Occurrence and Fate of Alternative Flame Retardants in the Environment

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3.2: Leaching of halogen-free and brominated flame retardants from polymers - Influence of leaching parameters

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Sicco H. Brandsma[1*], Jacob de Boer[1], Petra Krystek[1], Peter Clarke[2], Hidetaka Takigami[3], Go Suzuki[3] Parina Patel[2], Paul Cusack[2], and Pim E.G. Leonards[1]

[1] Institute for Environmental Studies (IVM), VU University, de Boelelaan 1087, 1081 HV Amsterdam, The Netherlands

[2] ITRI Ltd, Unit 3, Curo Park, Frogmore, St Albans, Hertfordshire AL2 2DD, UK

[3] Centre for Material Cycles and Waste Management Research, National institute for Environmental Studies (NIES), 16-2 Onogawa, Tsukuba, 305-8506 Ibaraki, Japan

Abstract

The ban and restrictions on some of the brominated flame retardants (BFRs) has led to an increase in use and production of alternatives such as halogenated free flame retardants (HFFRs). Limited information is available on the occurrence and fate of inorganic HFFRs. Inorganic HFFRs such as aluminum polyphosphinate (AlPi), melamine polyphosphate (MPP) and zincstannate (ZS), dissociate into ions in the environment and are difficult to trace back. Therefore, we studied the leachability of HFFRs from manufactured polymeric FR combinations in comparison with BFRs. Both HFFRs and BFRs leach from the polymers and may end up in the environment. Particle size, pH, porosity (adding synergist), surface structure, impact strength and strength of break are determining factors in the leaching behaviour of the FRs. Many of these parameters are related to the polymer type, which is the main parameter determining leaching behaviour. Differences in leaching behaviour between HFFRs and BFRs have been observed for the polymers polyamide (PA), polybutylene terephthalate (PBT) and epoxy resins (EPR). These polymer showed also the highest leaching properties. Almost no FRs leached from high impact polystyrene (HIPS)/polyphenylene ether (PPE/HIPS) and polycarbonate/acrylonitrile butadiene styrene (PC/ABS polymers). Therefore, no differences between HFFRs and BFRs were observed. This study contributes to a better understanding of the fate of inorganic HFFRs from polymers. In addition, it provides relevant information for reduction of the leaching of FRs from polymers.

Introduction

Manufacturers add flame retardants (FRs) to polymers in order to meet fire safety regulations. In electrics and electronics (EEE) brominated flame retardants (BFRs) are widely used and have been detected globally in the indoor and outdoor environment, which indicates that BFRs may leach from the polymer used in these products (de Wit et al., 2002, Kemmlein et al., 2003). Electric and electronic waste (WEEE) form the fastest growing stream of all waste types. Worldwide, every year approximately 20 to 50 tonnes of WEEE is generated, equivalent to more than 5% of all municipal solid waste (Kiddee et al., 2013, UNEP, 2006). It has been shown that BFRs can also leach from WEEE after disposal on landfills (Osaka et al., 2004, Odusanya et al., 2009, Choi et al., 2009). Due their persistent, bioaccumulative and toxic properties (De Wit et al., 2002, Law et al., 2014, Hites. 2004, Hamers et al., 2006, Kim et al., 2014) several BFRs, such as the Penta- and Octa-mix consisting of polybrominated diphenylethers (PBDEs) have been banned or restricted in many countries (BSEF. 2010, CEFIC. 2011). Therefore, manufacturers started searching for alternatives, which has led to an increase in use and production of alternative FRs (CEFIC. 2011). In the European Union funded project *ENFIRO* halogen-free flame retardants (HFFRs) were studied as viable alternatives to specific commercial BFRs such as decabromodiphenyl ether (Deca-BDE), tetrabromobisphenol A (TBBPA) and brominated polystyrene. Some of the selected HFFRs that were studied were inorganic FRs such as aluminum polyphosphinate (AlPi), melamine polyphosphate (MPP) and zincstannate (ZS) (Table 1).

