plastic are stated in the tables below (Table 28 to Table 29). A table for each type of examined material is listed. The average result of the two duplicate determinations is stated. It must be noted that migration to stomach acid was performed on the granulate (ABS-G1 and PS-G1) while migration to 20 % ethanol was performed on sample plates (ABS-G1-Pr and PS-G1-Pr). No migration above the detection limit was identified at any of the analyses. It is therefore the detection limit (0.01 and 0.02 mg/l respectively) which is stated in the tables below. In the last two columns, the converted values are stated where a migration corresponding to the detection limit is converted to per kg of toy material and per cm^2 of surface area of the toy material respectively.

Table 28. Migration of the residual monomers acrylonitrile, butadiene and styrene from one material of recycled ABS. The average result of the two duplicate determinations is stated.

Product no.	**Monomer**	**Migration conditions**	**Sample material used**	**Migration*** (mg/l)	**Migration*** (mg/kg)	**Migration*** (µg/cm^2)
ABS-G1	Acrylonitrile	Acc. to EN 71-3:	20 ml simulant	< 0.01	< 1.8	-
	Butadiene	Migration to	0.111 g	< 0.01	< 1.8	-
	Styrene	0.07 mol/L HCl		< 0.02	< 3.6	-
ABS-G1-Pr	Acrylonitrile	20 % ethanol	50 ml simulant	< 0.01	< 0.042	< 0.005
	Butadiene	30 minutes at 40°C	0.93 dm^2	< 0.01	< 0.042	< 0.005
	Styrene	Stirring	11.9 g	< 0.02	< 0.084	< 0.010

* The migration in the first column is stated in mg of monomer per litre of migration liquid, in second column in mg of monomer per kg of toy material and in third column converted to mg of monomer per cm^2 of toy material.

Table 29. Migration of the residual monomer styrene from one material of recycled PS. The average result of the two duplicate determinations is stated.

Product no.	**Monomer**	**Migration conditions**	**Sample material used**	**Migration*** (mg/l)	**Migration*** (mg/kg)	**Migration*** (µg/cm^2)
PS-G1	Styrene	Acc. to EN 71-3: Migration to 0.07 mol/L HCl	20 ml simulant 0.102 g	< 0.02	< 3.9	-
PS-G1-Pr	Styrene	20 % ethanol 30 minutes at 40°C Stirring	50 ml simulant 1.11 dm^2 6.78 g	< 0.02	< 0.15	< 0.009

* The migration in the first column is stated in mg of monomer per litre of migration liquid, in second column in mg of monomer per kg of toy material and in third column converted to mg of monomer per cm^2 of toy material.

9.3 Discussion of analysis results

Large variations in content (and migration) of the relevant residual monomers in recycled material are expected dependent on from where it originates. The sources for the recycled material are not necessarily the same all the time and thus variations in content (and migration) of residual monomers can be expected over time.

The examined recycled materials (in the form of industrial waste) in ABS and PS do not seem to be different than the examined virgin ABS and PS material in toys with regard to content and migration of the relevant monomers. See Table 30 below, where the content analyses of residual monomer from the 10 examined toy materials of ABS and the 5 examined toy material of PS are compared with the recycled material of ABS and PS respectively.

Table 30. Content of the residual monomers acrylonitrile, butadiene and styrene in toy materials of ABS (10 samples) and PS (5 samples) examined in this project (average, lowest and highest concentration) compared with recycled plastic material of ABS and PS.

Product no.	**Content acrylonitrile (mg/kg)**	**Content butadiene (mg/kg)**	**Content styrene (mg/kg)**
ABS			
Average	27	0.6	842
Minimum	8	0.23	590
Maximum	64	1.55	1350
ABS-G1	10	2.1	330
PS			
Average	-	-	351
Minimum	-	-	230
Maximum	-	-	490
PS-G1	-	-	270

With regard to migration of residual monomers from recycled material of ABS and PS, no migration above the detection limit for the examined monomers has been identified here.

It must be noted that the analyses of recycled material in this project is made on the “purest” form of recycled material which is available – namely industrial waste. With “pure” it means here solely (sorting of) plastic type, i.e. that industrial waste of ABS can be expected to consist of 100 % ABS.

10. Hazard assessment

Hazard assessment of the four relevant carcinogenic monomers

As described in section 6.2 ”Monomers and materials in focus”, it was decided to focus on four of the five relevant carcinogenic monomers, which according to the survey appear to be present in toy materials and which appear to be used frequently or in more types of toy materials. The four monomers are:
- Acrylonitrile (in e.g. ABS)
- 1,3-butadiene (in e.g. ABS, SBC)
- Styrene (in e.g. ABS, PS, SEBS, SBC)
- Vinyl chloride (in PVC)

Therefore, hazard assessment, exposure calculations and risk assessment have been carried out for these four monomers. The hazard assessment will primarily focus on the carcinogenic effects in line with the focus on carcinogenic monomers in this project.

10.1 Acrylonitrile

The primary references for the hazard assessment of acrylonitrile have been: ECHA opinion on scientific evaluation of occupational exposure limits for acrylonitrile which has been performed by RAC (Committee for Risk Assessment) (ECHA RAC, 2018a) and the associated annexes (ECHA RAC, 2018b), suggestion by ECHA regarding EU occupation exposure limit value for acrylonitrile (ECHA, 2017), EU risk assessment of acrylonitrile (EU RAR, 2004), toxicological review of acrylonitrile by US EPA (US EPA, 2011), ECHA database of registered substances (ECHA RSD, 2018) and toxicological profile for acrylonitrile by ATSDR (ATSDR, 1990).

Acrylonitrile has a harmonised classification as (ECHA C&L, 2018):
- Flam. Liq. 2, H225 ”Highly flammable liquid and vapour”
- Carc. 1B, H350 ”May cause cancer”
- Acute Tox. 3 *[19], H331 ”Toxic if inhaled”
- Acute Tox. 3 *, H311 ”Toxic in contact with skin”
- Acute Tox. 3 *, H301 ”Toxic if swallowed”
- STOT SE 3, H335 ”May cause respiratory irritation”
- Skin Irrit. 2, H315 ”Causes skin irritation”
- Eye Dam. 1, H318 ”Causes serious eye damage”
- Skin Sens. 1, H317 ”May cause an allergic skin reaction”
- Aquatic Chronic 2, H411 ”Toxic to aquatic life with long lasting effects”

The occupational threshold limit value (TLV) for acrylonitrile in Denmark is 2 ppm or 4 mg/m^3. The written remarks for acrylonitrile are H and K, which means that the substance can be absorbed through skin (H for “hud” (skin in Danish)) and that the substance is carcinogenic (K for “kræft” (cancer in Danish)) (AT, 2007). In 2017, the occupational TLV was assessed by RAC and the conclusion was that the lower TLVs as listed below should be established as an EU

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[19] The star (*) at these Actue Tox. 3 classifications indicates that this minimum classification must be used, but must be classified in a more severe hazard category in the event that further information is available which shows that the hazard meet the criteria for classification in a more severe category (according to Annex VI, section 1.2.1 of the CLP regulation).

TLV for acrylonitrile. However, this occupational TLV has not yet officially been approved in the EU, i.e. listed in Annex of EU Directive no. 164, 2017.

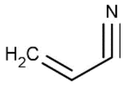
- TLV as TWA (time-weighted average) over 8 hours: 1 mg/m^3
- STEL (15 minutes) (Short Term Exposure Limit): 4 mg/m^3

Among other things, quality criteria for drinking water are established based on the Danish EPA. These quality criteria are used as indicative limit values and are health-related values that are based on toxicological assessments of the specific substances. Acrylonitrile is on the Danish list of quality criteria for drinking water with a drinking water quality criterion of 0.1 µg/l (Danish EPA, 2018).

10.1.1 Identification and physical-chemical parameters

Physical-chemical parameters for acrylonitrile are listed in Table 31 below.

Table 31. Physical-chemical parameters for acrylonitrile (ECHA RSD, 2018)

Chemical name	**Acrylonitrile**
Synonyms	Prop-2-enenitrile
CAS no. / EC no.	107-13-1 / 203-466-5
Structure	
Molecule formula	C_3H_3N
SMILES code	C=CC#N
Molecular mass	53.06
Physical state (at 20 °C)	Colourless liquid
Density	0.8 g/cm^3
Melting point	-83.5 °C
Boiling point (at 1013 hPa)	77.3 °C
Vapour pressure (at 20 °C)	115 hPa
Octanol-water partition coefficient (Log K_{OW}) (at 25 °C)	1.04 (at 21 °C)
Solubility in water (at 20 °C)	Very high 73 g/l
Solubility in ethanol (at 30 °C)	Is soluble[20] No data

10.1.2 Background levels

Acrylonitrile can be found in small concentrations in outdoor air but will primarily be concentrated nearby industrial production. ECHA RAC (2018b) reports levels of acrylonitrile in ambient air of unpolluted areas between 0.01 µg/m^3 (in the Netherlands in 2010 based on dispersion models) and 0.0052 µg/m^3 (in the USA in 2010 based on the average of 46 24-hours samples). Near industrial sites, levels between < 2.2 and up to 100 µg/m^3 have been reported.

Furthermore, acrylonitrile has been identified in indoor air in homes of smokers. ECHA RAC (2018b) reports levels between 0.1 and 8.2 µg/m^3 (in hospitals) and levels between 0.5 to 1.2 µg/m^3 in homes of smokers.

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[20] http://www.chemicalbook.com/ChemicalProductProperty_EN_CB8764818.htm

In EU RAR (2004), an estimate (modelled by EUSES) of a daily intake of acrylonitrile through the environment of 0.103 µg/kg bw/day is given, which is distributed on:

- Intake through drinking water: 0.0801 µg/kg bw/day
- Intake through consumption of food: 0.0077 µg/kg bw/day (of which the primary source is through intake of fish)
- Intake through air: 0.0152 µg/kg bw/day

Furthermore, EU RAR (2004) calculates the theoretical maximum intake of acrylonitrile through consumption of food based on migration of acrylonitrile from food contact materials made of ABS. This calculation was based on a migration limit value of 0.02 mg acrylonitrile/kg food, an assumption of 5 % of the food is wrapped in ABS-based material, an average intake of 2 kg food and a body weight of 70 kg. In this way, EU RAR (2004) calculates a maximum daily exposure of acrylonitrile through food contact materials of 0.03 µg/kg bw/day. However, it must be noted that the migration limit value for acrylonitrile today is reduced by half to 10 µg/kg food (0.01 mg/kg food) (see section 3.2 ”Legislation for monomers in food contact materials”).

In comparison, inhalation of acrylonitrile from indoor air in homes of smokers will result in a daily exposure of maximum 0.3 µg/kg bw/day for adults based on an inhalation ratio of 18 m^3/day, a body weight of 70 kg and based on the maximum listed concentration in indoor air of 1.2 µg/m^3. The corresponding value for small children (< 3 years) will be maximum 0.8 µg/kg bw/day based on an inhalation ratio of 7 m^3/day and a body weight of 10 kg (RIVM, 2014). This means that the daily exposure in homes of smokers seems to be the most significant contribution to exposure to acrylonitrile. In comparison, the US EPA (2011) has stated a RfC (Reference Concentration) of 0.9 µg/m^3, which means that RfC can be exceeded solely by the background exposure in homes of smokers.

The established drinking water quality criteria for acrylonitrile in drinking water of 0.1 µg/l will correspond to a daily exposure of 0.03 µg/kg bw/day for a child of 10 kg and 0.004 µg/kg bw/day for an adult of 70 kg (see Appendix 2.5 ”Used values in the exposure and risk calculations”, RIVM (2014)) and an assumption of intake of 3 litres of water per day (through food and drinking).

An adult worker will be exposed to a maximum daily exposure of 123 µg acrylonitrile/kg bw/working day when using the assumption of an inhalation rate of 1.08 m^3/hour for 8 hours (inhalation rate for adults doing light exercise (RIVM, 2014)), a body weight of 70 kg and when using the suggested EU occupational threshold limit value of 1 mg/m^3. However, this calculation of course assumes no use of personal protection equipment or exhaust ventilation.

10.1.3 Absorption and distribution

Acrylonitrile is rapidly and almost completely absorbed and widely distributed in the body after oral intake, inhalation or dermal exposure (EU RAR, 2004; US EPA, 2011). Human data show that dermal absorption of acrylonitrile is high and close to 100 % as for oral intake (ECHA RAC, 2018b).

Acrylonitrile is primarily excreted in the urine or by exhalation regardless of the exposure route, partly as acrylonitrile and partly as its metabolites (EU RAR, 2004; US EPA, 2011). Acrylonitrile metabolises by two different pathways in the body which may be dependent on the exposure level (EU RAR, 2004). The primary metabolite from both biotransformation pathways is cyanide which is part of the explanation of the toxic properties of acrylonitrile (ECHA RAC, 2018a).

For the exposure calculations, a dermal and oral absorption of 100 % is used, as also listed in ECHA RAC (2018b).

10.1.4 Acute and chronic effects

Acrylonitrile is acutely toxic and is regarded as being neurotoxic. Moreover, acrylonitrile causes irritation of skin, eyes and the respiratory system, and is regarded as a skin sensitiser. A part of this toxicity is caused by the fact that acrylonitrile is metabolised to cyanide in the body (ECHA RAC, 2018a). For this reason, acrylonitrile has a harmonised classification as STOT SE 3, H335 ” May cause respiratory irritation”, Skin Irrit. 2, H315 ”Causes skin irritation”, Eye Dam. 1, H318 ”Causes serious eye damage”, Skin Sens. 1, H317 ”May cause an allergic skin reaction”.

