Behavior of bromine content and low molecular weight emissions from decaBDE, HBCD and brominated polystyrene in polystyrene under artificial ageing in UV light

Jiří Samsonek[1], Franky Puype[1]
[1]Institute for Testing and Certification, Trida T Bati 299, 764 21 Zlín, Czech Republic

Introduction

Restriction of polybrominated diphenylethers (BDEs) and hexabromocyclododecane (HBCD) in the European Union by regulations like RoHS (European regulation 2002/95/ES) and REACH/SVHC has consequently motivated research on effective replacements of the restricted brominated flame retardants (BFRs). Compared to the organophosphor, chlorinated and inorganic flame retardants the BFRs are still the most effective ones. Bromine has a big capacity to capture effective free radicals during the initial combustion process and acts very quickly.

Several mechanisms can be applied to dope a plastic material by flame retardant. The easiest is the addition of the BFR additive into the polymer. Therefore the BFR needs to be soluble into the polymer matrix and big enough to avoid migration towards the surface. However, the long term migration into the environment cannot be avoided. A more sophisticated system is the incorporation of brominated monomers into the polymer. Usage of brominated monomers avoids direct migration of low molecular BFRs into the environment, depending only on the biodegradability and bioavailability of the polymer. The polymeric BFRs as last class are either bounded to the main matrix or simply mixed into the matrix.[1.] Main factors influencing the development of new brominated flame retardants are based on low production costs, reduced blooming defects, huge operating temperature range, big application range and low environmental impact. Therefore the use of high molecular weight and polymeric brominated flame retardants has been increased in the last few years.

This study is describing the impact of artificial ageing by ultraviolet (UV) light on flame retarded polystyrene (PS). Parameters like the total bromine content and low molecular weight emissions were checked on regular base. On the market lots of recycling plastics are used and many materials are still delivered without proper documentation. To face global problem of BFRs in the environment, long term studies on BFR behaviour in polymers are necessary.

Materials and Methods

<u>Polymers:</u> In this study, three BFRs were applied and mixed into additive free polystyrene obtained from SYNTHOS (Kralupy, Czech Republic). All compounds were solved in HLPC grade toluene, mixed and dried on a PP desk. The 3 BFR doped PS samples were compared with the additive free polystyrene and all had an average film thickness of about 3,5 mm. The PS samples were compounded with:

- *Brominated polystyrene* (SAYTEX HP-3010) from Albemarle corporation (Europe, Belgium). SAYTEX HP-3010 has an average bromination degree of 2,7 on the phenyl ring and was added for 5,1 % in additive free polystyrene. As polymeric BFR should give no migration from the polymer. It is supposed that all the BFR will stay in the polymer mixture.
- *Technical decabromo diphenylether* (decaBDE) SAYTEX 102E from Albemarle corporation (Europe, Belgium) which was added for 4,3 % in additive free polystyrene. This aromatic BFR additive might migrate from the polymer matrix and it is known to debrominate under UV radiation.
- *HBCD* doped polystyrene granulates with 0,5 % HBCD (Kralupy, Czech Republic) ready to use for

expanded polystyrene were solved in toluene for the preparation of the film. This is the only aliphatic BFR used in this study.

The artificial ageing of the polystyrene films was performed under UV light generated by a mercury UV-lamp. The samples were placed 30 cm under the lamp to avoid heating of the samples. Energy of the UV radiation was measured in the distance of the samples and was set at 120 W/m^2.

Characterization of the bromine content and identification of the low molecular weight organobromine compounds was done by X-ray fluorescence spectrometry (XRF) and thermal desorption-GC-MS (TD-GC-MS) respectively. The bromine content by XRF analysis (Oxford Instruments ED 2000 Ag instrument) was performed under the conditions for measuring of medium elements in hydrocarbon matrix. The intensity of Bromine (Kα at 11,9 KeV) was automatically corrected for potential overlapping lines of As, Hg and Ru. All identification experiments were carried out with a thermal desorption unit PY-2020iD (Frontier Laboratories Ltd., Japan) connected to a GC/qMS QP2010plus (Shimadzu, Japan). A special metal capillary separation column (Ultra ALLOY-PBDE; 0.25 mm i.d. x 15 m, Frontier Laboratories Ltd., Japan) coated with a very thin (0,05 um) film of immobilized-polydimethylsiloxane was used for separation of the thermal desorption products. The thermal desorption temperature for HBCD containing polystyrene was 200ºC. All other samples were thermally desorbed at 300ºC. Negative chemical ionization (NCI) was applied for the determination of the brominated compounds with methane as reaction gas (M/z 79 + 81). Electron impact ionization (EI) was applied for the identification of the degradation products. Unfortunately TD-GC-MS could not be used for quantification of emissions and was only used for identification.