Inorganic FRs are stable in the plastic product, but may leach and dissociate into ions in the environment. It is difficult to relate environmental levels of metals to inorganic FRs as they can have multiple sources (both natural and anthropogenic). Therefore, we studied the leaching of HFFRs from manufactured polymer-FR combinations to better understand the leaching properties, and to provide information on the environmental fate of HFFRs.

Table 1. Polymer-FR formulations tested in this study.

Polymer	Application	Code	Flame retardant (w/w percentage added)
Polybutylene terephthalate (PBT) + GF(30%)	Electrical & electronic equipment, connectors, switches etc.; encapsulated electronic components	PBT1 PBT2 PBT3 PBT4	No FR BPS (10%) + Sb_2O_3 (5%) AlPi (15.55%)+ Nanoclay (2.45%) AlPi (15%)
Polyamide 6.6 (PA) +GF (30%)	Electrical & electronic equipment, connectors, switches etc.; encapsulated electronic components	PA1 PA2 PA3 PA5	No FR BPS (21.3%) +Sb_2O_3 (10.7%) AlPi (13.3%) + MPP (6.7%) + ZS (3.0%) AlPi (16.67%) + MPP (8.33%)
High impact polystyrene (HIPS)/Polyphenylene ether (PPE) (55/45)	Housings for business machines, dashboards, toys, refrigerator, telephones, consumer electronics	PHB1 PHB2 PHB3	No FR DecaBDE (14%) + Sb_2O_3 (6%) PBDPP (15%)
Polycarbonate (PC) /Acrylonitrile butadiene styrene (ABS) (70/30)	Housings for business machines, dashboards, toys, equipment for refrigerator, telephones, and other consumer electronics	PCA1 PCA2 PCA3 PCA4 PCA5	No FR DecaBDE (10%) + Sb_2O_3 (5%) TBBPA (10%) + Sb_2O_3 (5%) BPA-BDPP (15%) + PTFE (3%) PBDPP (20%) + PTFE (20%)
Epoxy resins(EPR)	Wires & Cables	EPR1 EPR2 EPR3	No FR DecaBDE (20%) + Sb_2O_3 (10%) AlPi (20%) + MPP (20%)

Aluminium diethylphosphinate (AlPi); Melamine polyphosphate (MPP); Zinc stannate (ZS); Brominated polystyrene (BPS); Decabromodiphenyl ethers (DecaBDE); Antimony trioxide (Sb_2O_3); resorcinol bis (diphenylphosphate) (PBDPP); bisphenol A bis (diphenylphosphate) (BPA-BDPP): Tetrabromobisphenol A (TBBPA).

Several leaching protocols have been developed and used by regulatory agents for measuring leaching behavior from building and waste materials and to characterize the toxicity of waste and determine the compliance of the waste for deposition at landfills (USEPA, 1992, Keith et al., 2008, Lincoln et al., 2007). Some of the main differences between those leaching protocols are the waste particles size, leaching solvent, liquid to solid (L/S) ratio and the extraction time (Keith et al., 2008, Lincoln et al., 2007). For example, the German DIN 38414-S4 leaching protocol, which is widely applied in Europe, uses only deionized water as leaching solvent whereas the US EPA Toxicity Characteristics Leaching Procedure (TCLP) uses a mixture of acetic acid, sodium hydroxide and deionized water with a pH of 4.93 as leaching solvent. An alternative to the TCLP procedure is the US EPA Synthetic Precipitation Leaching Procedure (SPLP), which uses a leaching solvent with a pH of 4.22 containing sulfuric and nitric acid and simulating acidic rainwater. Comparable to the TCLP is the

Waste Extraction Test (WET), which also uses a buffered organic acid solution as extraction fluid. The WET protocol was adopted for the State of California. The Dutch norm EA NEN 7371 is based on repeatable extraction with a pH of 7 followed by a pH of 4. These differences have strong influence on the leaching behavior. Discrepancies in leaching behaviour of metals from WEEE and mobile phones using different leaching protocols have been observed earlier by Lincon et al. (2007) and Keith et al. (2008). For this study two types of leaching protocols, the TCLP and the DIN 38414-S4. The TCLP protocol uses worse-case leaching conditions (low pH) to simulate a municipal waste landfill and to study if waste is hazardous. The DIN 38414-S4 determines leaching by water, and has been widely used for regulatory purposes in Europe. It is a much milder protocol. The present study shows leaching properties of various HFFRs in comparison with those of BFRs. Influences of polymer type, pellets vs. moulded plates and pH on the leaching properties are taken into account.