Acrylonitrile has no effect on reproductive performance or fertility as the developmental toxicity of acrylonitrile is only observed at maternally toxic doses (ECHA RAC, 2018a).

RAC concludes that acrylonitrile is genotoxic *in vitro* and that its direct metabolite (by the metabolising pathway for low oral doses (EU RAR, 2004)) seems to be an acting mutagen. There is no clear evidence that acrylonitrile is an *in vivo* mutagen, but the available data are not sufficient to conclude the absence of a mutagenic hazard where a carcinogenic effect has been seen in animals (ECHA RAC, 2018a).

RAC states that the critical effect for acrylonitrile is its carcinogenic properties and that the potential most relevant effect for humans is brain tumours, which have been observed in rats exposed for acrylonitrile. Even though rather extensive epidemiological data exist, these studies do not support a causal association between occupational acrylonitrile exposure and increased cancer at a particular site in the body (ECHA RAC, 2018a).

RAC concludes that even though acrylonitrile may have a genotoxic potential and thus can be considered a genotoxic carcinogen, there is compelling evidence for indirect DNA damage as the main mechanism in rat brain tumour formation. This mechanism supports a non-linear dose-response relationship and is further supported by the epidemiological data for acrylonitrile (ECHA RAC, 2018a). However, RAC concludes that by exposure below the suggested occupational threshold limit value of 1 mg/m^3 no significant cancer risk for workers will be expected (ECHA RAC, 2018a).

10.1.5 Critical effect and calculation of DNEL/DMEL

The critical effect of acrylonitrile is its carcinogenic properties and the most relevant effect for humans is brain tumours (ECHA RAC, 2018a). As described above, RAC suggests an occupational threshold limit value of 1 mg/m^3 and underlines that no significant cancer risk may be expected for workers exposed to levels of acrylonitrile below this value. However, an established threshold limit value in the working environment cannot necessarily be converted to a continuous exposure for the general population. If this calculation is performed (as described above), this will result in a daily exposure of 123 µg acrylonitrile/kg bw/day.

In comparison, US EPA (2011) has listed a RfD (Reference Dose) of 0.3 µg/kg bw/day and a RfC (Reference Concentration) of 0.9 µg/m^3 – these levels are thus considerably lower than the occupational TLV proposed by RAC. However, these values cover non-carcinogenic effects.

In the ECHA registration dossier of acrylonitrile, the below listed DNEL (Derived No Effect Level) values are recorded for acrylonitrile (ECHA RSD, 2018). However, it should be noticed that DNELs listed in the registration dossiers are recorded by the industry and have not been reviewed by ECHA:

- Workers – long-term exposure via inhalation route, systemic effects: ”high hazard (no DNEL derived), most sensitive endpoint: carcinogenicity”
- Workers – long-term exposure via inhalation route, local effects: 1.8 mg/m^3
- General population – long-term exposure via inhalation route, systemic effects: 0.1 mg/m^3

- General population – long-term exposure via dermal route, systemic effects: 0.009 mg/kg bw/day or 9 µg/kg bw/day
- General population – long-term exposure via oral route, systemic effects: 0.009 mg/kg bw/day or 9 µg/kg bw/day

In a working document prepared by Germany for the EU Expert Group on Toy Safety (‘sub group chemicals’) and as described in Lenzner et al. (2018), a calculated oral dose of 1.9 ng/kg bw/day is used as an acceptable additional life time risk of cancer of 1 x 10^{-6}. This value originates from SCCS (Scientific Committe on Consumer Safety), SCHER (Scientific Committee on Health and Environmental Risks) and SCENIHR (Scientific Committee on Emerging and Newly Identified Health Risks), which in 2008 prepared an opinion on TTC (Threshold of Toxicological Concern). In this opinion, they established a range of limit values for chemical substances used in cosmetic products and other consumer products, including acrylonitrile. Here, they use a model with linear extrapolation and calculate this limit value of 1.9 ng/kg bw/day for acrylonitrile (SCCP, 2008). However, it should be noted that in 2018 RAC (ECHA RAC, 2018a) concludes that there is a non-linear dose-response relationship for acrylonitrile. Therefore, the question is whether this linear extrapolation would be carried out today.

Consequently, it is debatable which value is the most correct value to use in the calculation of the risk, as the value calculated by SCCP based on the TTC concept is considerably lower than other mentioned limit value, and assumes a linear dose-response relationship, where in 2018 RAC has concluded the opposite. However, as worst-case the value of **1.9 ng/kg bw/day** for an additional risk of life time cancer of 1 x 10^{-6} is used.

10.2 Butadiene

The primary references for the hazard assessment of butadiene have been: ”Concise International Chemical Assessment Document 30” for butadiene (WHO, 2001), ”Health Assessment of Butadiene” by US EPA (2002), EU’s risk assessment of butadiene (EU RAR, 2002) and a ”Substance Evaluation Report” for butadiene carried out by the German institute BAuA (Federal Institute for Occupational Safety and Health) for ECHA (BAuA, 2015).

Butadiene has a harmonised classification as (ECHA C&L, 2018):
- Flam. Gas 1, H220 ”Extremely flammable gas”
- Press. Gas
- Carc. 1A, H350 ”May cause cancer”
- Muta. 1B, H340 ”May cause genetic defects”

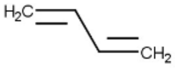
Butadiene is included in the CoRAP list (Community Rolling Action Plan), i.e. EU Member States have evaluated or will evaluate the substance. This has been carried out by the so-called ”Substance Evaluation Report” by BAuA (2015).

The occupational threshold limit value of butadiene in Denmark is 10 ppm or 22 mg/m^3. The written remarks for butadiene are K, which means that the substance is carcinogenic (K for “kræft” (cancer in Danish)) (AT, 2007).

10.2.1 Identification and physical-chemical parameters

Physical-chemical parameters for butadiene are listed in Table 32 below.

Table 32. Physical-chemical parameters for butadiene (ECHA RSD, 2018)

Chemical name	**1,3-Butadien**
Synonyms	Buta-1,3-dien
CAS no. / EC no.	106-99-0 / 203-450-8
Structure	
Molecule formula	C_4H_6
SMILES code	C=CC=C
Molecular mass	54.0916
Physical state (at 20 °C)	Colourless gas
Density	0.62 g/cm^3 (EU RAR, 2002)
Melting point	- 108.9 °C
Boiling point (at 1013 hPa)	- 4.4 °C
Vapour pressure (at 20 °C)	2440 hPa[21]
Octanol-water partition coefficient (Log KOW)	1.99
(at 25 °C)	Low water solubility 0.735 g/l
Solubility in water (at 20 °C)	Is soluble[22] No data

10.2.2 Background levels

Butadiene can be found in concentrations between 0.1 and 1.0 ppb in outdoor air (corresponding to between 0.2 and 2.3 µg/m^3). These data come from measurements carried out in the 1980ies and 1990ies in the USA (US EPA, 2002). WHO (2001) reports of similar levels in air in Canada between 0.2 and 1 µg/m^3 (50 % to 95 % percentile), but with higher concentrations in urban areas (up to 1.3 µg/m^3 for the 95 % percentile). This concentration is relatively constant according to US EPA (2002) even though butadiene relatively quickly decomposes (by oxidation) in air.

Exposure of butadiene to the environment happens exclusively through emissions to air. US EPA (2002) states that the total emissions of butadiene to the environment are due to industrial production (1.6 %), mobile sources like transportation (78.8 %) and other miscellaneous combustion sources (19.6 %). Butadiene is formed as a product of incomplete combustion of fossil fuels and for this reason transportation is one of the primary sources to emission of butadiene in the environment. For this reason, the concentration of butadiene in the indoor climate will also depend on a smoking or non-smoking environment, as butadiene also is formed by smoking of cigarettes (US EPA, 2002). WHO (2001) reports of levels of less than 1 µg/m^3 in non-smoking homes, but concentrations between 1.3 and 18.9 µg/m^3 in smoking environments. In exposure calculations, the EU RAR (2002) uses a background concentration in indoor air of 2.2 µg/m^3 on average, and states that this corresponds to a daily exposure of 11

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[21] According to the EU RAR report of 1,3-butadiene (https://echa.europa.eu/documents/10162/1f512549-5bf8-49a8-ba51-1cf67dc07b72)

[22] https://pubchem.ncbi.nlm.nih.gov/compound/1_3-butadiene#section=Top

µg/day (i.e. 1.1 µg/kg bw/day for a child of 10 kg). For children exposed to passive smoking the daily exposure will be higher.

EU RAR (2002) lists a theoretical worst-case oral intake of butadiene monomer migrating from food contact packaging material to food based on the limit value for migration at that time of 0.02 mg/kg food set in the legislation on food contact materials. This results in a worst-case intake for a small child of 1.2 µg/kg bw/day. BAuA (2015) points out that since then this migration limit value has been lowered to 0.01 mg/kg and that Germany does not report of levels of butadiene detected in food in their monitoring programme for food. Therefore, exposure by air (indoor or outdoor) can be expected to be the primary source of background exposure to butadiene.

10.2.3 Absorption and distribution

Butadiene is absorbed via the lungs in both human and animals, and this is considered to be the most important route of exposure. No data exist regarding the potential for oral or dermal absorption of butadiene. However, EU RAR (2002) describes that given the physicochemical characteristics of butadiene, the potential for dermal or oral uptake is unlikely.

Once butadiene is absorbed, it is widely distributed throughout the body. The main route of elimination of butadiene and its metabolites is urinary excretion or exhalation (EU RAR, 2002).

As no data exist regarding the absorption of butadiene in the human body, 100 % absorption is used as worst-case for all exposure routes – even though EU RAR (2002) points out that dermal absorption is not significant.

10.2.4 Acute and chronic effects

The acute toxicity of butadiene is low and butadiene is not classified as acutely toxic. There is no indication of butadiene being irritating for skin or eyes and butadiene is not regarded as a skin sensitiser (BAuA, 2015).

Butadiene is genotoxic both *in vitro* and *in vivo* and has therefore a harmonised classification as Muta. 1B, H340 ” May cause genetic defects” (BAuA, 2015).

Exposure to butadiene by inhalation has resulted in development of cancer in both mice and humans (observed at occupational exposure). In 2002, EU concluded in the risk assessment of butadiene that butadiene must be regarded as carcinogenic for humans. Later (in 2008), IARC has concluded that there is sufficient evidence in both humans and animals for the carcinogenicity of butadiene. One of the most frequent types of cancer reported in humans is leukaemia (BAuA, 2015). Butadiene is regarded as a genotoxic carcinogen and has a harmonised classification as Carc. 1A, H350 ”May cause cancer”.

Butadiene is regarded as having a low potential for effects on reproductive performance or fertility, as developmental toxicity of butadiene is only observed at maternally toxic doses (BAuA, 2015).

10.2.5 Critical effect and calculation of DNEL/DMEL

The critical effect of butadiene is its carcinogenic properties. BAuA (2015) states that butadiene is a genotoxic carcinogen, and that it has generally been accepted that genotoxic carcinogens have no dose threshold for their carcinogenic potential. Therefore, no DNEL value can be derived but instead a DMEL-value (Derived Minimum Effect Level) must be derived.

In the ECHA registration dossier of butadiene, the below listed DMEL values are recorded for butadiene (ECHA RSD, 2018). Only a DMEL value for exposure via the inhalation route is listed as “no hazard identified” is reported for hazard via dermal and oral route. However, it should be noticed that DNELs listed in the registration dossiers are recorded by the industry and have not been reviewed by ECHA:

- Workers – long-term exposure via inhalation route, systemic effects: 2.21 mg/m^3
- General population – long-term exposure via inhalation route, systemic effects: 0.265 mg/m^3

However, BAuA (2015) reports DMEL values that are considerably lower. They calculate a DMEL value of 11 µg/m^3 based on a lifetime risk for leukaemia of 1 to 100,000. This value is converted to a DMEL value of 1.5 µg/m^3 for consumers when taking 24 hours exposure into consideration (contrary to 8 hours working day) and 70 years of lifetime (contrary to 40 years of work). Similarly, these DMEL values are converted from inhalation to oral intake to a value of 0.43 µg/kg bw/day for adults (0.72 µg/kg bw/day for 3-year-old children) by using an inhalation rate of 20 m^3 for adults (7 m^3 for 3-year-old children) and a body weight of 70 kg for adults (14.5 kg for 3-year-old children). When using a body weight of 10 kg for a 1 to 2-year-old child (as generally used in this report), this results in a DMEL value of 1.05 µg/kg bw/day for small children.

In comparison, the US EPA (2002) states a RfC (Reference Concentration) for butadiene of 0.9 ppb (or 2.1 µg/m^3) based on atrophy in ovary in mice.

As worst-case the lowest described value, i.e. the DMEL value listed in BAuA (2015), is used. This value is also from the most recent assessment of butadiene. BAuA reports a value of **0.72 µg/kg bw/day** for 3-year-old children.

10.3 Styrene

The references for the hazard assessment of acrylonitrile have been: ECHAs 'Annex XV transitional report' on styrene (ECHA, 2009), which corresponds to the unfinished EU risk assessment report (RAR) from 2008 (was not completed before June 1 2008 (EU, 2008), Danish EPA LOUS (List of Undesirable substances) report of styrene (Kjølholt et al., 2014), 'Toxicological profile for styrene' by ATSDR (2010), assessment of styrene prepared by ECHA RAC (Risk Assessment Committee) (RAC, 2012), ECHA database of registered substances (ECHA RSD, 2018) and the reassessment by IARC of styrene regarding its carcinogenic properties (IARC, 2018).

