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ProScale applied in a Mistra SafeChem case study with BASF

A comparative assessment of the human toxicity potential via direct exposure of a polyamide produced with two different flame retardants

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MISTRA SAFECHEM

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Contents

Abstract

ProScale is a tool in the Mistra SafeChem (MSC) toolbox, providing a hazard and exposure based scoring system for comparing chemical risks associated with products in a life cycle perspective. Current scope of ProScale cover human toxicity via direct exposure, e.g., worker exposure during production. Together with BASF, an industry partner within the programme, a case study for testing ProScale was developed. The aim of the case study was to perform a ProScale assessment of the human toxicity potential of the life cycle of two flame retardant polyamides. The goal of the case study was to compare the cradle-to-gate ProScale score (PSP) (inhalation and dermal exposure) of the two flame retardant polyamides.

The first polyamide, herein referred to as Product A, is based on a brominated flame retardant and represents the reference product. The second, Product B, is a nitrogen-based flame retardant free from halogens. In this assessment the product systems are represented as branches of interconnected unit-processes, i.e., production steps from raw material outtake (cradle), coming together in a final product output (gate).

The results indicate that Product B has a lower toxicity potential than Product A, as the PSP per kg of product, inhalation and dermal, was 220 and 20 for Product A and 450 and 40 for Product be, respectively.

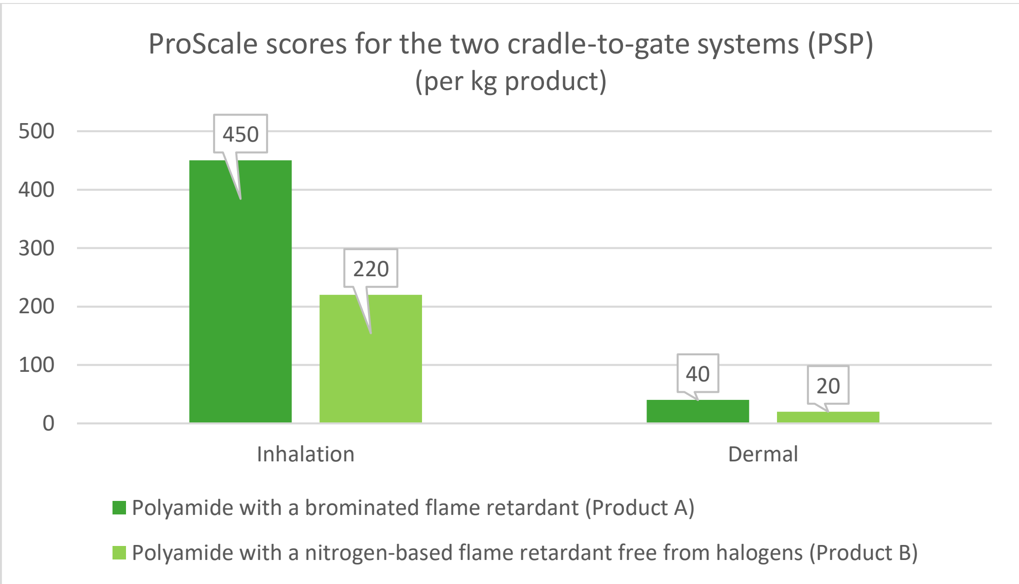

Figure 1. Visualization of the ProScale scores for the cradle-to-gate systems (PSP) of Product A and B.

Approximately 40% of the PSP from Product A came from the polyamide and its upstream processes. The contribution from this branch was the same in both systems, i.e., it was not this branch that caused the difference in the PSPs shown in Figure 1. Instead, 60% of the PSP from Product A came from the flame retardant, and mainly its upstream processes. Almost 100% of the PSP from the flame-retardant branch in Product A came from crude oil extraction and refining. Once crude oil is extracted it undergoes refining in which 20kg crude oil is required to produce 1kg of naphtha. Crude oil is classified as H350, placing the substance in the highest hazard class. The high mass flow contribution and the hazard class gave the oil refining a high ProScale score for the unit process (PSU), resulting in a major contributing to the total PSP. Product B is also produced from substances that originates from naphtha from oil refining. However, as the downstream mass flows were lower, the contribution from the oil refining to the final PSP of Product B system was lower.