Material and Methods

Materials

The solvents and chemicals used were all pro-analysis quality or HLPC grade, unless otherwise stated. Hexane and methanol used for the extraction and cleanup were from Promochem (Wesel, Germany)) and toluene from Fisher Scientific (Loughborough, UK). PBDPP (Fyrolflex RDP, technical grade, 95.5% purity) and BPA-BDPP (Fyrolflex BDP, technical grade, 96.5% purity) were obtained from ICL (Amsterdam, the Netherlands). Native and mass labeled ($^{13}C_{12}$) decabromodiphenyl ether (^{13}C-BDE209) and tetrabromobisphenol A (^{13}C-TBBP-A) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). The internal standard TPHP-$_{d15}$ were supplied by respectively, Sigma-Aldrich Chemie B.V. (Zwijndrecht, the Netherlands).

Polymer-FR formulations

Five different polymer formulations were selected and prepared (Table 1). Information on the selected HFFRs as well as the various applications as alternative for BFRs are given in Table 1. For each polymer type a formulation with and without HFFR was prepared, and a BFR was used as reference.

All prepared polymer-FR formulations were tested for flammability using the UL-94 flammability standard (Blaszkiewicz et al., 2007), and were optimized for the V-0 criteria, which implies that burning should stop within 10 seconds and no flaming drips are allowed. All formulations that passed the V-0 criteria, were tested for the leaching properties.

Moulded plates

Moulded plates were prepared for each polymer-FR formulation using injection moulding. These moulded plates actually represent the final product such as the housing of a television or electric consumer product. For this leaching test the TCLP protocol was used (USEPA, 1992). This protocol was

modified as followed. Instead of using 100 g plastic pellets, leaching was focused on the surface of the plate to better mimic the environmental fate of FRs leaching from plastics. The moulded plates were attached to a plastic (5.940 cm^2, Ø=2.75 cm) or stainless steel tube (5.309 cm^2, Ø=2.6 cm) that contained the leaching solvent (Fig. 1). The plastic tubes were used for leaching inorganic flame retardants and metal tubes for organic flame retardants. The liquid/solid ratio was set at 7:1 mL/cm^2. The TCLP solution was prepared as described in the protocol, by adding 64.3 mL of sodium hydroxide (1 M) and 5.7 mL of glacial acetic acid to 500 mL of milli-Q water. It was further diluted to a volume of 1L with milli-Q water. The pH of this solution was 4.93. The TCLP protocol prescribes a leaching period of 18h. After 18h the levels in the leachate were compared with the TCLP regulatory levels to determine if the waste should be characterized as hazardous. In this study we were interested in the kinetics of leaching and the maximum concentrations that leach after a certain period of time. Seven time points were selected: 1h,18h, 2.5d, 5d, 10d, 20d and 30d. Three time points were performed in duplicate; 18h, 10d and 30d. The polymer without FR was used as a blank and was leached for 30d.

Extraction and Analysis of the FR

BDE209

At the end of the leaching period the solvent was transferred into a 60 mL glass tube. Hundred µL of ^{13}C-BDE209 (150 ng/mL in acetone) was added as internal standard. The metal leaching tube was rinsed 3 times with in total 10 mL of 30% toluene in hexane (v/v) to ensure that no BDE209 was left in the tube. The total volume of 10 mL was used for the first liquid-liquid extraction (LLE). Extraction was repeated two times with 5 mL of 30% toluene in hexane (v/v). The organic layers were combined and evaporated under nitrogen until 2 mL. Each LLE was performed in glass tubes on a rotary shaking machine for 15 minutes. The extract was dried over a sodium sulfate column and rinsed with 8 mL 30% toluene in hexane (v/v) and concentrated under nitrogen until 0.6 mL and transferred into a GC-vial. The extraction efficiency of BDE209 was tested by a duplicate spike experiment. The recovery for BDE209 was >86%. BDE209 was analyzed with HP6890 gas-chromatography (GC) coupled to a mass-spectrometer (MS) (Agilent Technologies, Amstelveen, The Netherlands) running in the electron capture negative chemical ionization (ECNI) mode. Detailed information on the method can be found in Brandsma et al. (2013).