Styrene has a harmonised classification as (ECHA C&L, 2018):

- Flam. Liq. 3, H226 ”Flammable liquid and vapour”
- Repr. 2, H361d ”Suspected of damaging the unborn child”
- Acute Tox. 4 *[23], H332 ”Harmful if inhaled”
- STOT RE 1, H372 (hearing organs) “Causes damage to organs through prolonged or repeated exposure” – here specifically damage to the hearing organs
- Skin Irrit. 2, H315 ”Causes skin irritation”
- Eye Irrit. 2, H319 ”Causes serious eye irritation”

The occupational threshold limit value of styrene in Denmark is 25 ppm or 105 mg/m^3. The written remarks for styrene are L, H and K, which means that the substance is a short-term exposure limit that at no point must be exceeded (L for ‘upper’ limit (in Danish)), that the substance can be absorbed through skin (H for “hud” (skin in Danish)) and that the substance is carcinogenic (K for “kræft” (cancer in Danish)) (AT, 2007).

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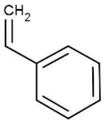
[23] The star (*) at these Actue Tox. 3 classifications indicates that this minimum classification must be used, but must be classified in a more severe hazard category in the event that further information is available which shows that the hazard meet the criteria for classification in a more severe category (according to Annex VI, section 1.2.1 of the CLP regulation).

In the former Danish Statutory Order on drinking water (Stat. Ord. no. 1024, 2011), styrene was restricted in drinking water by a limit value of 1 µg/l water measured at the water tap of the consumer. However, in the existing Danish Statutory Order on drinking water (Stat. Ord. no. 1068, 2018), no specific limit value for styrene has been established. On the other hand, a drinking water quality criterium for styrene of 1 µg/l has been established (Danish EPA, 2018). This drinking water quality criterium is used as an indicative limit value and is a health-related value, which has been established based on a toxicological assessment of the substance. WHO (2003) has established a limit value of styrene in drinking water of 20 µg/l.

10.3.1 Identification and physical-chemical parameters

Physical-chemical parameters for styrene are listed in Table 33 below.

Table 33. Physical-chemical parameters for styrene (ECHA RSD, 2018; IARC, 2018)

Chemical name	**Styrene**
Synonyms	Ethenyl benzene, phenyl ethylene, vinyl benzene
CAS no. / EC no.	100-42-5 / 202-851-5
Structure	
Molecule formula	C_8H_8
SMILES code	C=CC1=CC=CC=C1
Molecular mass	104.15
Physical state (at 20 °C)	Colourless to yellow liquid, pungent odour
Density	0.9 g/l
Melting point	- 31 °C
Boiling point (at 1013 hPa)	145 °C
Vapour pressure (at 20 °C)	6.67 hPa
Octanol-water partition coefficient (Log KOW)	2.96
(at 25 °C)	Low to insoluble 0.32 g/l (at 25 °C)
Solubility in water (at 20 °C)	Is soluble[24] No data

10.3.2 Background levels

Low levels of styrene occur naturally in food such as fruits, vegetables, nuts and meats. Moreover, small amounts of styrene can be transferred from styrene-based packaging material for foods (ATSDR, 2010).

Furthermore, styrene can be found in small concentrations in air because of sources like automobile exhaust and chemical industry (IARC, 2018; ATSDR, 2010). ATSDR (2010) reports background levels of styrene in urban air of 0.06 to 4.6 ppb (corresponding to 0.29 to 19.6 µg/m^3) and 0.06 to 0.1 ppb in rural/suburban air (corresponding to 0.26 to 0.43 µg/m^3). Indoor concentrations of styrene are reported to be between 0.07 to 11.5 ppb (corresponding to 0.29 to 49 µg/m^3). The primary sources for styrene in indoor air are cigarette smoke and photocopiers (ATSDR, 2010).

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[24] https://pubchem.ncbi.nlm.nih.gov/compound/styrene#section=Flash-Point

The general daily exposure to styrene for the general population is estimated to be 8.2 – 55.2 µg/day (corresponding to 0.3 – 0.8 µg/kg bw/day for a person of 70 kg). Breathing of air constitutes the largest exposure (ATSDR, 2010):

- Air: 18 - 54 µg/person/day
- Food: 0.2 – 1.2 µg/person/day

In the risk assessment of styrene (EU, 2008), a few higher values for the daily exposure for styrene through food are given: 3 µg/person/day for food and 8 µg/person/day for chewing gum. However, the value for food may contain indirect intake of styrene in the food transferred from food contact materials.

EU RAR (2008) estimates a total daily exposure from sources like food, air and drinking water of 58 µg/kg bw/day, where the main part of the exposure is caused by breathing of air. However, it is pointed out that the contribution from the air is very high. In comparison, WHO (2003) reports a total daily exposure for styrene of 0.57 µg/kg bw/day for non-smokers in non-industrial areas based on an amount of 2 µg/person/day from air, 10-50 µg/person/day from automobile exhaust and 5 µg/person/day from food and a body weight of 70 kg. For smokers, the daily exposure will be much higher (500 µg/person/day corresponding to 7.1 µg/kg bw/day), and likewise the daily exposure from air in industrial areas will be much higher (400 µg/person/day corresponding to 5.7 µg/kg bw/day).

If these above exposure levels are converted to exposure levels for a child of 10 kg, this will result in the following background exposure levels (based on data from ATSDR (2010), EU RAR (2008) and WHO (2003)):

- Air: 1.8 – 5.4 µg/kg bw/day
- Food: 0.02 – 0.5 µg/kg bw/day

In comparison, WHO has reported a TDI (Tolerable Daily Intake) of 7.7 µg/kg bw (WHO, 2003), which means that the TDI will be exceeded (for adults) solely based on the background exposure for smokers or persons living in industrial areas. However, Kjølholt et al. (2014) states that this comparison should be made with reservations, as the total daily exposure primarily is based on inhalation whereas the TDI has been calculated based on oral intake.

With an assumption of an inhalation rate of 1.08 m^3/time for 8 hours (inhalation rate for adults at light activity (RIVM, 2014)), an adult worker will be exposed to a maximum daily exposure of 12,960 µg styrene/kg bw/working day by use of the occupational TLV of 105 mg/m^3 and an assumption of a body weight of 70 kg. This calculation assumes no use of personal protective equipment or local exhaust ventilation.

10.3.3 Absorption and distribution

The uptake of styrene in the body is rapid (based on animal testing). By inhalation the uptake of styrene is about 59-70 % according to ATSDR (2010). Uptake by oral intake is regarded to be rapid and complete (ATSDR, 2010), whereas absorption through skin is considered to be low (based on the physical-chemical properties and an assumption of styrene will evaporate quickly and thereby not absorbed through the skin). Based on the physical-chemical properties of styrene and experimental values in animals, the EU RAR (2008) assumes an absorption of 100 % by oral intake. Values between 0.1 and 2 % are listed for absorption through skin compared to absorption at inhalation (ATSDR, 2010; EU RAR, 2008).

For use in the exposure calculations, a dermal absorption of 2 % is used and an oral absorption of 100 %.

After uptake of styrene, the substance is completely absorbed in the body and styrene and/or its metabolites are distributed in the entire body with the highest concentration in fatty tissue.

Styrene is metabolised to a high degree in humans and is primarily excreted via the urine (ATSDR, 2010; Kjølholt et al., 2014).

10.3.4 Acute and chronic effects

Styrene has a moderate to low acute toxicity in rats and guinea pigs by inhalation and oral exposure. There are no data regarding the acute dermal toxicity of styrene, but according to EU RAR (2008) this can be assumed to be low (EU RAR, 2008). Styrene has a harmonised classification as Acute Tox. 4, H332 " Harmful if inhaled".

After inhalation of styrene, acute effects such as irritation of eyes and nose, CNS (central nervous system) depression and changes in the lungs have been observed (EU RAR, 2008). In humans, CNS depression after inhalation of styrene is the primary effect observed. However, this effect is only found at high concentrations far above the established occupational TLV (EU RAR, 2008; Kjølholt et al., 2014).

Limited data exist regarding the irritative and sensitising properties of styrene. However, the available data suggest that liquid styrene is not skin irritating after a single exposure, but repeated exposure suggests skin irritation (EU RAR, 2008). Styrene has a harmonised classification as Skin Irrit. 2, H315 ”Causes skin irritation”. Similarly, liquid styrene and styrene vapour demonstrate eye irritation, but only at levels far above the occupational TLV. Styrene has a harmonised classification as Eye Irrit. 2, H319 ”Causes serious eye irritation”.

Based on the extensive occupational use of styrene, EU RAR (2008) concludes that styrene does not have a significant sensitising potential either for skin or by inhalation.

A large amount of data concerning the repeated human exposure to styrene exist through occupational studies. The most frequent reported symptoms are eye or nose irritation and CNS disturbance (in the form of drowsiness, headache and light-headedness). However, EU RAR (2008) concludes that even though it is well-documented that styrene is a potent neurotoxicant in animals, there is no clear relationship between repeated exposure to styrene and persisting damage to the nervous system. Effects in the form of hearing impact (ototoxicity) have also been observed for styrene, but only at high concentrations (far above the established occupational TLV) (EU RAR, 2008).

Some studies state that inhalation of styrene can influence colour vision, i.e. the ability to distinguish colours. However, the effect is only observed at concentrations far above the established occupational TLV (EU RAR, 2008; Kjølholt et al., 2014).

According to RAC (ECHA Risk Assessment Committee), the EU commission has acknowledged that occupational styrene exposure above 50 ppm (i.e. twice the established occupational TLV of 25 ppm or 105 mg/m^3) for a period of 5-10 years may induce chronic encephalopathy (damage to the brain) (RAC, 2012).

WHO (2003) reports a NOAEL of 7.7 mg/kg bw/day based on a 2-year oral toxicity study with rats being exposed to styrene through drinking water. The only observed effect (at the highest dose) was a significant reduced body weight. This NOAEL-value has been used for establishing the TDI-value for styrene of 7.7 µg/kg bw/day.

Based on inhalation studies in animals, EU RAR (2008) concludes that ototoxicity is the most sensitive and relevant effect of repeated styrene exposure by inhalation. Styrene has a harmonised classification as STOT RE 1, H372 (hearing organs) “Causes damage to organs through prolonged or repeated exposure” – here specifically damage to the hearing organs.

In 2008, the EU concluded in their risk assessment of the substance that there is no convincing evidence that styrene has shown mutagenic activity in humans or no convincing evidence of styrene possessing carcinogenic potential in humans. Previously (in 2002), IARC has concluded that styrene is possibly carcinogenic to humans (group 2B). However, recently, IARC has re-evaluated styrene and concluded that styrene is probably carcinogenic to humans (group 2A) based on limited evidence in humans and adequate evidence in animals (IARC, 2018). IARC (2018) concludes that overall, the epidemiological studies provide credible evidence that exposure to styrene causes leukaemia or lymphohematopoietic malignancies, but confounding, bias, or chance in data cannot be ruled out.

In the long term, this re-assessment of styrene as probably carcinogenic may result in a harmonised classification according to CLP as Carc. 1B. However, first and foremost, such a re-classification requires that a proposal of classifying styrene as carcinogenic is submitted and subsequently that RAC (ECHAs Committee for Risk Assessment) also interprets data in the same way as IARC before a potential harmonised classification as carcinogenic will enter into force.

EU RAR (2008) concludes that styrene does not cause developmental effects in animals at exposure levels below 600 mg/m^3 (a level far above the established occupational TLV). Styrene has a harmonised classification as Repr. 2, H361d ”Suspected of damaging the unborn child”.

Styrene is listed in category 1 of the EU list of potential endocrine disruptors, i.e. substances for which endocrine activity has been documented in at least one study of a living organism. These substances are given the highest priority for further studies. However, EU RAR (2008) concludes that there is no evidence that styrene possesses significant endocrine disruption activity in humans. In 2015 DTU Food (Danish National Food Institute) has carried out a screening of the existing data that supports the conclusion of the EU RAR (Danish EPA, 2015).

10.3.5 Critical effect and calculation of DNEL

WHO (2003) has established a TDI value of 7.7 µg/kg bw/day which is based on a NOAEL value of 7.7 mg/kg bw/day in a 2-year drinking water study with rats, where the effect was reduced body weight. An uncertainty factor of 1000 was used (100 for differences within and between species and a factor of 10 for the cancer risk and genotoxicity of the metabolite of styrene). This TDI value was used to establish a limit value for styrene in drinking water of 20 µg/l. However, it should be noted that, according to the Danish EPA (2015), this TDI value has been questioned. The 2-year drinking water study (from 1980), which is used to derive the TDI value is for example not even described in the EU risk assessment (EU RAR, 2008).

In comparison EU RAR (2008) uses a NOAEL of 150 mg/kg bw/day based on necrosis of the liver observed in a 2-year oral carcinogenicity study with mice. However, EU RAR notices that study with mice should be used carefully as the metabolism in mice is different from the human metabolism, and as mice have a higher sensitivity towards liver toxicity compared to e.g. rats. Based on a 2-year oral carcinogenicity study with rats, the EU RAR (2008) derives a NOAEL value of 1000 mg/kg bw/day (the effect was here also necrosis of the liver at high doses). The lowest NOAEL values reported in EU RAR (2008) are 120 mg/kg bw/day for developmental effects in rats and 32.6 mg/kg bw/day for changes in colour vision. However, these values are both inhalation values that have been converted. Most NOAEL values reported in EU RAR (2008) are based on inhalation studies and are reported as NOAEC values.

