Legacy flame retardants in polymeric products, recycling and analysis

Various legacy flame retardants used in the past in products made of thermoplastic materials have been classified or are currently assessed as substances of concern, among these hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBP-A) and polybrominated diphenylethers (PBDE) and polybrominated biphenyls (PBB).

WEEE contains on average 20 % plastics. The EEE (electrical and electronic equipment) industry accounts for 5-7 % of the total European plastic demand, i.e., 2.7 million tons out of a total 47.8 million tons. These plastics often contain flame retardants. It is estimated that flame retarded plastics make up around 5.5 % of WEEE by weight, or 25 % of all plastic used in EEE (Hedemalm et al, 1995). Of these flame retarded plastics, approximately 80 % are treated with brominated flame retardants (ENEA, 1995). Polystyrene foams (PSFs) have a large market share - in Germany alone around 62.3 x 10^6 m^3 PSFs have been sold in the last 30 years, based on performance and cost efficiency in construction. Due to national fire regulations in EU countries a large portion has been manufactured with flame-retardant additives: the former chemical of choice for foam was HBCD. In 2008 HBCD was classified as PBT (persistent, bio accumulative and toxic) and was also later classified as a POP (persistent organic pollutant) under the UNEP Stockholm Convention, leading many countries to set up plans for recycling HBCD building panels. Today, the WEEE plastics' recyclers are able to separate plastics containing brominated flame retardants (BFR) from the mainstream thanks to the sink/float technology within the heavy fraction of mixed waste. As the BFR plastics cannot be purified with the current recycling technologies, the material cannot be further recycled and is therefore incinerated, as prescribed in the POPs Regulation. Among other funding agencies, the European Commission's funding framework Horizon 2020 funds several projects developing new technologies to remove these substances of very high concern (SVHC) from the plastic matrix to enable their recycling. To promote the development of such processes, it is essential to have a steady system and threshold that enables a feasible quality control. However, the analysis of the POPs substances such as the PBDEs is complex due to the lack of verified method at concentration below 1000 ppm.

As of for bromine containing non-compliant flame retardants, recyclers have mainly relied on simple XRF analysis. By only analyzing on total Bromine content, recyclers do not discriminate between regulated and non-regulated Brominated substances. With some actors pushing for lower regulation limits for e.g. PBDEs, recyclers cannot rely on XRF only anymore, and will need to rely on chemical analysis. Experience with measurements on recycled WEEE plastics, have shown large variations in results. The heterogenous character of recycled plastics can lead to problems with representativity of the sample analysed. But considering the small amount of material that is analysed, it also raises questions on robustness of the method used.

In the framework of the EU -funded CREAToR and PRIMUS projects, the analysis of these materials is a major task, as CREAToR is developing new technologies for the removal of these substances and

PRIMUS is setting up sound methodologies for waste plastic sampling, pre-treatment and characterisation, a most accurate detection needs to be ensured.

As the CREAToR partners have experienced difficulties in the reproducibility and reliable measurement of the concentration, an additional effort was made to refine the analysis procedure and to assess the major influences on the measurement to be able to come up with a new best practice guideline.

During the project results evaluation of the extraction efficiency for the process it became obvious that a defined HBCD detection method for the precise evaluation is required, as different laboratories using mass spectroscopy techniques (ESI/LCMS, APPI/LCMSMS and GC-MS) result in different value levels and trends. Furthermore, there exists no official protocol or even scientific publication to determine and compare HBCD contents of polymer samples. Therefore, the CREAToR partners Centexbel, Transfercenter für Kunststofftechnik and Fraunhofer ICT started to develop and approve a common protocol for the HBCD extraction including sample preparation, pre-treatment of the samples, extraction and evaluation. As different mass spectroscopy techniques were available in the individual labs the effect on the technology was investigated additionally.

As a summary of the work carried out, following general statements can be concluded:

- The sample preparation (size, storage) and pre-treatment (type of comminution and time) before analysis already have a significant impact on the measured HBCD content independent on the used mass spectroscopy method or detector for the analysis
- The number of extractions on the samples is crucial. At least two extractions should be carried out in order to result in high HBCD detection accuracy
- The results showed a good detection accuracy for a HBCD content of 1 +/- 0,05 wt.-% (10.000 ppm +/- 500 ppm)

In the next step the analytical techniques will be validated to identify the individual minimum detection limits and the influence of the total HBCD content in the polymer on the accuracy of the analysis.

In parallel PRIMUS works on the development of a correlation tool for this analysis with X-ray fluorescence (XFR) and mass spectroscopy (MS) to enable plastics recyclers to monitor the recycled plastics to indicate the presence or absence of SVHC above the legislative threshold as already done with the PRE 1000 tool.

The update of the POPs Regulation Annex IV and coming Annex I foresee the lowering of the threshold for the HBDC and PBDEs significantly.

As can be seen from the work carried out by the two projects, the measurement accuracy does not allow for plastics recyclers to obtain results with high confidence that the HDCB concentration would be below 500 ppm in the recycled output.

Actual investigation in the projects result as well in doubting to be able to measure reliable PBDEs concentration be below 500 ppm in the recycling output. However more research is needed to confirm the first results. To sum up, it is expected that only an accuracy as described above, even using high-tech measurement systems as described above, is achievable.

Therefore, in order to be able to assess the content and to be able to reuse this material in a circular economy, we need to assure that reproducible and precise results can be obtained by the testing laboratories. Therefore, standardization is a prerequisite to enable this, accompanied by an extensive

cross-check in different laboratories. As soon as all laboratories are able to detect accurate quantities at different concentration levels, confidence can be given to the recyclers.

Specially to ensure high confidence for materials containing 200 ppm, still further research needs to be carried out to verify the quality and the deviation margin of the analysis. CREAToR and PRIMUS will collaborate to contribute to this and will encourage further projects in this field to join the initiative.

CREAToR consortium, November 2022