TBBPA

Extraction of TBBPA from the leaching solvent was done as described for BDE209, with the exceptions hexane was used as extraction solvent. As internal standard ^{13}C-TBBPA was used. The extraction efficiency of the duplicated spike experiment for TBBPA was > 95%.

Analysis of TBBPA was performed on a HP6890 GC (Agilent Technologies, Amstelveen, The Netherlands) with a BPX5 capillary column (50 m x 0.25 mm ID, 0.25 µm film thickness, Agilent

Technologies , Amstelveen, the Netherlands). The injector temperature was 275 °C and the samples were injected in the pulsed splitless mode with a pulse pressure of 277 KPa for 1.5 min. Helium was used as a carrier gas with a flow of 3 mL/min. The initial oven temperature was 90 °C and held for 3 min, followed by an increase of 30 °C min^{-1} to 210 °C, held for 20 min. The temperature was then increased to 310 °C (5 °C min^{-1}) and held for 26 min. The temperatures of the source and quadrupole were 200 and 106 °C, respectively. The MS was run in ECNI mode with methane as reagent gas. Selective ion monitoring (SIM) was performed for m/z 544 and 542 for TBBPA, and m/z 554 and 556 for the internal standard ^{13}C-TBBPA.

PBDPP and BPA-BDPP

The leaching solvent was spiked with the internal standards TPHP-$_{d15}$ (75 ng). Extraction was performed with solid phase extraction (Oasis SPE MCX 150 mg/6 mL). Before the sample was transferred to the SPE cartridge, it was washed and conditioned with 5 mL methanol followed by 5 mL ultrapure water. After transferring the sample to the SPE cartridge, the SPE cartridge was washed with 3 mL ultrapure water. After drying the cartridge for 30 min, RBDPP and BPA-BDPP were eluted with 6 mL methanol, which was evaporated and transferred into a 1 mL LC-vial.

Analysis of PBDPP and BPA-BDPP was performed on a 1260 infinity high performance liquid chromatograph (HPLC) (Agilent Technologies, Amstelveen, The Netherlands) with a 150 x 3 mm Luna C18 3 µm column (Phenomenex, Utrecht, The Netherlands). The HPLC was coupled to the MS and run in the MS-MS mode using multiple-reaction monitoring (MRM) of the parent and the daughter ions (Brandsma et al., 2013).

Inorganic FRs

Four hundred µL of concentrated nitric acid was added to the leachates of the metal based FRs before analysis to improve the solubility of the metals. Analyses was performed with the Element 2 high resolution inductively coupled plasma mass spectrometer (ICP-HRMS) (Thermo Scientific). Rhodium was used as internal standard (concentration of 1 µg/L). A cyclone spray chamber with MicroMist nebulizer of 0.2 mL/min was used. Selective ion monitoring (SIM) was performed for m/z 27 for aluminum, m/z 31 for phosphate, m/z 66 and 68 for zinc, and m/z 103 for the internal standard rhodium.

Metal - based   Organic

Figure 1. Set-up of the leaching moulded polymer plates using a plastic (left) or metal tube (right).

Calculations

The leaching process of the FRs from the polymer material was considered to be a first order process (Choi et al. 2009, Zhou et al., 2013) according to equation 1.