ATSDR (2010) reports a so-called acute MRL (Minimum Risk Level) of 0.1 mg/kg bw/day for styrene based on a LOAEL value of 100 mg/kg bw/day and an uncertainty factor of 1000. ATSDR (2010) states that, in 2009, the US EPA has established a so-called RfD (Reference Dose) of 0.2 mg/kg bw/day based on a NOAEL value of 200 mg/kg bw/day for a subchronic study and an uncertainty factor of 1000).

In the ECHA registration dossier of styrene, the below listed DNEL (Derived No Effect Level) values are recorded for styrene (ECHA RSD, 2018). However, it should be noticed that the Danish EPA (2015) states that it seems that the wrong method for determining safety factors has been applied, and for this reason the reported DNELs are probably too high:

- Workers – long-term exposure via inhalation route, systemic effects: 85 mg/m^3
- General population – long-term exposure via inhalation route, systemic effects: 10.2 mg/m^3
- General population – long-term exposure via dermal route, systemic effects: 343 mg/kg bw/day
- General population – long-term exposure via oral route, systemic effects: 2.1 mg/kg bw/day

According to the ECHA guidance documents (2012), use of the NOAEL value of 120 mg/kg bw/day for developmental effects for rats (reported by EU RAR (2008)) would result in a total assessment factor of 200 (4 for interspecies differences (rats to humans), 2.5 for additional interspecies differences, 10 for intraspecies differences, 2 for subchronic to chronic). Hence, the DNEL value can be calculated as 600 µg/kg bw/day.

According to the ECHA guidance documents (2012), a use of the NOAEL value of 32.6 mg/kg bw/day for changes in colour visions in humans (reported in EU RAR (2008)) would result in a total assessment factor of 60 (0 for interspecies differences, 10 for intraspecies differences, 6 for sub-acute to chronic). Hence, the DNEL value can be calculated as 543 µg/kg bw/day.

Both these DNEL values are far above the TDI value of **7.7 µg/kg bw/day** set by WHO. Even though this TDI value can be questioned, it has been used in this report as a worst-case DNEL value in the risk assessment calculations.

10.4 Vinyl chloride

The primary references for the hazard assessment of vinyl chloride have been: SIDS Initial Assessment Report" for vinyl chloride (OECD, 2001),"Toxicological Profile for Vinyl Chloride" by ATSDR (ATSDR, 2006), and the ECHA database of registered substances (ECHA RSD, 2018).

Vinyl chloride has a harmonised classification of (ECHA C&L, 2018):

- Flam. Gas 1, H220 "Extremely flammable gas"
- Press. Gas
- Carc. 1A, H350 "May cause cancer"

The use of vinyl chloride is restricted by the REACH Regulation Annex XVII entry no. 2, where it is stated that vinyl chloride shall not be used as propellant in aerosols for any use (REACH Regulation no. 1907, 2006).

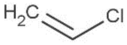
The occupational threshold limit value of vinyl chloride in Denmark is 1 ppm or 3 mg/m^3. The written remarks for vinyl chloride are E, H and K, which means that the substance has an EU threshold limit value (E), that the substance can be absorbed through skin (H for "hud" (skin in Danish)) and that the substance is carcinogenic (K for "kræft" (cancer in Danish)) (AT, 2007).

Vinyl chloride is restricted by the Danish Statutory Order on drinking water (Stat. Ord. no. 1068, 2018) by a limit value of 0.5 µg/l water measured at the water tap of the consumer.

10.4.1 Identification and physical-chemical parameters

Physical-chemical parameters for vinyl chloride are listed in Table 34 below.

Table 34. Physical-chemical parameters for vinyl chloride (ECHA RSD, 2018)

Chemical name	**Vinyl chloride**
Synonyms	Chloroethylene Chloroethene
CAS no. / EC no.	75-01-4 / 200-831-0
Structure	
Molecule formula	C_2H_3Cl
SMILES code	ClC=C
Molecular mass	62.496 g/mol
Physical state (at 20 °C)	Colourless gas
Density	0.97 g/cm^3
Melting point	- 153.8 °C
Boiling point (at 1013 hPa)	- 13.4 °C
Vapour pressure (at 20 °C)	3330 hPa (OECD SIDS)
Octanol-water partition coefficient (Log KOW)	1.58 (at 22 °C)
(at 25 °C)	High water solubility 9.15 g/l
Solubility in water (at 20 °C)	Is soluble[25] No data

10.4.2 Background levels

According to OECD (2001), vinyl chloride is present in the air near production facilities, but generally at very low concentrations of < 0.1 mg/m^3. Vinyl chloride concentrations in ground water are expected to be below the detection limit of 0.001 ppm.

The Danish EPA has measured and reported the quality of the Danish drinking water for several years. According to the latest results for the period 2014 to 2016 (Danish EPA, 2017), all 71, 118 and 125 measurements of vinyl chloride, respectively, conducted in these years were below the limit value of 0.5 µg/l water measured at the water tap of the consumer. The actual concentrations are not reported.

The established limit value for vinyl chloride in drinking water of 0.5 µg/l will correspond to a daily exposure of 0.15 µg/kg bw/day for a child of 10 kg (see Appendix 2.5 ”Used values in the exposure and risk calculations”, RIVM (2014)) and an assumption of intake of 3 litre of water per day (through food and drinking). However, the actual intake is expected to be much lower as recent migration analysis measurements reported in this survey are at a level of < 0.006 – 0.020 µg/l (Walter et al., 2011) corresponding to a daily exposure of < 0.002 – 0.006 µg/kg bw/day for a child of 10 kg.

ATSDR (2006) reports that vinyl chloride has been identified in cigarette smoke and smoke from small cigars in concentrations of 5.6 – 27 ng per cigarette. Therefore, smokers will be exposed to a higher concentration of vinyl chloride compared to non-smokers.

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[25] https://pubchem.ncbi.nlm.nih.gov/compound/vinyl_chloride#section=Solubility

10.4.3 Absorption and distribution

The primary and most relevant exposure route for vinyl chloride is by inhalation. After inhalation, vinyl chloride is rapidly absorbed in humans, but in general there is limited information (OECD, 2001). A few measurements carried out on humans illustrate that on average 42 % vinyl chloride is absorbed (difference between inhaled and exhaled concentration). No human data exist regarding absorption through skin or orally, but animal testing illustrates that oral absorption of vinyl chloride is rapid and virtually complete. Animal testing illustrates that dermal absorption of gaseous vinyl chloride through the skin is not significant (ATSDR, 2006).

For use in the exposure calculations, an absorption of 100 % for both dermal and oral absorption is used even though dermal absorption is not considered significant.

10.4.4 Acute and chronic effects

Generally, the acute toxicity of vinyl chloride is low but anaesthetic effects have been reported in humans at short time exposures (5 minutes) at very high concentrations (> 30,000 mg/m^3). Liquid vinyl chloride may freeze tissue and produce a chemical burn as it evaporates (OECD, 2001). No data exist regarding the sensitising properties of vinyl chlorides (ECHA RSD, 2018).

The liver is the critical target organ at long-term oral exposure. A lifetime NOAEL value of 0.13 mg/kg bw/day has been observed for rats (OECD, 2001).

Vinyl chloride is not regarded as being toxic to reproduction, as no observed negative effects of this type have been observed for human exposure to vinyl chloride (OECD, 2001).

Vinyl chloride (and/or its metabolites) produces DNA damage and the substances have been tested positive as a mutagen in both *in vitro* and *in vivo* studies. Vinyl chloride is regarded as being carcinogenic to humans, i.e. it is known that long-term exposure in experimental animals and humans causes liver cancer (OECD, 2001). Therefore, vinyl chloride has a harmonised classification as Carc. 1A, H350 ” May cause cancer”.

10.4.5 Critical effect and calculation of DNEL/DMEL

The critical effect of vinyl chloride is liver cancer according to OECD (2011). OECD does not report a safe dose for the substance (RfD, DNEL or similar).

ATSDR (2006) reports that the US EPA has listed a RfD (Reference Dose) for vinyl chloride of 3 µg/kg bw/day based on a NOAEL for liver cell polymorphisms (variation of DNA sequence) in rats that orally were administered vinyl chloride during their entire lifetime. Based on this RfD, the US EPA derived a RfC (Reference Concentration) of 0.1 mg/m^3.

In the ECHA registration dossier of vinyl chloride, the below listed DMEL (Derived Minimu Effect Level) values are recorded for vinyl chloride (ECHA RSD, 2018). However, it should be noticed that DNELs listed in the registration dossiers are recorded by the industry and have not been reviewed by ECHA:

- Workers – long-term exposure via inhalation route, systemic effects: 7.7 mg/m^3
- General population – long-term exposure via inhalation route, systemic effects: 0.002 mg/m^3
- General population – long-term exposure via dermal route, systemic effects: ”hazard unknown”
- General population – long-term exposure via oral route, systemic effects: 1.4 ng/kg bw/day

In a working document prepared by Germany for the EU Expert Group on Toy Safety (subgroup chemicals’), and described in Lenzner et al. (2018), a calculated oral dose of 1.4 ng/kg bw/day is used as an acceptable additional lifetime risk of cancer of 1 x 10^{-6}. This value originates from SCCS (Scientific Committe on Consumer Safety), SCHER (Scientific Committee on Health and Environmental Risks) and SCENIHR (Scientific Committee on Emerging and

Newly Identified Health Risks), which in 2008 prepared an opinion on TTC (Threshold of Toxicological Concern). In this opinion, they established a range of limit values for chemical substances used in cosmetic products and other consumer products, including vinyl chloride. Here, they use a model with linear extrapolation and calculate this limit value of 1.4 ng/kg bw/day for vinyl chloride (SCCP, 2008).

It is debatable which value that is most correct to use in the risk assessment, as the value from SCCP based on the TTC concept is about 2,100 times lower than the limit value (RfD) established by ATSDR (2006). However, the same value as established by use of the TTC concept is also reported as a DMEL value for vinyl chloride in the ECHA database of registered substances. For this reason, and as a worst-case, the value of **1.4 ng/kg bw/day** is used for an additional lifetime risk of cancer of 1 x 10^{-6}.

11. Risk assessment

Risk assessment of residual monomers in toy materials as well as estimation of migration of monomers from toy materials that will not constitute a health risk for children

The migration analyses performed in this project showed no migration of the selected monomers from the examined toy products for any of the examined exposure scenarios. This means that no migration was measured in this project above the detection limit – either to artificial sweat when children are holding the toy in the hand, or to artificial saliva when small children are placing the toy in the mouth, or to stomach acid if children by accident swallow a small piece of toy material. In practise, no actual measurable exposure to residual monomers from the toy material takes place, and therefore, in practise, there is no exposure to base the exposure and risk calculations on.

However, some of the examined monomers have relatively low DNEL/DMEL values, which means that the exposure must be low to be able to eliminate a risk. Therefore, a method for exposure and risk calculations is described in Appendix 2 ”Risk calculations”, and exposure and risk calculations have been carried out for a range of hypothetical scenarios where it is assumed that migration takes place identically to the detection limit. Therefore, the calculations in these hypothetical scenarios are based on the detection limit, but the actual migration will be lower - how much lower is unknown, as it is not measurable.

In this chapter, the ‘backward’ calculation of the migration which is not expected to constitute a risk (or a minimal risk) for children is calculated. The estimate of the so-called ‘acceptable’ migration, which does not expect to constitute a risk for children, is based on the listed DNEL/DMEL values from the chapter ”Hazard assessment” and is described and calculated below. The point of reference is the situation, where small children are placing the toy in their mouth (i.e. sucking on the toy without swallowing the toy material) as it is assumed that this scenario will constitute a larger exposure compared to the situation where children are holding the toy in their hand because potential substances migrating will be ingested directly through the mouth.

11.1 Calculation of acceptable migration

The ‘backwards’ calculation of the so-called ‘acceptable’ migration of monomers from toy materials is carried out on the basis of the concentrations (exposures) that are regarded as not constituting a health risk for children (the used DNEL/DMEL values). In practise, this is an estimate of which migration of monomers from toy materials that will not constitute a health risk for children or will constitute a minimal health risk for children.

