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METHODS TO STUDY THE DEGRADATION OF THE POLYMERIC BROMINATED FLAME RETARDANT POLYFR BY UV IRRADIATION

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1. Introduction

Since 2014, PolyFR (polymeric flame retardant) is used as a substitute for HBCD on a commercial scale. Different to HBCD, it is chemically bonded to the base material (reactive FR) and a persistent polymer by design. Thus, PolyFR is claimed to be more environmental friendly. However, almost all governmental risk evaluations focus only on the polymer itself and leave potential degradation products disregarded. Considering the long life time and various life cycle stages of EPS and XPS, abiotic and biotic environmental factors need to be taken into account. These factors may lead to a degradation of the commercial polymer and could result in smaller molecules with a different toxic potential. An environmental factor that is well known for altering the structure of brominated flame retardants (BFR) is ultraviolet (UV) radiation [1–3].

The goal of this study was to establish an adequate procedure to investigate the possible degradation of bulk PolyFR and PolyFR incorporated in EPS under UV irradiation. Besides the search for a suitable marker with regard to the level of decomposition, it was also of interest to determine the structure of molecules that may derive from PolyFR during degradation and are water soluble. Due to the polymeric structure and the fact that PolyFR is a reactive FR and insoluble in water, well-trying methods that were applicable when working with BFRs like HBCD, had to be exchanged in order to accomplish this goal.

2. Material and methods

A broad overview of the applied methods and intentions for using them is given in Figure 1.

Due to the broad extent, to which methods have been applied, it is not possible to list all methods in detail.

3. Results

3.1 Total Bromine concentration increases after UV irradiation

Measurements using ICP-MS showed that UV irradiation caused the bromine concentration to increase over time in the 150 mL samples containing 3.33 g EPS with PolyFR per litre. After irradiating for 60 minutes, the bromine concentration raised to 69.21 µg/g EPS (standard deviation (SD) ± 0.98 µg/g) of which 2.48 µg/g were bromine that leaches out without UV treatment. Treating the 150 mL samples containing bulk PolyFR (3.33 g/L) caused an almost linear increase of the bromine concentration as well, but to a much higher extent. After 60 minutes, the concentration increased to 17,300 µg/g (SD ± 3370 µg/g) PolyFR including 57 µg/g bromine that can be detected without previous UV treatment.

3.2 Low percentage of adsorbable organically bound bromine

Analyses of the adsorbable organically bound bromine in the 350 mL PolyFR samples via CIC, revealed comparably low concentrations of organically bound bromine in contrast with the total bromine concentrations. The adsorbable organically bound bromine accounted on average only for 0.96 % (SD ± 0.06 %) of the total bromine measured with ICP-MS.

3.3 Degradation products are observable after UV irradiation

After irradiating the samples for 60 minutes, different degradation products were detectable via LC-MS.

3.4 Changes to the solid PolyFR fraction after UV irradiation

The mean contact angle flattens with increasing duration of UV treatment. Without UV treatment, the mean contact angle was 78.95 ° (SD ± 4.34 °). After irradiating for 60 minutes, the mean contact angle decreased to 22.23 ° (SD ± 3.25 °).

After 60 minutes of UV treatment, the mean molecular mass of the solid fraction, measured via GPC, stays almost the same compared to untreated bulk PolyFR (untreated: 127,300 g/mol; treated: 125,900 g/mol). The density of PolyFR did not significantly change after UV treatment (untreated: 0.58 g/cm³ compared to treated: 0.59 g/cm³).

After irradiating the samples for 60 minutes, changes can be analysed using ¹H-NMR in the solid fraction of the polymer, mainly within the signals with the chemical shift in the range of 0.5 to 2.5 ppm. These

signals correspond to protons in the polymer main chain without adjacent bromine atoms and broaden after UV treatment for 60 minutes.

4. Discussion

4.1 Bromine concentration as a marker for degradation

Bromine has been chosen as a marker for a possible degradation of PolyFR, because, different to the AOB_r, it is time efficient and convenient to measure. The bromine concentration raises to over 17,000 µg/g bulk PolyFR. This equates to 2.84 % of the bromine content of 1 g bulk PolyFR (where the bromine content is 61 %). To account for possible free, thus unreacted bromine during industrial manufacturing, experiments were carried out without UV treatment. As a result of these, it was calculated, that only 0.33 % of the total bromine concentration leaches out of bulk PolyFR without UV irradiation.

EPS, thus the final insulation product and arguably more realistic scenario, around 1 % per mass PolyFR. After UV treatment for 60 minutes, the bromine concentration rose to almost 70 µg/g EPS, which is much lower compared to bulk PolyFR. However, when taking the PolyFR content of 1 % into account, the bromine concentration gets much closer (40 %) to the observed bromine concentration in the bulk PolyFR experiments. The remaining difference might be due to the thicker layer in the EPS experiments (PolyFR is shielded against the UV irradiation by the surrounding matrix).