Eq. 1:

$$C = C_{max} \times [1-\exp(^{-kt})]$$

Based on the leaching concentrations measured (C) the maximum concentration (C_{max}) leaching from the polymer after a certain period of time (t), and the rate constant (K) were calculated (Eq. 1). The program Prism Graphpad 5.0 was used for the statistically analyses of C_{max}, k and the regression (r^2) of the best line of fit. An example of the fitting of the leaching behavior of zinc stannate from a PA moulded plate is given in Fig. 2.
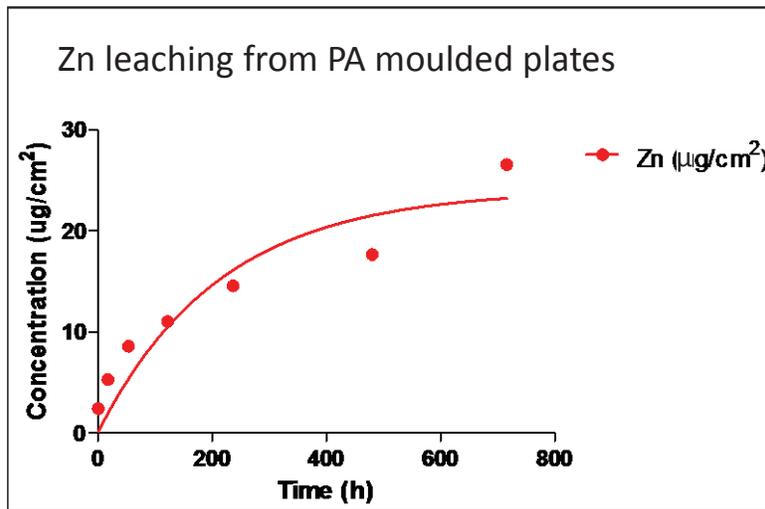
Figure 2.Concentrations of zinc from zinc stannate in µg/cm² after leaching from polyamide (PA) moulded plate.

Because leaching is carried out on the surface of the moulded plate, the concentration of the leached compound is expressed in µg/cm². Calculating the percentage of FR leaching from the polymer was done with equation 2.

Eq. 2:

$$FR\ (\%) = \frac{Cmax\ \left(\frac{\mu g}{cm2}\right) * D\ (cm2)}{P(\%)\ * \left(A\ (cm3)\right) * 1000000 * \rho(\frac{g}{cm3})}$$

In which FR (%) is the percentage of FR leaching from the moulded plate. D (cm) is the leaching surface (cm2), P (%) is the percentage FR added to the plate, A (cm³) is the total volume of the leached plate (cm3), and ρ (g/cm³) is the density of the polymer.

Leaching properties

Polymer properties

The following properties of the polymers-FR moulded plates were selected to investigate if these were relevant for the leaching behavior: the tensile (ISO 527) and impact properties (ISO 180), viscosity and polymer-FR density. In addition, the surface structures of the moulded plates were characterized using 3D laser microscope (OLS4100 Olympus) .

Particle size; pellets versus moulded plates

To study the influence of the particle size on the leaching behaviour of the FR, leaching studies were performed with pellets of PBT3 and PBT4 and PA3 and PA5 (Table 1). Instead of leaching the surface of the moulded plates, pellets (~5 mm) were added to the leaching solvent. The TCLP protocol was slightly modified for the pellets by downsizing the sample intake from 100 g to 0.6 g, but keeping the L/S ration similar to that of the protocol.

<u>*pH; TCLP versus DIN 38414-S4 (moulded plates and pellets)*</u>

To investigate the influence of the pH on the leaching behaviour two methods with different pH were used. The TCLP protocol uses a buffered leaching solution with a pH of 4.93, and the DIN 38414 uses only deionized water. Leaching experiments were performed with pellets of PBT3 and PBT4 and moulded plates of PA3 and PA5. For the pellets the DIN 38414-S4 and TCLP protocols were modified by downsizing the sample intake from 100 g to 1.2 g for the DIN, and 0.6 g for TCLP. The L/S ratio was kept similar as described in the protocols. For the moulded plates the DIN 38414-S4 protocol was modified similar as described previously for to the TCLP method; instead of using 100 g plastic material, leaching was focused on the surface of the plate (5.3 cm^2 ($\emptyset$=2.6 cm) for the metal tubes and 5.9 cm^2 ($\emptyset$=2.75 cm) for the plastic tubes).