The point of departure is the formulas described in the REACH guidance document on consumer exposure assessment (ECHA, 2016a), which deals with exposure from substances that migrate from a product (appendix R.15.5), but modified for oral intake and for migration analysis performed for a specific surface of toy material in a specific amount of time (see if necessary the method descriptions in Appendix 2 ”Risk calculations”):

$$D_{oral} = \frac{A_{prod} \times MG_{prod} \times F_{contact} \times F_{abs} \times n}{BW}$$

where

D_{oral}	The dermal dose, i.e. the amount of substance that potentially can be absorbed per kg body weight. By use of F_{abs} the oral absorption rate of the substance is taken into consideration.	µg/kg bw/day
A_{prod}	Area of toy product used	cm^2
MG_{prod}	Amount of the substance that migrates per area unit (and for the time unit used at the migration analysis)	$µg/cm^2$
$F_{contact}$	Fraction of the product that is placed in the mouth to account for the fact that the product may only partially be in contact with the mouth (default value = 1)	-
F_{abs}	Fraction of substance absorbed by oral intake	-
n	Average number of incidents per day	/day
BW	Body weight	kg bw

As described in Appendix 2 ”Risk calculations”, the risk is expressed as Risk Characterisation Ratio (RCR) and is calculated as the ratio between the size of the exposure (D_{oral}) and the Derived No Effect Level (DNEL) – or as is the case of most examined substances in this project the Derived Minimum Effect Level (DMEL). The RCR value is calculated after the formula below:

$$RCR = \frac{Exposure\ (D_{oral})}{DMEL}$$

where

D_{oral}	The oral dose, i.e. the amount of substance that potentially can be absorbed per kg body weight. By use of F_{abs} the oral absorption rate of the substance is taken into consideration.	µg/kg bw/day
DMEL	The acceptable exposure i.e. the acceptable amount of substance that will not constitute a risk or a minimal risk for children	µg/kg bw/day

The DMEL value for the single monomers is regarded as being the ’acceptable’ exposure and is equivalent to the exposure D_{oral}, i.e. the RCR value is equivalent to 1. When it is assumed that the migration conditions are as described in EN 71-10, where a surface area of toy of 10 cm^2 for 100 ml migration fluid (simulant) for 1 hour is used, the so-called acceptable migration $MG_{prod\ acc.}$ will be equivalent to the DMEL value multiplied by the body weight of 10 kg as long as the toy placed in the mouth is 100 % in contact with the mouth ($F_{contact}$ = 1), and that 100 % of the monomers are absorbed by oral intake (F_{abs} = 1), as described in chapter 10 ”Hazard assessment” for de separate monomers.

However, it is suggested that the contact time should be 3 hours instead of 1 hour as this is the time it is assumed that a small child will place a toy in its mouth each day as worst case. This time is for example used for establishing the limit value for bisphenol A in toys (EU Directive no. 898, 2017) and it is the exposure time suggested by ANEC (2018).

As a standard mouthing time, 3 hours has been used (as described in Appendix 2.5) in this project, as the worst-case value for the time that small children are placing the toy in their mouth each day. If migration analyses are carried out on 10 cm^2 to 100 ml simulant for 3 hours at 37 °C, the calculation of the so-called acceptable migration can be simplified to the described formula below.

$$D_{oral} = \frac{MG_{prod\ acc.} \times F_{contact} \times F_{abs} \times n}{BW}$$

can be simplified to the formula below when $F_{contact}$ and F_{tabs} are equal to 1, and when migration analysis is carried out for 3 hours:

$$MG_{prod\ acc.} = DMEL \times BW$$

where

$MG_{prod\ acc.}$	Amount of acceptable substance that migrates per litre simulant (and for the time used at the migration analyses)	µg/l
DMEL	The exposure, i.e. the amount of substance that is acceptable (does not constitute a risk or a minimal risk for children)	µg/kg bw/day
BW	Body weight	kg bw
$F_{contact}$	Fraction of the product that is placed in the mouth, to account for the fact that the product may only partially be in contact with the mouth (default value = 1)	-
F_{abs}	Fraction of substance absorbed by oral intake (here 100 % = 1)	-
n	Average number of incidents per day	/day

The estimated ’acceptable’ migrations of the individual monomers are listed in Table 35 below. In the table the values and assumptions used in the calculations are listed as well. It should be noted that for the calculations it has been assumed that the exposure from the toy can represent 100 % of the DMEL value. In some cases (and as assumed by ANEC (2018) in their calculation of their suggested threshold limit value for styrene), it is assumed that the toy as a maximum may represent 10 % of the daily exposure.

When it is assumed that the ’acceptable’ exposure is the exposure that as a maximum is allowed to migrate into the used amount of migration fluid of 100 ml, the concentration of the ‘acceptable’ migration per litre migration fluid is calculated by multiplying by a factor of 10.

Table 35. Estimated ’acceptable’ migration of the individual monomers

Monomer	DMEL (µg/kg bw/day)	Body weight BW (kg bw)	F_{abs} (-)	Acceptable exposure (µg in total in 100 ml)	Acceptable migration $MG_{prod\ acc.}$ (µg/l simulant)
Acrylonitrile	0.0019	10	1	0.019	0.19
Butadiene	0.72	10	1	7.2	72
Styrene	7.7	10	1	77	770
Vinyl chloride	0.0014	10	1	0.014	0.14

Table 36 below contains the acceptable migrations for the individual monomers as calculated above as well as the used detection limits used for the migration analysis. In this project, the migration analyses to artificial saliva were carried out for 3 hours, but the amount of toy material used was as high as possible in proportion to the 100 ml simulant in order to obtain as high a migration as possible. This was a deliberate choice in order to increase the probability of detecting a migration. In practice, a surface area between 46 and 147 cm^2 toy material has been used for the migration analyses to artificial saliva.

Obviously, when more than 10 cm^2 toy material is used for the migration analyses, a higher migration is expected compared to migration from 10 cm^2 toy material. How much higher the migration is expected to be is not known for certain as linear correlation between surface area of toy material and amount migrated does not necessarily exist. Many other factors will play a role, like material thickness and the initial concentration of the monomer in the material.

Table 36. Estimated 'acceptable' migration of the individual monomers compared to the detection limit for the migration analyses to artificial saliva

Monomer	Estimated 'acceptable' migration $MG_{prod\ acc.}$ (µg/l simulant)	Detection limit for the migration analyses (µg/l simulant)
Acrylonitrile	0.19	10
Butadiene	72	10
Styrene	770	20
Vinyl chloride	0.14	10*

* It must be pointed out that no migration analyses have been carried out for vinyl chloride in this project, however, Eurofins has provided the information that the detection limit for vinyl chloride will be the same as for acrylonitrile and butadiene.

The detection limit for styrene and butadiene for the migration analyses is lower than the estimated 'acceptable' migration for these two monomers. Hence, migration of styrene and butadiene from toys at levels of the detection limit will not constitute a risk for children. Therefore, butadiene and styrene are not regarded as constituting a risk for children playing with the toy materials investigated in this project (ABS, PS, SBC and SEBS).

For vinyl chloride, it seems that the detection limit is too high in order to be able to assess whether a possible migration would be acceptable. However, no migration analyses have been performed in this project, as no content of the residual monomer vinyl chloride was identified above the detection limit of 0.1 mg/kg. Therefore, it is expected that a possible migration of vinyl chloride from PVC will be very low as well – and most likely non-detectable.

For acrylonitrile the detection limit is also too high to assess whether there is a risk when children are placing toy material of ABS in their mouth. The detection limit is too high compared to the estimated 'acceptable' migration. However, it should be noticed that for the calculated situation, the lowest identified DMEL value has been used. Moreover, a much higher surface area than the prescribed 10 cm^2 in the EN 71-10 standard has been used, which means that the probability of detecting a migration if acrylonitrile should migrate, ought to be higher under the used conditions.

In this project, a standard analysis for migration from food contact materials has been used. In this standard analysis the detection limit is 10 µg/l. It might be possible to obtain a lower detection limit for identification of acrylonitrile in solid materials, but it will then be necessary to develop the method further and use non-standardised analysis methods (based on the information received when contacting other institutes performing chemical analyses).

11.2 Discussion of the hypothetical scenarios

As formerly described, none of the selected monomers migrates from the examined toys in any of the examined scenarios. Therefore, in practice, no actual measurable exposure of residual monomers from the toys exists, and therefore, in practice, there is no exposure to carry out exposure and risk calculations on. However, in Appendix 2 "Risk calculations", exposure and risk calculations have been carried out for the hypothetical scenarios where a migration is assumed to take place from toy materials identical with the detection limit. Hence, the calculations of these hypothetical scenarios are based on the detection limit, but the actual migration will be lower – how much lower is unknown as it is not measurable

These calculations demonstrate that the detection limit is not low enough to be able to comment on the potential risk of migration of acrylonitrile from toy materials as the calculated RCR values for acrylonitrile are higher than 1 for some of the hypothetical scenarios. However, it is not possible to determine whether a risk occurs or not as no migration of acrylonitrile from toys (above the detection limit) has been measured. We do not know what the actual migration of acrylonitrile from toy materials would be as the detection limit when using the standardised methods is not adequately low. However, it should be noted that differences in the approach of establishing the DMEL value exist. For this reason, it is necessary with an updated reassessment of the DMEL value for children. This assessment has been out of the scope of this project.

The calculated daily hypothetical exposure to acrylonitrile from ABS toy materials for the different scenarios of between 0.02 and 0.101 µg/kg bw/day is based on the detection limit (described in Appendix 2) and is less than the maximum daily background exposure for the general population (including children) of 0.103 µg acrylonitrile/kg bw/day listed by different sources. This background exposure covers exposure from food, outdoor air etc.

For the other monomers (vinyl chloride, butadiene and styrene), the risk calculations in Appendix 2.6 illustrate that no health risk will occur for these monomers by either dermal exposure (holding toy in the hand) or oral exposure (swallowing a small part of a toy material or when placing the toy in the mouth) if they were to be released from the toy materials in amounts corresponding to the detection limit.

11.3 Discussion and conclusion

An essential conclusion of this project is that no migration of any of the examined monomers (acrylonitrile, butadiene and styrene) has been measured above the detection limit of 10 µg/l migration fluid (corresponding to 0.01 mg/l) from any of the two examined ABS toy materials or the two examined PS toy materials at any of the five performed migration analyses, including migration to stomach acid simulant.

The detection limit for migration to stomach acid has been used as an expression of the maximum amount of monomer that hypothetical can be released to the stomach if a child should swallow a small part of a toy material[26]. This is a hypothetical scenario as the detection limit has been used as the level of the migration even though the actual migration (below the detection limit) is unknown. This exposure calculation showed that migration (or the content in the situations where migration to stomach acid was not analysed) of the residual monomers from the examined toy materials will not constitute a risk for any of the examined monomers or any of the examined toy materials (ABS, PS, PVC, SEBS and SBC).

Regarding the assessment of the risk by oral exposure when small children have toy placed in their mouth, an ‘acceptable’ migration from the toy material was estimated. The detection limit for both butadiene and styrene is much lower than the estimated ‘acceptable’ migration from toy materials for these two monomers. Therefore, these two monomers are not regarded as constituting a risk for children playing with toy materials based on these monomers.

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[26] The following comment to the report was received: The analysis method described in EN 71-3 regarding migration to stomach acid is not applicable as worst-case for organic compounds. Instead a digestion model simulating real life should be used. However, no such validated model is available today.

However, for acrylonitrile, the used detection limit for the migration analyses is too high to assess whether there is a potential risk. A lower detection limit is needed in order to demonstrate if the risk is acceptable. However, the same detection limit as for migration of acrylonitrile from food contact materials has been used which could indicate that at present it is not possible to obtain a lower detection limit unless the method is further developed and non-standardised analyses methods are used. However, it should be noted that differences in the approach of establishing the DMEL value exist. For this reason, it is necessary with an updated reassessment of the DMEL value for children.

Existing data in the literature regarding migration of these monomers from toy materials are limited. Only two former investigations of migration of these monomers have been identified and in both cases ABS toy materials have been analysed:

- One investigation has been carried out by a toy producer. Several migration analyses have been carried out during the last 5 to 6 years. During this period, migration of the three monomers have been measured to 3 % acetic acid for 24 hours at 40 °C from in all 20 products. The result was that no migration of any of the monomers was identified in any of the samples. The detection limit was the same as in this project, i.e. 10 µg/l migration fluid (TIE, 2018b).
- The other investigation is a Japanese survey (Abe et al., 2013), where 10 migration analyses of ABS toy materials to water for 30 minutes at 40 °C were carried out. Here, migration of acrylonitrile was identified in 1 case out of 10 (the migration was equal to the detection limit of 3 µg/l) and styrene migrated in 9 cases out of 10 (in concentrations between 6 and 40 µg/l). Here, the detection limit was 3 µg/l for acrylonitrile and 1 µg/l for styrene. Migration of butadiene was not investigated.

Hence, it is only in the Japanese survey by Abe et al. (2013) that migration of these monomers has been identified above the detection limit. However, Abe et al. (2013) emphasises that their method most likely has measured too high migration levels, as methanol was added as a solvent for the internal standard which may have increased the migration of both acrylonitrile and styrene from the toy materials. Regardless of whether this is true, the migration of styrene from these 10 toy materials is below the estimated ‘acceptable migration’ for styrene, i.e. the migration that will not constitute a risk for children – and for acrylonitrile, no migration was identified in 9 cases out of 10.

12. Discussion in relation to ANEC's proposal

As described in section 3.3 ”Proposal from ANEC for legislation on monomers in toys”, the European consumer organisation ANEC has proposed the following limit values for five selected monomers (ANEC, 2018) in toys for children below 3 years and for toys intended to be placed in the mouth:

- A content limit of 1 mg/kg for vinyl chloride in toys of PVC
- A content limit of 1 mg/kg for 1,3 butadiene when the substance is used as a monomer in toy materials
- A content limit of 1 mg/kg for acrylonitrile when the substance is used as a monomer in toy materials
- A content limit of 1 mg/kg for acrylamide when the substance is used as a monomer in toy materials
- A migration limit value of 0.077 mg/l simulant for styrene following 3 hours extraction of the toy material or one third of this value if the extraction procedure as described in EN 71-10 is used (where extraction for 1 hour is used).

It must be noted that these proposed content limit values of 1 mg/kg for four of the monomers are based on an assumption that the entire amount of residual monomer which is contained in 8 mg toy material that is swallowed will be released in the body. The migration analyses carried out in this project show that this is not the case as no migration above the detection limit of the migration analyses to stomach acid is measured.