4.2 Changes to the polymer

Although UV irradiation does not seem to change the mean molecular mass distribution or density of the solid fraction of PolyFR, changes are observable via ¹H-NMR. Broadening within the signals with the chemical shift in the range of 0.5 to 2.5 ppm indicate a degradation of the main chain. Possible explanations are changes in aromatic compounds or abstraction of bromine containing fragments, which would be in line with the increasing bromine concentration and the typical stepwise reductive debromination that BFRs undergo when exposed to UV radiation [1,3].

As mentioned previously, these changes are reflected in the alteration of the contact angle. The smaller the contact angle with water, the more hydrophilic a surface is [4]. Thus, PolyFR becomes more hydrophilic when exposed to UV radiation. This is especially important when considering other environmental factors, like biodegradation.

4.3 Degradation products and their toxicity

All of the detected degradation products were brominated. Taking into account that the parent compound PolyFR does not have brominated aromatic structures, bromine needs to be added to these structures. Based on the fact, that only brominated molecules were found in the samples, this addition might either occur to the aromatic structure while still attached to the polymer itself or very rapidly in solution. Another possible explanation would be, that non brominated molecules are present, but only in a concentration lower than the detection limit.

A literature research in the C&L inventory of the European Chemicals Agency (ECHA) gave a first impression on the hazard associated with these substances. Many of the detected products cause some kind of irritation (e.g. skin or eye irritation). One of the identified substances, 2,4,6-tribromophenol, is currently under re-evaluation in regard to persistent, bioaccumulative and toxic (PBT), and carcinogenic, mutagenic and reprotoxic (CMR) characteristics.

4.5 Future experiments

This study gives a first approach for studying the environmental degradation of BFRs, particularly polymeric ones, as an effect of exposure to UV radiation. However, further studies should be conducted to use this approach in an environmentally more relevant scenario, because possible degradation caused by UV irradiance is important to take into account when assessing the risk at all life cycle stages of bulk PolyFR and products that contain this BFR, for instance installation or disposal of EPS.

5. Acknowledgement

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6. References

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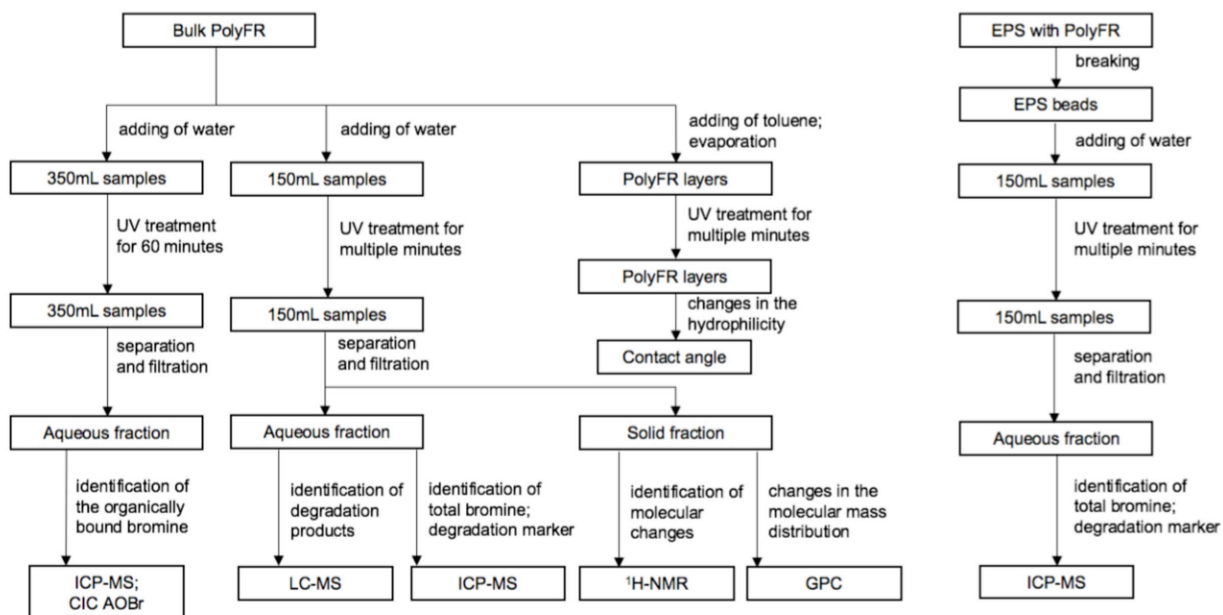


Figure 1: Overview of the applied methods and procedures