Results

<u>*Polybutylene terephthalate (PBT)*</u>

Brominated polystyrene is a common FR used in PBT polymers for different applications (see Table 1). As a viable halogen-free alternative in PBT AlPi is used. Three different polymer-FR formulations were prepared and all formulations passed the V-0 flammability test (UL-94). The first formulation PBT2 contained 10% brominated polystyrene + 5% antimony trioxide (synergist). The two other formulations, PBT3 and PBT4, contained 15.55% AlPi + 2.45% nanoclay, used as synergist or 15% AlPi only, respectively.
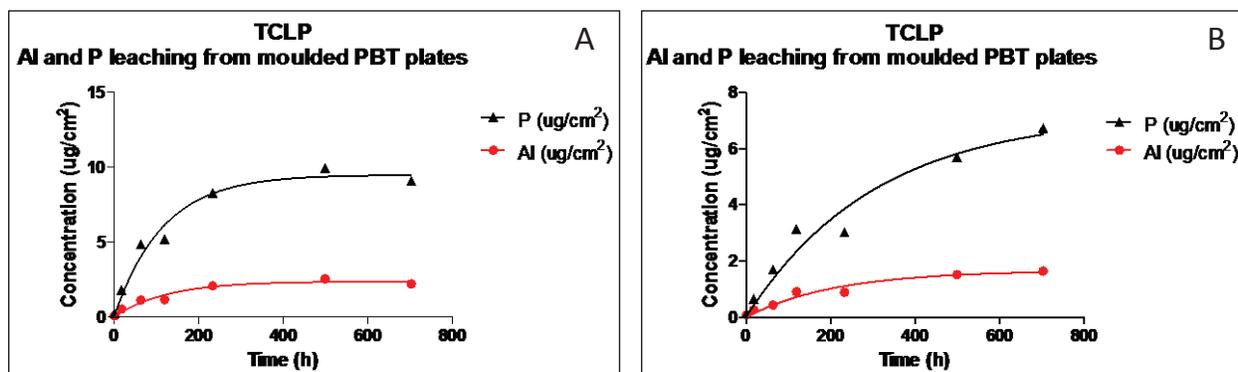

Figure 3. Concentrations of Al and P ($\mu g/cm^2$) leaching from PG plates containing AlPi using the TCLP method. A) PBT3: PBT + 15.55% AlPi + 2.45% nanoclay. B) PBT4: PBT + 15% AlPi.

Leaching was tested with moulded plates. When AlPi leached from the PBT polymer it dissociated into Al and P in a ratio of 1:3.4 (w/w), corresponding to the theoretical value for AlPi. AlPi leached from both PBT polymer formulations (Table 2 and Fig 3). AlPi leached fast in the beginning and reached a steady state after ca. 400-600 h. This first order process was also observed for the PBDEs leaching from WEEE by Choi et al. (2009) and Zhou et al. (2013).

Table 2. Calculated results of C_{max}, k and TCLP concentration after 18h for the different polymer-FR formulations.

Polymer	Compound	Cmax ($\mu g/cm^2$)	k (h^{-1})	r^2	FR (%) leached
PBT3	Al	2.4 ± 0.2	0.008 ± 0.002	0.95	0.030*
PBT3	P	9.5 ± 0.5	0.009 ± 0.001	0.97	
PBT4	Al	1.7 ± 0.2	0.005 ± 0.001	0.95	0.021*
PBT4	P	7.2 ± 1.0	0.003 ± 0.001	0.96	
PA3	Al	20 ± 15	0.002 ± 0.002	0.75	0.31*
PA3	P	258 ± 50	0.004 ± 0.002	0.88	
PA3	Zn	24 ± 3.7	0.005 ± 0.002	0.86	0.41**
PA5	Al	25 ± 58	0.001 ± 0.002	0.63	0.32*
PA5	P	636 ± 147	0.002 ± 0.001	0.97	
PCA3	TBBPA	0.13 ± 0.02	0.09 ± 0.1	0.63	0.00019
EPR2	BDE209	0.027 ± 0.003	0.07 ± 0.05	0.77	0.000019
EPR3	Al	7.6 ± 1.1	0.004 ± 0.001	0.95	0.11*
EPR3	P	103 ± 12	0.007 ± 0.003	0.88	