It was concluded that i) Product B is indicated to have a lower toxicity potential compared to Product A (the reference) with regards to human toxicity via direct exposure in the defined cradle-to-gate systems, and ii) The use of raw materials originating from crude oil can have a high impact on the PSP in downstream processes even though the value chain is rather long. This is important to keep in mind when defining the system boundaries for a ProScale assessment.

Background

Mistra SafeChem (MSC) is a research programme with a vision to enable and promote the expansion of a safe, sustainable and green chemical industry. Together with BASF, an industry partner within the programme, a case study for testing ProScale was developed. ProScale, www.proscale.org, is a method providing a hazard and exposure based scoring system for comparing chemical risks associated with products in a life cycle perspective. The aim of the case study was to perform an assessment of the human toxicity potential for the respective cradle-to-gate system of two flame-retardant polyamides.

Goal and Scope of the ProScale assessment

The goal of the case study was to compare the cradle-to-gate ProScale score (inhalation and dermal exposure) of the two flame retardant polyamide systems, herein referred to as Product A and Product B. The gate of the system is the material manufacturing, Figure 2. For simplicity, catalysts and transports was left out of the study.

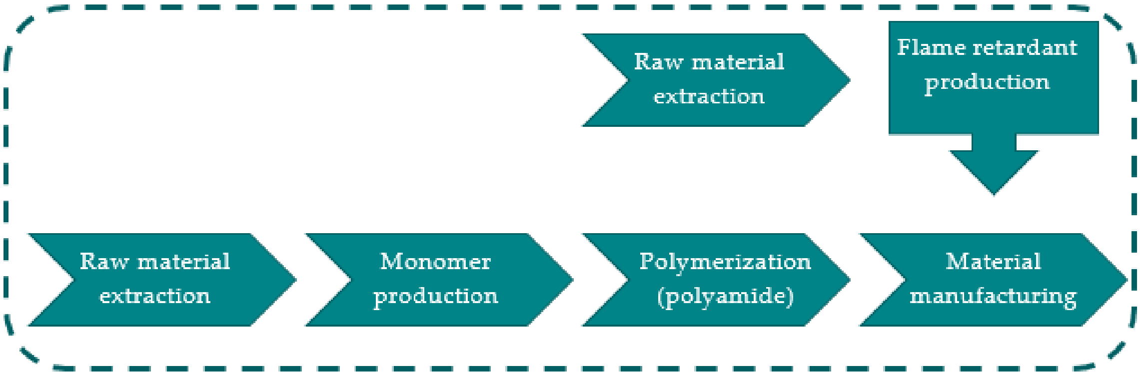

Figure 2. Simplified flowchart of the system for Product A and B.

Introduction to Product A and Product B

Two different types of flame-retardant polyamides, Product A and B, is being produced by BASF. Product A is based on a brominated flame retardant and represents the reference product. The second, Product B, is a nitrogen-based flame retardant free from halogens.

Introduction to ProScale

ProScale is an easy-to-use, hazard and exposure-based quantitative scoring system for assessing human toxicity (via direct exposure) of a product system with a life cycle perspective focusing on workers and professionals. A consumer exposure is also possible to include in a ProScale assessment (ProScale 2017), but not implemented in this case study.

The ProScale score is calculated from the combination of hazards and exposure for a unit process and aggregated across unit processes for the life cycle. The hazard is determined by the hazard factor, which in turn is based on substances classification according to the Globally Harmonized System of Classification and Labelling (GHS) and the legally defined Occupational exposure limits (OELs) or

Derived- No-effect levels (DNELs). Using the tier 1 exposure modelling in ECETOC TRA gives the exposure (ProScale 2017; ECETOC 2012).

When using ProScale, the toxicological potential (via direct exposure) of all substances in one or several unit processes are assessed. The ProScale score for a unit process is referred to as ProScale of Unit process (PSU) and the ProScale score for all unit processes of a product life cycle is referred to as ProScale of Product (PSP). The latter can also be calculated for a cradle-to-gate system for which the PSP includes all upstream processes for the specific substance. All these ProScale scores are route specific, meaning that a PSU or PSP is obtained per exposure route (dermal, inhalation or oral).