Results and Discussion

XRF analysis: The intensity of bromine signal in the 4 polystyrene samples was monitored regularly during the UV radiation. The PS without additives was proved to be bromine free and suitable for the experiments (Fig.1a). The ageing under UV light seemed to have a little influence on the loss of bromine (Fig.1 b,c,d), however the samples were all visibly yellow and strongly degradated after 65 hours of UV radiation. Yellowing of the additive free PS was far slower compared to the flame retarded PS samples. Yellowing of the polymers during the UV degradation is often linked to the creation of conjugated system of double bonds (like with PVC, that creates conjugated double bond system after dehydrochlorination). Strong yellowing (or browning) of polystyrene with the presence of BFR probably have origin in inter and intra-molecular bromine radical transfer on the polystyrene chain and releasing of low-molecular brominated organic substances. Bromine reactivity can also help to create light by Charge-Transfer (CT) complexes. [2]

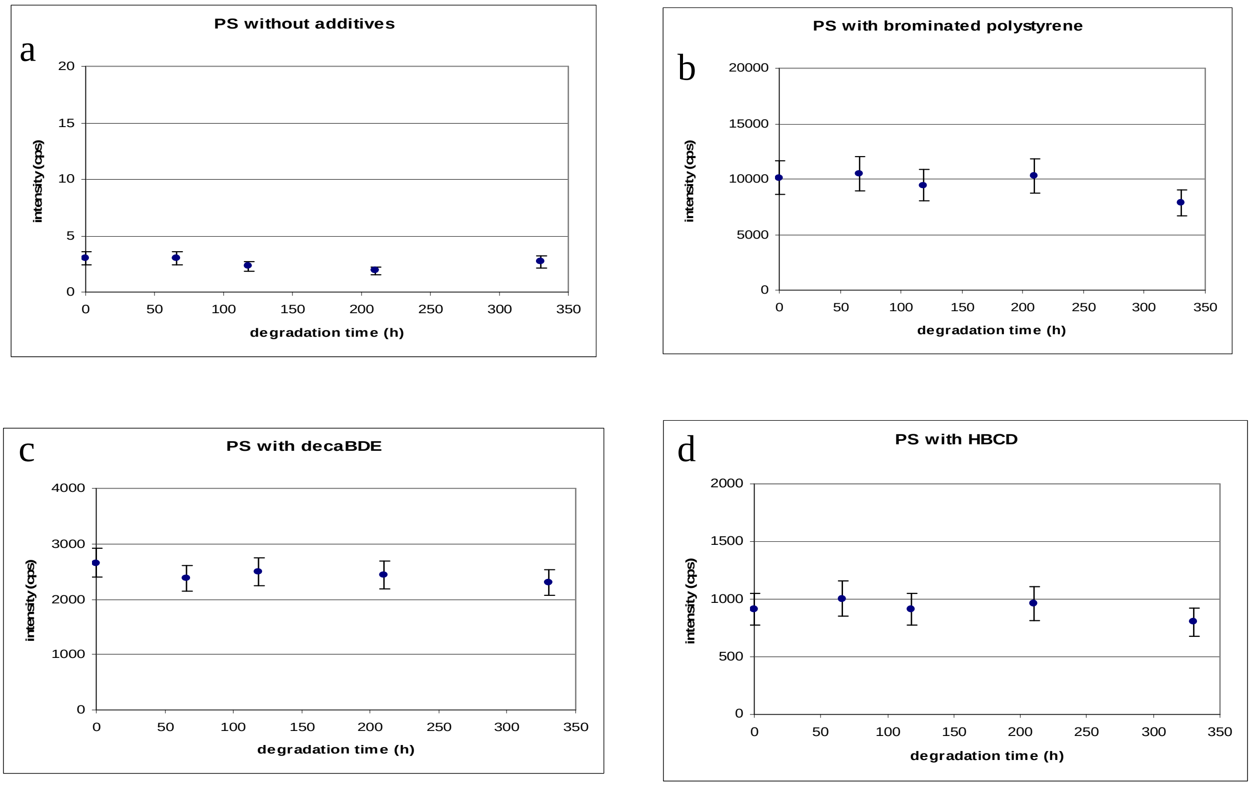

Figure 1: XRF measurement of Bromine during artificial ageing under UV light in:
a) PS without additives, b) PS with brominated polystyrene, c) PS with decaBDE, d) PS with HBCD.

<u>TD-GC-MS analysis:</u> The emissions of organobromine compounds were measured by TD-GC-MS in NCI mode. The use of NCI was necessary due to the huge amount of degradation/oxidation products evolved from the polymer matrix and the low concentration level of the brominated emissions. Thermal desorption analysis of PS without additives gave no peaks in NCI mode coming from brominated compounds. In EI mode were discovered huge amounts of free styrene, toluene, benzophenone and benzoic acid which are degradation and oxidation products from the sample matrix.