* Represent the amount of AlPi leached from the Polymer

** Represent the amount of ZS leached from the polymer

The maximum concentrations (C_{max}) of Al and P from AlPi leachates from PBT3 were 2.4±0.2 and 9.5±0.5 $\mu g/cm^2$, respectively. These levels were lower for PBT4 with a C_{max} of 1.7±0.2 and 7.2±1.0 $\mu g/cm^2$ for Al and P, respectively. This corresponds to 0.030% and 0.021% of AlPi leaching from the PBT3 and PBT4 plates, respectively (Eq.2). We have assumed that brominated polystyrene is not leaching as it is a polymer material which is completely insoluble in water.

Polyamide 6.6 (PA)

Three PA polymer-FR formulations were prepared (Table 1). The first, PA2, contained 21.3% brominated polystyrene + 10.7% antimony trioxide (synergist). As halogen-free alternative for brominated polystyrene the following two formulations were made: PA3 containing 13.3% AlPi +6.7% MPP + 3% ZS (synergist), and PA5 which contained 16.67% AlPi +8.33% MPP.

Both Al and P leach from the PA polymer-FR formulations and also Zn was detected in the leachates from PA3 (Table 2). The k, C_{max} and the TCLP concentration after 18h were calculated for PA3 and PA5 (Table 3). The C_{max} values of Al and P in the leachates from PA3 were 20±0.15 $\mu g/cm^2$ and 258±50

µg/cm^2, respectively, and from PA5 these were 25±58 µg/cm^2 and 636±147 µg/cm^2, respectively. These levels correspond to 0.31% and 0.32% of AlPi leaching from the PA3 and PA5 plates after 30 days, respectively. The Al:P ratio for AlPi was 1:3.5. However, in the leachates from PA3 this ratio was 1:13 and for PA5 a ratio of 1:25 was observed. The PA3 and PA5 formulations contain a mixture of AlPi with MPP both containing phosphor, so the ratio 1:3.4 for AlPi is being influenced by the P originating from MPP as well. These results therefore show that both AlPi and MPP leach from the PA moulded plates.

Epoxy resins (EPR)

BDE209 is used as an additive FR in EPR. Substitution of BDE209 in EPR is feasible with a mixture of AlPi and MPP. For both EPR3 (EPR +20% AlPi + 20% MPP) and EPR2 (EPR + 20% BDE209 + 10% antimony trioxide) leaching experiments were performed and the k and C$_{max}$ were calculated (Table 3).

The AlPi, MPP and BDE209 leach from the polymer-FR formulations. The Al:P ratio is higher than 1:3.4, with indicates that not only AlPi leaches but also MPP from the EPR formulation. AlPi and MPP leached slower than BDE209; k for Al is 0.004 h^{-1}, and 0.07 h^{-1} for BDE209. However, the maximum concentration of AlPi leached after 30 days is more than 100 times higher than of BDE209. The percentage leached after 30 days is 0.11% for AlPi and 0.000019% for BDE209 from the EPR moulded plates.

Polyphenylene ether/ High-impact polystyrene (PHB)

PBDPP can be used as an alternative FR for BDE209 in PHB. The leaching behavior of PBDPP and BDE209 from PHB was tested. The first formulation, PHB2, contained PHB + 14% BDE209 + 6% antimony trioxide and the second, PHB3, contained (PHB + 15% RBDPP). A very small amount of BDE209 (0.8 ng/cm^2) leached from the PHB2 formulation after 30 days and no PBDPP (<8.0 ng/cm^2) leached from the PHB at all.