All details on the ProScale method documented in this report originate from the ProScale guidance (ProScale 2017).

ProScale score for a unit process

For each exposure route and substance (i), a ProScale score (PS) is calculated within a unit process by multiplying its hazard factor (HF), exposure concentration factor (ECF), mass flow (MF) and person-hour-factor (PHF) (Eq. 1). Summarizing the products of these multiplications gives the PSU of the unit process (Eq. 2).

$$PS_{i,route} = \sum_i HF_{i,route} * ECF_{i,route} * MF_i * PHF \quad \text{Eq. 1}$$

$$PSU_{route} = \sum_i PS_{i,route} \quad \text{Eq. 2}$$

The following sub-section introduces the details of determining the factors used in Eq 1.

Hazard factor (HF)

The hazard factor of a substance describes the substance's hazard and is based on the hazard class (A-E) and acceptable level of exposure (occupational exposure levels (OEL) or derived-no-effect-levels (DNEL)).

OELs below 0.1 mg/m3 or above 250 mg/m3 result in the maximum or minimum HF respectively in each hazard class. For substances with OELs between 0.1-250 mg/m3, the HF is a value between the maximum and minimum value in each hazard class. This is illustrated in Figure 3. The underlying mathematical equation for this figure is left out of this report.

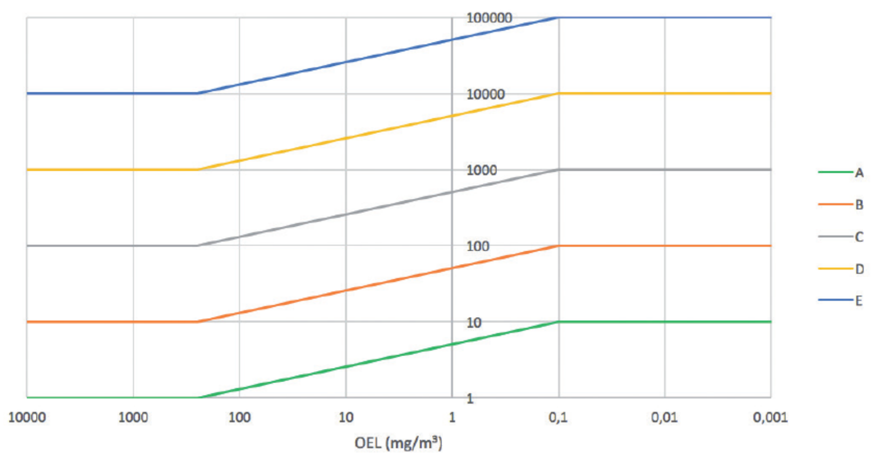

Figure 3. Function for deriving a Hazard Factor. Figure borrowed from ProScale (2017).

Determining the hazard class

The first step in calculating the hazard factor is to determine the hazard class, which is done by identifying the substance classification according to GHS. The ProScale guidance has set a hierarchy of data sources for determining the H-phrases.

The H-phrases assigned to a substance are sorted based on type and exposure route. Only health hazards are of interest for ProScale assessments, hence only H-phrases in the series of H3XX are documented. Exposure via dermal, oral and inhalation are all possible to assess via ProScale, although oral exposure is not included in this case study as it is of limited relevance in an industrial setting considering the direct exposures.

The ProScale hazard classes are divided into A-E, A being the least harmful and E the most severe. The H-phrases are used to place the substance in one of these classes, Figure 4. If a substance is classified with more than one H-phrase, it is the most severe one that determines the hazard class.