Based on the results in this report, the following can be concluded in relation to the limit values proposed by ANEC:

- PVC toys seem to be able to easily comply with the content limit value of 1 mg/kg for vinyl chloride in PVC. All 11 PVC products examined in this project had a content of vinyl chloride under the detection limit of 0.1 mg/kg. Today, a corresponding content limit value of 1 mg/kg exists for food contact materials.
- The majority of the examined toys seem to be able to comply with the content limit value of 1 mg/kg for butadiene. Eight out of 10 ABS products and both SBC products examined in this project had a content of butadiene below this value. Today, a corresponding limit value of 1 mg/kg exists for food contact materials.
- ABS materials will not be able to apply with the content limit value of 1 mg/kg for acrylonitrile. All of the 10 examined ABS products in this project had a content of acrylonitrile above this value. Data from the literature also indicate that the content of acrylonitrile typically is above 1 mg/kg even though a few data show level below this proposed limit value. In practice, adoption of this proposed limit value will actually result in a ban on the use of ABS as a material for toys for children under 3 years or for toys intended to be placed in the mouth. It must be noted that for food contact materials no corresponding limit value for the content of acrylonitrile is established but only a limit value for migration of the monomer corresponding to the detection limit which is used in this project.
- The monomer acrylamide has not been examined in this project.
- Toy materials which contain styrene as residual monomer seem to be able to easily comply with the migration limit value for styrene of 77 µg/l simulant (for 3 hours migration of 10 cm^2 toy material). No migration of styrene above the detection limit of 10 µg/l simulant has been measured in this project and data from the literature do not either indicate any migration of styrene above this proposed value.

13. Economic impact

What will the economic impact be for the toy industry if the selected monomers would be banned or regulated in toys?

During this survey, the producers and importers of toys were asked which economic impact it would have on the toy industry if the selected monomers would be banned or regulated in toys. Limited information was received from the toy industry, but TIE sent a collective answer based on information received from its members (TIE, 2018b).

The economic impact would depend on which kind of ban or regulation that potentially would be adopted. The discussion is therefore divided in two parts:
1. Economic impact of limit values for migration of residual monomers
2. Economic impact of limit values for content of residual monomers

13.1 Economic impact of limit values for migration

The proposal for a restriction of the five monomers in toys as presented by ANEC (described in section 3.3 ”Proposal from ANEC for legislation on monomers in toys”) only suggests a specific migration limit value for styrene (of the five monomers). However, TIE (2018b) states that a regulatory restriction ought to be based on the actual exposure, i.e. migration and not content, if this restriction should be established for residual monomers in toys. TIE makes it clear that limit values for migration of residual monomers should only be established if based on a risk assessment (performed by SCHEER), it is deemed necessary in order to protect the health of children.

According to TIE, establishing limit values for migration of residual monomers from toy materials will involve additional expenses for testing in order to be able to demonstrate compliance for the toy materials with the established legal requirements. TIE points out that the toy industry primarily consists of small companies (SMEs) and for this reason additional testing expenses will constitute a substantial economic impact for the industry.

13.2 Economic impact of limit values for content

The proposal for a restriction of the five monomers in toys presented by ANEC (described in section 3.3 ”Proposal from ANEC for legislation on monomers in toys”) suggests a content-based limit value for each of the monomers acrylonitrile, butadiene, vinyl chloride and acrylamide of 1 mg/kg. Acrylamide has not been in focus in this project and is therefore not discussed any further.

Regarding vinyl chloride, the analyses carried out in this project together with the results of the survey show that the content of vinyl chloride in PVC in general is very low. Therefore, PVC toy materials seem to comply with the suggested limit value. TIE (2018b) points out that an adoption of this content limit value for vinyl chloride in PVC will not result in an additional protective effect of children and will only impose additional costs for chemical analyses to be able to demonstrate compliance with the potential legislation.

Concerning the proposed content limit value for butadiene, the results of this project show that the content of butadiene in materials such as SBC and SBS is far below the suggested limit value whereas the content of butadiene in ABS in some cases is found to be above the suggested limit value of 1 mg/kg. In the literature, levels of butadiene of up to about 5 mg/kg have been identified. The chemical analyses performed in this project have also identified levels above 1 mg/kg (1.05 and 1.55 mg/kg respectively). However, it should be noticed that the main part of the investigated ABS toy materials – both in the literature and in this project – will be able to comply with the proposed limit value of 1 mg/kg.

However, for acrylonitrile in ABS material, it is only a few of the results of the chemical analyses – both in this project and results identified in the survey – that have a content level below the proposed limit value of 1 mg/kg. Most of the chemical analyses concerning the content of acrylonitrile in ABS materials have values above 1 mg/kg. Both in this project and in the literature, levels of acrylonitrile up to about 50 to 64 mg/kg have been identified, i.e. significantly higher than the proposed limit value. In practice, adoption of a limit value of 1 mg/kg for acrylonitrile used as co-monomer would result in a ban on the use of ABS for toys to children below the age of 3 years or for toys intended to be placed in the mouth (e.g. music instruments). TIE (2018b) points out that ABS mainly is used due to its mechanical resistance and that it allows toys for children under 3 years to comply with the mechanical and physical safety requirements of the Toy Safety Directive for toys for this age group. In fact, this is one of the reasons why a large part of toys for children in this category (below the age of 3 years) is manufactured in ABS.

It is evident that ceasing to use ABS in toy products for children below the age of 3 years and in toy products intended to be placed in the mouth will have tremendous economic consequences for the toy industry as a lot of toy products would have to be developed in completely different materials. As described in the survey, ABS is a material that is used for a lot of toys and also used for a lot of toys for toddlers (like rattles, teething rings, bath toys) and music instruments intended to be placed in the mouth (see also Appendix 1 ”Information from TIE” and Table 8). Four out of the seven producers that supplied information about materials used in toys (see Table 4) have stated that the main part of the toys consists of ABS. A content limit value for acrylonitrile of 1 mg/kg which in practice will result in a ban on the use of toy products made of ABS for children below the age of 3 years (and for toy products intended to be placed in the mouth) will therefore not only have consequences for a small part of the toy industry, but will widely affect the entire toy industry and will have enormous far-reaching consequences.

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Appendix 1. Information from TIE

This appendix contains information received from TIE regarding materials used for toys.

On the next pages, three tables are listed. Table 37 (Part 1) and Table 38 (Part 2) contain information on the type of polymer material used in different categories of toys. The table is split into two tables in order to fit in the page. ‘Part 1’ shows the materials which contain one or more of the five monomers, whereas ‘Part 2’ shows the materials which do not contain any of the five monomers, i.e. materials like PE and PP. In order to fit in the table to the page, empty lines without any data for either materials with or without the five monomers have been deleted.

The next table (Table 39) contains an estimated percentage distribution (when information was available) of the use of these materials distributed on different categories of toys. For this table it was possible to list all materials on one page and in one table.

It should be noted that all three tables contain information about toys which fall under Appendix C of the Statutory Order on Toys, i.e. toys intended for use by children below 36 months or in other toys intended to be placed in the mouth. This means that toys for the age of 3-14 years are not included in these tables – neither are materials (internal components) which are not accessible to children (exposure-wise).

It should also be noted that TIE asked their members to respond to the materials ASA, NBR and PAM, but none of the members have stated that they use these materials in toys intended for children under the age of 3 years or in toys intended to be placed in the mouth. These empty columns (as received from TIE) are therefore not included in the tables below in order to fit in the tables to the page.

Table 37. Part 1: Available polymer materials in toys intended for children of the age 0 to 3 years or toys intended to be placed in the mouth (Appendix C of the Danish Statutory Order on Toys). Content of polymer materials that contain one or more of the carcinogenic monomers.

Toy category	Toy for children below the age of 3 years	Toy (children > 3 years) intended to be placed in the mouth	PVC	ABS	MABS	SBS	SEBS	SBC	SAN	PS (including HIPS, MIPS, etc.)	TPE
Stuffed toys with soft plastic, baby dolls	Yes		X (head, body, limbs)								
Dolls	Yes		X (head, limbs, accessories)	X (body, limbs, accessories)							X (closure gasket, accessories)
Stuffed toys with hard plastic	Yes			X (collar, buttons, body)						X (buttons)	
Toy Cars (Set)	Yes		X (figurine)	X (body, wheels, buttons)							X (tire)
Push/pull–along Toys	Yes			X (body, wheels, buttons)	X (clear covers)						X (tire)
Baby/infant Stimulation Toys	Yes		X (cable, figurine)	X (wheels, buttons, and part of body)	X (clear covers)					X (hinge)	
Educational Toys	Yes		X (cable)	X (body and buttons)	X (clear covers)					X (hinge)	X (soft handle, watch waist)
Walkers	Yes			X (body, buttons)	X (clear covers)						X (tire)
Bath/pool Toys	Yes		X (head, body, limbs)	X (body and buttons)							
Bath toys	Yes		X (entire toy, suction cup)				X (suction cup)				
Inflatable toys	Yes		X (entire toy, suction cup)								

Toy category	Toy for children below the age of 3 years	Toy (children > 3 years) intended to be placed in the mouth	PVC	ABS	MABS	SBS	SEBS	SBC	SAN	PS (including HIPS, MIPS, etc.)	TPE
Inflatable toys	Yes	Yes	X (air inflation inlet)								
Magnetic drawing board	Yes		X (drawing board, cover sheet, cable)	X (body and buttons)							
Scooter	Yes										X (foot deck cover, handle grip, seat cover)
Scooter/ride-on toys			X (wheels, handles)	X (structure)			X (wheels, handles)	X (transparent windscreen)	X (sprocket)		X (wheels, handles)
Ride-on toys	Yes										
Animal figurines	Yes		X (entire toy)								X (entire toy)
Teethers	Yes			X (entire toy)		X (entire toy)	X (entire toy)				X (entire toy)
Teethers	Yes			X (entire toy)							
Teethers	Yes							X			
Teethers				X (body)							
Rattles	Yes			X (non-transparent parts)	X (transparent parts)						
Rattles				X (entire toy)							
Construction toys	Yes										
Construction toys	Yes			X (entire toy)			X (components)				
Creative toys: stamps	Yes										
Foam shapes	Yes										

Toy category	**Toy for children below the age of 3 years**	**Toy (children > 3 years) intended to be placed in the mouth**	**PVC**	**ABS**	**MABS**	**SBS**	**SEBS**	**SBC**	**SAN**	**PS (including HIPS, MIPS, etc.)**	**TPE**
Musical instruments (trumpet, saxophone)		Yes								X (entire toy)	
Musical instruments (drum)	Yes									X (entire toy)	
Activity toys	Yes			X (casing)				X (LED cover)			
Puzzles	Yes									X (entire toy)	
Educational toys (colours and shapes)	Yes									X (components)	
Sand toys	Yes			X (components)							

Table 38. Part 2: Available polymer materials in toys intended for children of the age 0 to 3 years or toys intended to be placed in the mouth (Appendix C of the Danish Statutory Order on Toys). Content of polymer materials that do not contain one or more of the carcinogenic monomers.

Toy category	Toy for children below the age of 3 years	Toy (children > 3 years) intended to be placed in the mouth	Nylon	PUR	PP	PE (PEHD or PELD)	EVA
Stuffed toys with soft plastic, baby dolls	Yes						
Dolls	Yes				X (accessories)	X (limbs)	
Stuffed toys with hard plastic	Yes						
Toy Cars (Set)	Yes						
Push/Pull–along Toys	Yes						
Baby/Infant Stimulation Toys	Yes						
Educational Toys	Yes						
Walkers	Yes						
Bath/ Pool Toys	Yes						
Bath toys	Yes						
Inflatable toys	Yes						
Inflatable toys	Yes	Yes					
Magnetic Drawing board	Yes						
Scooter	Yes		X (foot deck frame, pivot, seat frame, seat body)	X (wheel)	X (foot deck cover, brake, wheel core, seat cover, footrest)		
Scooter/ride-on toys							
Ride-on toys	Yes				X (components)	X (main body)	
Animal figurines	Yes						
Teethers	Yes						
Teethers	Yes				X (entire toy)		
Teethers	Yes						

Toy category	Toy for children below the age of 3 years	Toy (children > 3 years) intended to be placed in the mouth	Nylon	PUR	PP	PE (PEHD or PELD)	EVA
Teethers							X (parts to be bitten)
Rattles	Yes					X (entire toy)	
Rattles					X (entire toy)		
Construction toys	Yes					X (entire toy)	
Construction toys	Yes						
Creative toys: stamps	Yes				X (entire toy)		
Foam shapes	Yes						X (entire toy)
Musical instruments (trumpet, saxophone)		Yes					
Musical instruments (drum)	Yes						
Activity toys	Yes						
Puzzles	Yes						
Educational toys (colours and shapes)	Yes				X (components)		
Sand toys	Yes				X (components)	X (components)	

Table 39. Available polymer materials in toys intended for children of the age 0 to 3 years or toys intended to be placed in the mouth (Appendix C of the Danish Statutory Order on Toys). Estimated percentage distribution of use of materials.