The thermal desorption measurement of PS with brominated polystyrene gave during UV radiation a shift from tribromotoluene, tetrabromobenzene and tribromomethylstyrene towards bromotoluenes, dibromotoluene, bromobenzenes and bromostyrenes (fig. 2). DecaBDE doped PS samples show an evolution starting from debromination of the decaBDE to lower BDEs, followed by a bromine radical capture from degradation products from the polystyrene forming: bromotoluene, dibromotoluene, bromobenzaldehyde (fig. 3)[3.]. The bromine capture by PS degradation products was also happening in the PS sample doped with brominated polystyrene however the degradation products from the BFR and the bromine capture products are similar and therefore difficult to differentiate. It seems that the HBCD is not debrominating under UV radiation. There are no recombination peaks detected in such excess like the PS samples with brominated polystyrene and decaBDE. The HBCD, as aliphatic BFR, might rather decompose (fig. 4). UV degradation of the BRF seems to lead to various changes in the whole polymeric system. Study of behavior of most typical BFR under UV radiation in polymer matrixes can help to understand behavior of various types of BFR in the products as UV exposition is ever-present.

References

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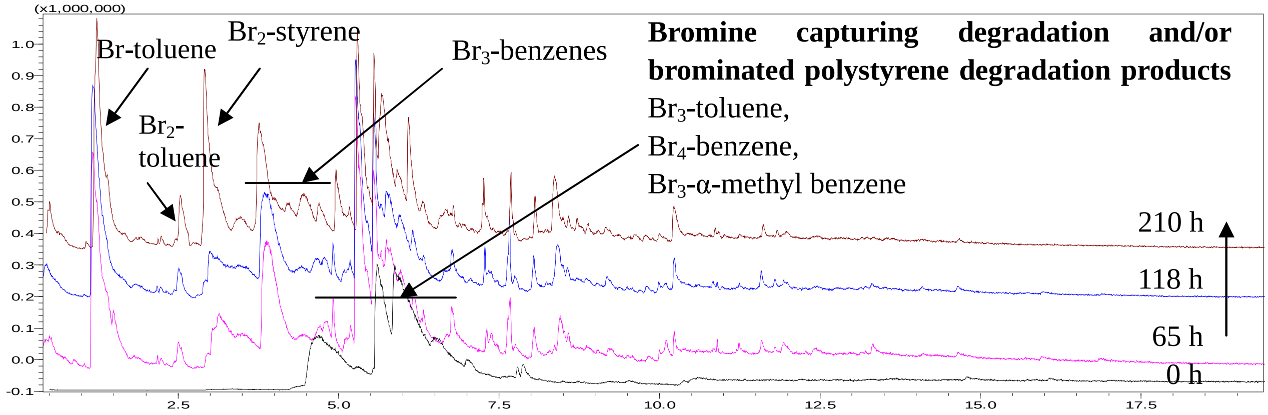