ProScale hazard class	H-phrases according to GHS/CLP, grouped by exposure route
E - "CMR" **10 000 – 100 000** (highest hazard)	All routes : H340, H350, H360, H362*
D – "Fatal" 1000 – 10 000	Dermal: H310 Inhalation: H330, H334, EUH032 Oral: H300 All routes: H341, H351, H361, H372
C – "Toxic" **100 – 1 000**	Dermal: H311, H314, H317, H318, EUH070 Inhalation: H331, EUH029, EUH031, EUH071 Oral: H301, H304 All routes: H370, H373
B – "Harmful" **10 - 100**	Dermal: H312, H315, H319, Inhalation: H332, H335 Oral: H302 All routes: H371
A – "Maybe harmful" **1 - 10** (lowest hazard)	Dermal: H313, H316, H320, EUH066 Inhalation: H333, H336 Oral: H303, H305

Figure 1. ProScale hazard classes corresponding to the hazard classes in the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Table borrowed from ProScale (2017).

Identifying an OEL (or DNEL)

The identification number (e.g., CAS number) of the substance is used to identify an acceptable level of exposure, i.e., an OEL or DNEL. The ProScale guidance (ProScale 2017) has a priority list for which data sources to use when determining the OEL.

Exposure Concentration Factor (ECF)

The ECF is calculated from the Exposure Concentration (EC) via an (route specific) algorithmic transformation function. The EC is determined in a stepwise approach.

The first step is to determine a process category (PROC) for the unit process as defined in ECHA (2015). Thereafter the fugacity level (high, moderate, low or very low) is determined based on the substance vapor pressure or dustiness (depending on its physical state). The PROC and fugacity level are thereafter used to determine the EC using the tables in Appendix A-C in ECETOC (2012) in which the EC for industrial and professional workers are separated.

Mass flow (MF)

The MF of the specific substance in each unit process, in relation to the functional unit (FU) for the system, is determined either via the use of firsthand data from industry, databases or via stochiometric mass balances.

Person-hour-factor (PHF)

The PHF is the annual hours worked per annual production volume. It is possible to calculate the factor manually, however ProScale (2017) strongly recommends the ProScale user to use the default PHFs as listed in the guidance.

ProScale score for a cradle-to-gate system

In this assessment the product systems are represented as branches of interconnected unit-processes, i.e., production steps from raw material outtake (cradle), coming together in a final product output (gate).

The ProScale score for the cradle-to-gate system is calculated by summarizing the PSUs of unit processes (u) in the system, scaled to the FU of the system, Eq 3. Calculating pre-chain scores for all upstream processes results in a total PSP (per exposure route) for the cradle-to-gate system.

$$PSP_{Route} = \sum_u PSU_{u,route} = \sum_u \sum_i (HF_{i,route} * ECF_{i,u,route} * MF_{i,u} * PHF_u) \qquad \text{Eq. 3}$$

Example: 0.8 kg of substance A and 0.2 kg of substance B are required in unit process C, Figure 5. The PSUA is multiplied with 0.8 and PSUB with 0.2 before added to PSUC. Applying the same approach for the rest of the system gives the PSP per exposure route.

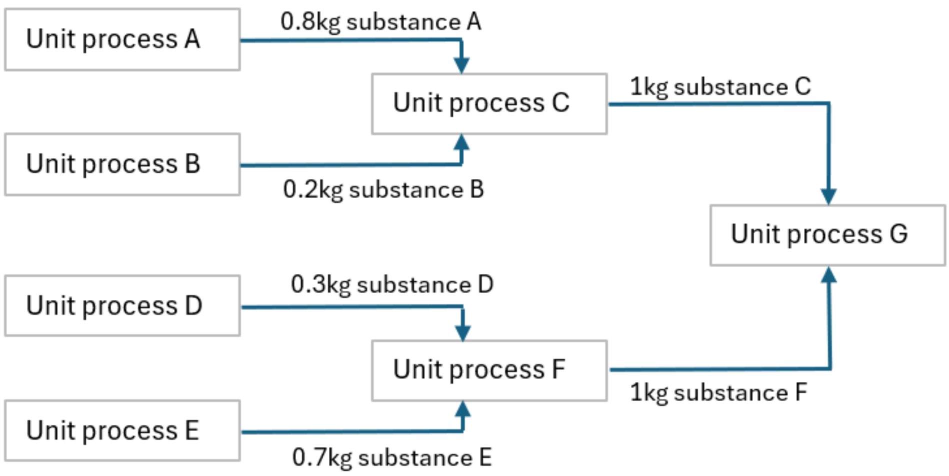

Figure 5. Example of pre-chain calculations to get a PSP. FU = 1 kg of substance G.