Toy category	Toy for children below the age of 3 years	Toy (children > 3 years) intended to be placed in the mouth	PVC	ABS	MABS	SEBS	PS (including HIPS, MIPS, etc.)	TPE	Nylon	PUR	PP	PE	EVA
Stuffed toys with soft & hard plastic, baby dolls, toy cars, bath toys, push/pull toys, stimulation and educational toys	Yes		1.7 %	60 %	3 %		1 %	1.5 %			30 %	2 %	
Bath toys			90 %										
Dolls	Yes		30 %	60 %				2 %			5 %	3 %	
Inflatable toys		Yes	100 %										
Scooter	Yes							10 %	50 %	10 %	25 %	5 %	
Ride-on toys	Yes										17 %	83 %	
Animal figurines	Yes		50 %					50 %					
Teethers	Yes			55 %							40 %		
Rattles				48 %			5 %				35 %		
Construction toys	Yes											100 %	
Construction toys	Yes			80 %		3 %							
Creative toys: stamps	Yes										100 %		
Foam shapes	Yes												100 %
Musical instruments (trumpet, saxophone)		Yes					100 %						
Musical instruments (drum)	Yes						100 %						
Sand toys	Yes			25 %							40 %	18 %	

Appendix 2. Risk calculations

This appendix contains a description of the method used in the exposure and risk calculations, and the actual calculations carried out for a range of hypothetical use scenarios. The scenarios are called hypothetical as the detection limit has been used as the amount of substances migrating from the toy materials even though no real migration has been measured for any of the examined monomers above the detection limit.

First, the method used for the calculations is presented together with the used values, and secondly, the actual calculations and the results are presented.

In principle, exposure to residual monomers in toy materials can take place through the different exposure routes: dermal, oral and inhalation. However, exposure by inhalation is a route of exposure which has not been a focus point in this project. All monomers are, by definition, volatile organic compounds where vinyl chloride and butadiene are the most volatile substances of the four examined monomers. Moreover, vinyl chloride and butadiene are the two monomers that have been identified in the lowest concentrations in the examined toy materials. Exposure from the toy materials through the inhalation route is considered to be negligible as this exposure will be diluted by the surrounding air. Therefore, the focus points in this project have been oral exposure – either when the small children are placing the toy in their mouth or when they accidently swallow a small part of the toy material, and dermal exposure, i.e. when children hold their favorite toy in their hand for several hours each day.

The hypothetical scenarios which have been described and calculated are:

- Dermal exposure for 8 hours (children who hold their favourite toy in their hand for a large part of the day)
- Oral exposure for 3 hours for children who place the toy in their mouth (suck the toy)
- Oral intake of 8 mg toy material which is the prevailing amount of toy assumed to be swallowed each day (Lenzner et al., 2018). In this scenario, the actual migration to the stomach (by use of the results for the migration analyses to stomach acid) has been taken into account.

No actual migration has been measured for these scenarios in the conducted migration analyses. Therefore, it should be noticed that these scenarios are sheer hypothetical. Even for migration to stomach acid, no migration above the detection limit was detected. Therefore, in the case where a child accidently swallows a small part of a toy material, it is not expected that a potential content of residual monomer will be released into the body (at least not in amounts above the detection limit). Therefore, the calculations in these scenarios are based on the detection limit, but the actual migration will be lower – how much lower is unknown as it is not measurable. However, the exposure calculations for these hypothetical scenarios have been carried out as some of the examined monomers have relatively low DNEL/DMEL-values which means that the exposure must be relatively small to be able to eliminate a risk.

The calculations and results are presented in this appendix but are discussed in chapter 11 ”Risk assessment”.

Appendix 2.1 Method for calculation of the dermal exposure

For calculation of the dermal exposure to which small children will be exposed by use of toy that contains materials with the relevant monomers, the model for calculation of dermal exposure as listed by ECHA is used as a starting point. According to the REACH guidance document on consumer exposure assessment (ECHA, 2016a), the exposure for a substance migrating from a product can be described by use of the following equation (appendix R.15.5).

$$D_{der} = \frac{Q_{prod} \times F_{prod} \times F_{migr} \times F_{contact} \times T_{contact} \times 1000\, mg/g \times n}{BW}$$

where

D_{der}	The dermal dose, i.e. the amount of substance that potentially can be absorbed per kg body weight. Later in the calculations, the dermal absorption rate of the substances is taken into consideration	mg/kg bw/day
Q_{prod}	Amount of product used	g
F_{prod}	Weight fraction of the substances in the product	g/g product
F_{migr}	Migration rate of substance migrating to skin per unit time (hours)	g/g/hours
$F_{contact}$	Fraction of contact area for skin to account for the fact that the product is only partially in contact with the skin (default value = 1)	cm^2/cm^2
$T_{contact}$	Contact duration between product and skin	hours
n	Average number of incidents per day	/day
BW	Body weight	kg bw

In this project, the migration analyses have been carried out for the specific time assumed to be the worst-case contact time for the different scenarios. Therefore, the result from the migration analysis (measured in $\mu g/cm^2$) can be used directly instead of the weight fraction of the substance in the product (F_{prod}), the migration rate (F_{migr}) and the contact time ($T_{contact}$). In this project, the migration analyses have been carried out for a specific surface area of the toy material. For this reason, the analysis result from the migration (migrated substance per cm^2 product) can be multiplied by the total area of toy material (A_{prod}) and thereby correspond to the total amount of substance migrating from the toy material, when the exposure is calculated for a specific area in contact with skin. Moreover, it will not be the entire amount of the migrated monomer that in fact will be absorbed through the skin. The modified formula for the exposure calculations carried out in this report is therefore:

$$D_{der} = \frac{A_{prod} \times MG_{prod} \times F_{contact} \times F_{abs} \times n}{BW}$$

where

D_{der}	The dermal dose, i.e. the amount of substance that potentially can be absorbed per kg body weight. By use of F_{abs} the dermal absorption rate of the substance is taken into consideration	µg/kg bw/day
A_{prod}	Area of toy product used	cm^2
MG_{prod}	Amount of the substance that migrates per area unit (and for the time unit used at the migration analysis)	$\mu g/cm^2$
$F_{contact}$	Fraction of contact area for skin to account for the fact that the product is only partially in contact with the skin (default value = 1)	-
F_{abs}	Fraction of substances that are absorbed through the skin	-
n	Average number of incidents per day	/day
BW	Body weight	kg bw

As part of this worst-case scenario, it is assumed that e.g. the measured migration is constant during the used exposure time.

Appendix 2.2 Method for calculation of the oral exposure (toy placed in the mouth)

Calculation of the oral exposure to which small children will be exposed by placing the toy in their mouth (suck the toy), which contains materials with the relevant monomers uses as a starting point the calculation model as outlined above for dermal exposure but modified for oral exposure. Here, migration from the toys is still relevant.

$$D_{oral} = \frac{A_{prod}\ (Q_{prod}) \times MG_{prod} \times F_{contact} \times F_{abs} \times n}{BW}$$

where

D_{oral}	The oral dose, i.e. the amount of substance that potentially can be absorbed per kg body weight. By use of F_{abs} the oral absorption rate of the substance is taken into consideration	µg/kg bw/day
A_{prod} (Q_{prod})	Area of toy product used (or amount of product used)	cm^2 (or g)
MG_{prod}	Amount of the substance that migrates per area unit (and for the time unit used at the migration analysis) (or per amount)	µg/cm^2 (or µg/g)
$F_{contact}$	Fraction of contact area for skin to account for the fact that the product is only partially in contact with the skin (default value = 1)	-
F_{abs}	Fraction of substance absorbed by oral intake	-
n	Average number of incidents per day	/day
BW	Body weight	kg bw

Appendix 2.3 Method for calculation of oral exposure (swallow toy)

Calculation of the oral exposure to which small children will be exposed by swallowing a little part of a toy material which contains materials with the relevant monomers uses as a starting point the calculation model as outlined above. However, the calculation model has been modified for oral exposure and for migration analyses conducted for a specific surface area of toy material for a specific amount of time.

As worst-case the content concentrations of residual monomers identified by the chemical content analyses carried out in this project are used. This means that it is assumed that the entire amount of residual monomers which is contained in the toy material being swallowed will be released in the stomach. However, for some products it is the actual migration from the toy material to the stomach[27] which is used (instead of the content). In fact, it is the detection limit for the migration analyses which is used, as no migration of residual monomers above the detection limit was identified in any of the cases.

$$D_{oral} = \frac{MG_{prod}\ (Q_{prod} \times F_{prod}) \times F_{abs} \times n}{BW}$$

where

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[27] The following comment to the report was received: The analysis method described in EN 71-3 regarding migration to stomach acid is not applicable as worst-case for organic compounds. Instead a digestion model simulating real life should be used. However, no such validated model is available today.

D_{oral}	The oral dose, i.e. the amount of substance that potentially can be absorbed per kg body weight. By use of F_{abs} the oral absorption rate of the substance is taken into consideration	µg/kg bw/day
MG_{prod}	Amount of the substance that migrates per amount of product (and for the time unit used at the migration analysis)	µg/g
Q_{prod}	Amount of toy product swallowed	g
F_{prod}	Weight fraction of the substance in the product	µg/g product
F_{abs}	Fraction of substance absorbed by oral intake	-
n	Average number of incidents per day	/day
BW	Body weight	kg bw

Appendix 2.4 Method for calculation of risk

According to the REACH guidance document for risk characterisation, it is assessed in each single case whether there is a risk of health effects based on the formula below. The risk is expressed as Risk Characterisation Ratio (RCR) which is calculated as the ratio between the size of the exposure (D_{oral}) and the Derived No Effect Level (DNEL) – or in the case of most of the examined substances in this project the Derived Minimum Effect Level (DMEL). The DMEL is used in cases where it is not possible to establish a lower limit for effects – instead a limit for minimal effects or a minimal risk is established:

$$RCR = \frac{Exposure\ (D_{der}\ or\ D_{oral})}{DMEL}$$

If RCR > 1 (i.e. the exposure is larger than the DMEL), a risk occurs for the specified scenario. If RCR < 1, the exposure is not considered to constitute a health risk.

Appendix 2.5 Used values in the exposure and risk calculations

The following values have been used for the exposure and risk calculations carried out in this project:

Dermal (D_{der}) / Oral (D_{oral}) exposure

D_{der} and D_{oral} are the calculated dermal and oral exposure of a specific substance, respectively. This exposure is used in the risk assessment. The dermal exposure illustrates the exposure when a child holds a piece of toy in its hand, and the oral exposure illustrates the exposure when a child either has part of the toy material placed in the mouth or where the child swallows a little piece of the toy material.

Amount of product (Q_{prod}) / Surface area of product (A_{prod})

Q_{prod} is the total weight of the toy material, which is e.g. swallowed per day (oral intake). Here it is assumed that an amount of 8 mg is swallowed each day, which corresponds to a little piece scraped of the toy when the child has placed the toy in its mouth. This value of 8 mg toy material is the value which is used as a default value in the toy directive for amongst other things calculation of limit values for metals (Lenzner et al., 2018).

A_{prod} is the total surface area of the toy material with which the child is in skin contact by holding the toy in its hand or when the child is placing the toy in the mouth (sucking on the toy). It is assumed that a small child below the age of 3, when sucking a toy, will have a surface area of 10 cm^2 in its mouth. This is the same value as was used by the EU Commissions appointed expert group on “Toy Safety” (sub-group Chemicals) to establish the specific limit value for e.g. bisphenol A in toys (EU Directive no. 898, 2017).

The surface area A_{prod} with which a child below the age of 3 years is in skin contact when holding a piece of toy in its hand, is assumed to be 67.5 cm^2. This value corresponds to half of the surface area of a hand of a 1-2-year-old child. The entire surface area of a 1-2-year-old child's hand is 135 cm^2 (or the total surface area of both hands is listed as 270 cm^2 in table 31 in RIVM (2014)).

Migration (MG_{prod})

MG_{prod} is the amount of a substance that by chemical analysis has demonstrated to migrate from the product to the used migration medium (artificial saliva) at 37 °C during the time $T_{contact}$. MG_{prod} is equal to the result of the migration analysis – or in practice, equal to the detection limit for the migration analysis (for a specific surface area of toy material (A_{prod})).

$T_{contact}$ is not used directly in the calculations but is automatically included in the result of the migration analyses where the migration has been carried out for a specific time. In this project, an exposure time of 2 hours has been used for the migration analysis to stomach acid as prescribed by the standard. In other migration analyses, the following worst-case exposure times are used: 8 hours per day for dermal exposure (holding the toy in the hand) and 3 hours per day for oral exposure (placing the toy in the mouth). The 3 hours used for mouthing time of the toy (sucking the toy) is the same value which is used by the EU Commissions appointed expert group on "Toy Safety" (sub-group Chemicals) to establish the specific limit value for e.g. bisphenol A in toys (EU Directive no. 898, 2017).

Weight fraction of the substance in the product (F_{prod})

F_{prod} is the weight faction of the substances in the product, i.e. the result of the content analysis of the residual monomers in the products. For vinyl chloride, where no content above the detection limit was identified, the detection limit has been used as an expression of the maximum content.

Fraction of area in contact with skin/mouth ($F_{contact}$)

$F_{contact}$ is the fraction of the product, which is in contact with the skin or the mouth.

For skin contact a value of 0.5 is used as it is assumed that the palm of a child's hand will not be in 100 % contact with the toy material at all time. This compensates for the fact that it is not the entire surface area of the palm (A_{prod}), which is in contact with the toy when squeezing the toy. It should be noticed that the surface area of a palm is calculated as half of the total surface area of a hand, i.e. including the surface area between the fingers. In practice, this area between the fingers will not be in contact with the toy, when the child is squeezing it. This means that the area, for which a small 1-2-year-old child is in contact with a toy by holding it in one hand will be 33.75 cm^2 (67.5 cm^2 x 0.5) or corresponding to an area of about 5 x 6.8 cm.