Figure 2: TD-GC-NCI/MS chromatogram of PS /brominated polystyrene during UV radiation (M/z 81)

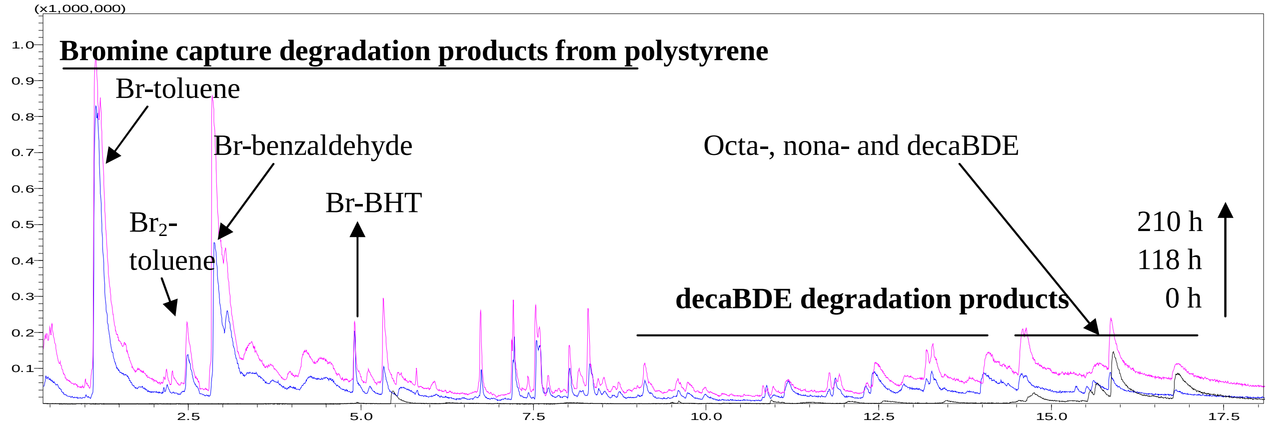

Figure 3: TD-GC-NCI/MS chromatogram of PS with decaBDE during UV radiation (M/z 81)

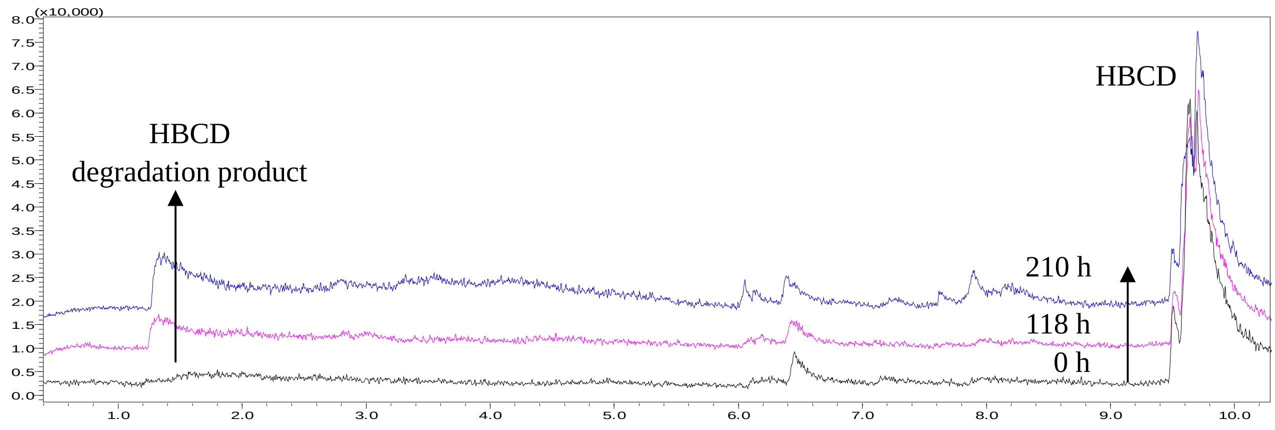

Figure 4: TD-GC-NCI/MS chromatogram of PS with HBCD during UV radiation (M/z 81)