Result

The Proscale assessment shows that Product A has roughly twice the PSP than Product B for both exposure routes, Figure 6.

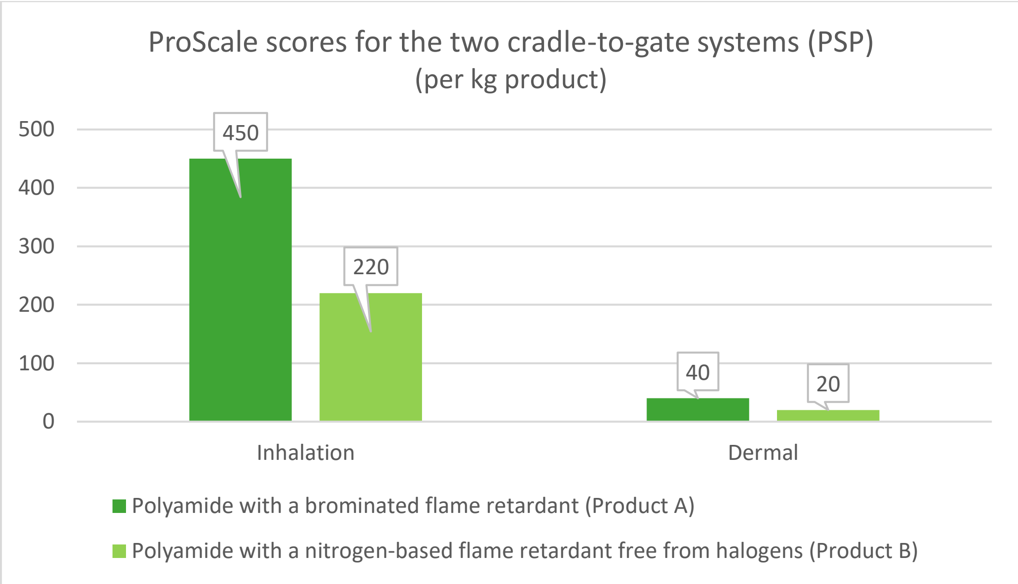

Figure 6. Visualization of the ProScale scores for the cradle-to-gate systems (PSP) of Product A and B.

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Simplifications and assumptions

As there was a limited amount of time and resources available for the ProScale assessment, some simplifications and assumptions have been made, Table 1.

Table 1. A summary of the main simplifications and assumptions made in the ProScale assessment.

Simplifications/assumptions	Motivation
Catalysts was excluded	It was difficult to find data on which catalysts (if any) was being used in each unit process.
Transports was excluded	Time did not allow deep investigation on transport means and distances.
In those unit processes where no information on energy and electricity consumption has been possible to identify, below assumption was made: Endothermic reactions: 5MJ energy and 1MJ electricity Exothermic reactions: 0MJ energy and 1MJ electricity.	Based on expert judgement.
If no data on energy source was identified, heavy fuel oil was assumed.	Worst-case scenario.
Some unit processes and its upstream processes were excluded.	Time did not allow to include all upstream value chains. Those that were excluded are the same in both products, hence it does not affect the comparison.

Conclusions

Based on the ProScale assessment the following conclusions were drawn:

- Product B is indicated to perform better than Product A (the reference) with regards to human toxicity via direct exposure in the defined cradle-to-gate systems.
- The use of raw materials originating from crude oil can have a high impact on the PSP in downstream processes even though the value chain is rather long. This is important to keep in mind when defining the system boundaries for a ProScale assessment.

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About Mistra SafeChem

Mistra SafeChem is a research programme with the vision
to enable and promote the expansion of a safe, sustainable, and green chemical industry.

The programme is developed with the twelve principles of green chemistry as a fundament.

The research combines the potential of innovative manufacturing processes,
tools for hazard and risk screening, and life cycle assessment
with ambitions and opportunities for the development and growth
of a safe and sustainable chemical industry.

More information:
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