For contact with the mouth, a default value of 1 is used, as it is assumed that the child has the entire used area in their mouth. The used area of 10 cm^2 is a default value for the assumed surface area of a toy, which a small child is expected to be able to place in the mouth.

Absorption (skin absorption/oral intake (F_{abs}))

F_{abs} is the fraction of the substance which is absorbed through the skin or orally. The fraction is listed in 10 "Hazard assessment" for the different monomers and specific values are used if they exist. Otherwise, 100 % is used as a worst-case in case of lack of data.

Incidents per day (n)

The average number of incidents per day, n, where small children swallow a piece of toy material, have the toy in their mouth or hold the toy in their hand is assumed to be 1 per day.

Body weight (BW)
A value of 10 kg has been chosen as the body weight of a child of the age below 3 years. This value is also used by the EU Commissions appointed expert group on “Toy Safety” (sub-group Chemicals) to establish the specific limit value for e.g. bisphenol A in toys (EU Directive no. 898, 2017). A body weight of 10 kg corresponds to small children of the age of 1 to 2 years (according to table 19 in RIVM (2014)).

DMEL (µg/kg bw/day)
DMEL (Derived Minimum Effect Level) is the exposure determined in the hazard assessment in chapter 10, where no health-related effects are expected or where a minimum health-related effect is expected to occur.

Appendix 2.6 Exposure and risk calculations

The exposure and risk calculations are carried out as described in chapter 11 ”Risk assessment” for the below hypothetical scenarios:

- Dermal exposure for 8 hours (children who hold their favourite toy in their hand for a large part of the day)
- Oral exposure for 3 hours for children who place the toy in their mouth (suck the toy)
- Oral intake of 8 mg toy material, which is the prevailing amount of toy assumed to be swallowed each day (Lenzner et al., 2018). In this scenario, the actual migration to the stomach (by use of the results for the migration analyses to stomach acid) has been taken into account.

The scenarios are hypothetical as no actual migration has been measured in the migration analyses performed for these scenarios. Therefore, the calculations in these scenarios have been based on the detection limit, but the actual migration will be lower – how much lower is not known, as it is not measurable. Obviously, if an analysis method with a lower detection limit was used and if a lower migration was in fact measured (lower than the detection limit for the migration analyses performed in this project), the calculated RCR values would be correspondingly lower.

It should be noticed that the differences between the migration result of the residual monomers of ABS4 and ABS10, as well as PS1 and PS4 in the tables below solely are due to the differences in the amount of toy materials used for the analysis and the volume of the migration fluid used to cover the toy materials. Among other things, the ratio between the amount of toy material and the volume of migration fluid depends on the shape of the toy material as the toy material has been cut into as few pieces as possible when performing the migration analyses.

Exposure and risk calculations for dermal exposure D_{der}

The different parameters and values used in the exposure and risk calculations for the scenario where a child is holding its favourite toy in its hand for a large part of the day (8 hours) are listed in Table 40 and Table 41 below. The result, the dermal exposure D_{der} is also listed and the RCR values have been calculated.

Table 40. Exposure calculation of dermal absorption D_{der} for selected ABS toy materials

Product no.	**ABS4**			**ABS10**		
Monomer	**Acrylonitrile**	**Butadiene**	**Styrene**	**Acrylonitrile**	**Butadiene**	**Styrene**
A_{prod} (cm^2)	67.5	67.5	67.5	67.5	67.5	67.5
MG_{prod} (µg/cm^2)	0.03	0.03	0.06	0.011	0.011	0.021
$F_{contact}$ (-)	0.5	0.5	0.5	0.5	0,5	0.5
F_{abs} (-)	1	1	0.02	1	1	0.02
n (per day)	1	1	1	1	1	1
BW (kg bw)	10	10	10	10	10	10
D_{der} (µg/kg bw/day)	**0.101**	**0.101**	**0.004**	**0.037**	**0.037**	**0.001**
DMEL (µg/kg bw/day)	0.0019	0.72	7.7	0.0019	0.2	7.7
RCR (-)	**53.3**	**0.14**	**0.0005**	**19.5**	**0.05**	**0.0002**

Table 41. Exposure calculation of dermal absorption D_{der} for selected PS toy materials

Product no.	**PS1**	**PS4**
Monomer	**Styrene**	**Styrene**
A_{prod} (cm^2)	67.5	67.5
MG_{prod} (µg/cm^2)	0.03	0.10
$F_{contact}$ (-)	0.5	0.5
F_{abs} (-)	0.02	0.02
n (per day)	1	1
BW (kg bw)	10	10
D_{der} (µg/kg bw/day)	**0.002**	**0.007**
DMEL (µg/kg bw/day)	7.7	7.7
RCR (-)	**0.0003**	**0.0009**

Exposure and risk calculations for oral exposure (toy in the mouth) $D_{oral\ suck}$

The different parameters and values used in the exposure calculations for the scenario where a child is placing its favourite toy in the mouth (suck on toy) for 3 hours each day are listed in Table 42 and Table 43 below. The result, the oral exposure $D_{oral\ suck}$ is also listed, and the RCR values have been calculated.

Table 42. Exposure calculation of oral intake $D_{oral\ suck}$ for selected ABS toy materials

Product no.		**ABS4**			**ABS10**	
Monomer	**Acrylonitrile**	**Butadiene**	**Styrene**	**Acrylonitrile**	**Butadiene**	**Styrene**
A_{prod} (cm^2)	10	10	10	10	10	10
MG_{prod} (µg/cm^2)	0.02	0.02	0.03	0.007	0.007	0.014
$F_{contact}$ (-)	1	1	1	1	1	1
F_{abs} (-)	1	1	1	1	1	1
n (per day)	1	1	1	1	1	1
BW (kg bw)	10	10	10	10	10	10
$D_{oral\ suck}$ (µg/kg bw/day)	**0.02**	**0.02**	**0.03**	**0.007**	**0.007**	**0.014**
DMEL (µg/kg bw/day)	0.0019	0.72	7.7	0.0019	0.72	7.7
RCR (-)	**10.5**	**0.03**	**0.004**	**3.7**	**0.01**	**0.002**

Table 43. Exposure calculations of oral intake $D_{oral\ suck}$ for selected PS toy materials

Product no.	**PS1**	**PS4**
Monomer	**Styrene**	**Styrene**
A_{prod} (cm^2)	10	10
MG_{prod} (µg/cm^2)	0.03	0.05
$F_{contact}$ (-)	1	1
F_{abs} (-)	1	1
n (per day)	1	1
BW (kg bw)	10	10
$D_{oral\ suck}$ (µg/kg bw/day)	**0.03**	**0.05**
DMEL (µg/kg bw/day)	7.7	7.7
RCR (-)	**0.004**	**0.006**

Exposure and risk calculations for oral intake D_{oral}

The exposure calculations are carried out for the following toy materials:

- ABS4 and ABS10, where the highest concentrations of content of residual monomers acrylonitrile, butadiene and styrene have been measured, and where migration analyses to stomach acid have been performed
- PS1 and PS4, where the highest concentrations of content of residual styrene monomer have been measured, and where migration analyses to stomach acid have been performed
- PVC1-11, where no content of vinyl chloride above the detection limit was measured – for this reason the detection limit is used as a worst-case value for the content of vinyl chloride

- SBC2, where the highest concentrations of content of residual monomers styrene and butadiene have been measured
- SEBS1-2, where no content of styrene above the detection limit was measured – for this reason the detection limit is used as a worst-case value for the content of styrene

The different parameters and values used in the exposure calculations for the scenario where a child accidently swallows 8 mg of toy material each day are listed in Table 44 and Table 45 below. The results of the oral intake D_{oral} are also listed, and the RCR values are calculated.

For two products of ABS and PS respectively, it has not been assumed that all residual monomers contained in the products are released – instead the detection limit from the migration analyses to stomach acid has been used as no actual migration above the detection limit was detected. In these cases, MG_{prod} has been used as the amount of substance migrating per g of toy material (and for the time used when performing the migration analyses). Thus, a fairer calculation of the actual amount of residual monomer released into the stomach when a child is accidently swallowing a small piece of toy material is performed. For the other investigated materials (PVC, SBC and SEBS), where no migration analyses have been performed, the maximum measured concentrations of the content of residual monomers have been used. For PVC this means that the detection limit for vinyl chloride has been used as the maximum content. For the other investigated materials, it has been assumed as worst-case that 100 % of the measured content (or 100 % of the detection limit) will be released from the material into the stomach and will be absorbed into the body. To illustrate the difference, the results for the ABS and PS products are described as $D_{oral\ stomach}$, and for PVC1-11, SBC2 and SEBS1-2 the exposure is described as D_{oral}.

Table 44. Exposure and risk calculation of release of monomers to the stomach $D_{oral\ stomach}$ for selected ABS toy materials

Product no.		**ABS4**			**ABS10**	
Monomer	**Acrylonitrile**	**Butadiene**	**Styrene**	**Acrylonitrile**	**Butadiene**	**Styrene**
Q_{prod} (g)	0.008	0.008	0.008	0.008	0.008	0.008
MG_{prod} (µg/g)*	2.0	2.0	3.9	1.8	1.8	3.6
F_{abs} (-)	1	1	1	1	1	1
n (per day)	1	1	1	1	1	1
BW (kg)	10	10	10	10	10	10
$D_{oral\ stomach}$ (µg/kg bw/day)	**0.0016**	**0.0016**	**0.0031**	**0.0014**	**0.0014**	**0.0029**
DMEL (µg/kg bw/day)	0.0019	0.72	7.7	0.0019	0.72	7.7
RCR (-)	**0.84**	**0.002**	**0.0004**	**0.76**	**0.002**	**0.0004**

* In practice, the detection limit of the migration analysis has been used as no actual migration of the monomer above the detection limit has been measured.

Table 45. Exposure and risk calculation of release of monomers to the stomach $D_{oral\ mave}$ for selected PS toy materials

Product no. **Monomer**	**PS1** **Styrene**	**PS4** **Styrene**
Q_{prod} (g)	0.008	0.008
MG_{prod} (µg/g)*	3.4	3.6
F_{abs} (-)	1	1
n (per day)	1	1
BW (kg)	10	10
$D_{oral\ stomach}$ (µg/kg bw/day)	**0.0027**	**0.0029**
DMEL (µg/kg bw/day)	7.7	7.7
RCR (-)	**0.0004**	**0.0004**

* In practice, the detection limit of the migration analysis has been used as no actual migration of the monomer above the detection limit has been measured.

Table 46. Exposure and risk calculation of oral intake D_{oral} for PVC toy materials

Product no. **Monomer**	**PVC1-11*** **Vinyl chloride**
Q_{prod} (g)	0.008
F_{prod} (µg/g)	0.1
F_{abs} (-)	1
n (per day)	1
BW (kg)	10
D_{oral} (µg/kg bw/day)	**0.00008**
DMEL (µg/kg bw/day)	0.0014
RCR (-)	**0.06**

* This exposure calculation is valid for all the analysed PVC products as no content of vinyl chloride above the detection limit of 0.1 mg/kg (0.1 µg/g) was measured. Therefore, the detection limit has been used as the maximum assumed content.

Table 47. Exposure and risk calculation of oral intake D_{oral} for selected SBC and SEBS toy materials

Product no.	**SBC2**		**SEBS1-2***
Monomer	**Styrene**	**Butadiene**	**Styrene**
Q_{prod} (g)	0.008	0.008	0.008
F_{prod} (µg/g)	7.95	0.2	0.2
F_{abs} (-)	1	1	1
n (per day)	1	1	1
BW (kg)	10	10	10
D_{oral} (µg/kg bw/day)	**0.0064**	**0.0002**	**0.0002**
DMEL (µg/kg bw/day)	7.7	0.72	7.7
RCR (-)	**0.0008**	**0.0002**	**0.00002**

* This exposure calculation is valid for both analysed SEBS products as no content of styrene above the detection limit of 0.2 mg/kg (0.2 µg/g) was measured. Therefore, the detection limit has been used as the assumed maximum content.

Survey and investigation of migration of monomers in toy materials

The production of plastics leave behind residual mon-omers, some of which are classified as hazardous sub-stances. Especially monomers with genotoxic car-cinogenic properties are unwanted in plastic materials used in toys. With this report, the Danish Environmen-tal Protection Agency wishes to gain further knowledge on the migration of such monomers and an assess-ment on their potential health risk. After the preliminary survey, 29 different toy materials and products were selected for content analysis of one or more of four monomers (vinyl chloride, butadiene, acrylonitrile and styrene). The following materials were investigated: ABS, PVC, PS, SEBS and SBC. The content of vinyl chloride in PVC and styrene in SEBS as well as of bu-tadiene and styrene in SBC was below the detection limit or detected at low levels. For ABS, residual mon-omers were identified in all products with an average of 26.7 mg/kg for acrylonitrile, 0.57 mg/kg for butadiene and 842 mg/kg for styrene. The styrene content in PS was on average 351 mg/kg. Migration analyses con-ducted under different conditions on two products of ABS and two of PS showed no migration above the detection limit. Exposure and risk assessment were per-formed with the assumption that the monomers migrate at a rate identical to the detection limit. The risk as-sessment showed that there is no risk related to play-ing with the toys containing vinyl chloride, butadiene or styrene. For acrylonitrile, the detection limit is not low enough to comment on any possible risk.

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