Acrylonitrile butadiene styrene terpolymer (PCA)

In PCA polymers, PBDPP and BPA-BDPP can be used as alternative FRs for BDE209 or TBBPA. The first test formulation, PCA2, contained PCA + 10% BDE209 + 5% antimony trioxide and the second, PAC3 contained PCA + 10% TBBPA + 5% antimony trioxide., The third formulation, PCA4, contained PCA + 15% RBDPP + 3 %PTFE and the fourth formulation, PCA5, contained (PCA + 20% BPA-BDPP + 20%PTFE). No differences in leaching were observed between the BFR (BDE209) and the alternative HFFRs PBDPP and BPA-BDPP. After 30 days no BDE209 (<0.1 ng/cm^2), PBDPP (<8.0 ng/cm^2) or BPA-BDPP (<0.5 ng/cm^2) were detected in the leaching solutions. TBBPA was the only FR that leached from PCA polymer with an C$_{max}$ of 0.13 µg/cm^2.

Discussion

Polymer and FR comparison

The addition of synergists (nanoclay or zinc stannate) to the polymer with AlPi changed the structure and leaching behavior of the moulded plates. Nanoclays (PBT3) caused an increase in leaching of Al which can be seen from the increased leaching rate and maximum concentration after 30 days (Table 2). The addition of ZS in the PA3 formulation besides AlPi increased the leaching rate of Al, but a difference in C_{max} was not observed. Therefore, ZS had less influence on the leaching behaviour of AlPi from PA than the addition of nanoclay on the PBT polymer. Yet, the concentration of Zn leaching from PA3 is relatively high compared to the leaching of AlPi and MPP (Table 1). Only 3% ZS was added to PA3 compared to 20% AlPi + MPP. The Zn levels were, however, higher than the Al levels in the leachates of PA3.

AlPi and BDE209 have been added to different polymer types which allowed a comparison in leaching behavior between the polymers. AlPi was added to three polymers (PA, PBT and EFR) in five formulations (Table 1). The percentages AlPi leaching from each of the polymers based on the Al concentrations are shown in Fig. 4. Differences in leaching behavior were observed for AlPi from the different polymer formulations. The highest percentage of AlPi leached from the polyamide polymer (PA3, 0.31%) and PA5, 0.32%), which was more than 10-fold higher than from polybutylene terephthalate (PBT3, 0.030%). This indicates that besides the presence of a synergist, the polymer type has a strong influence on the leaching behaviour of FR from moulded plates.
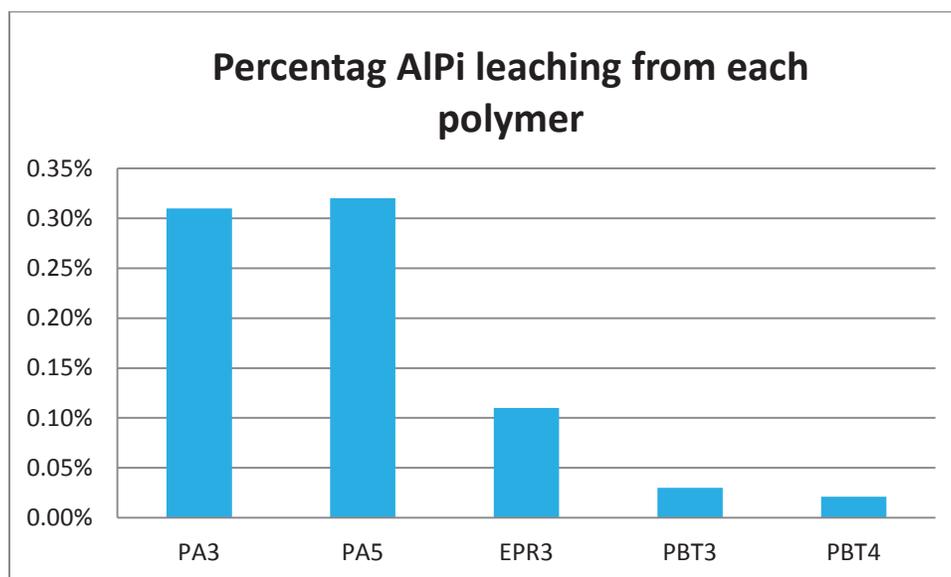

Figure 4. Percentage AlPi (%) leaching from five different polymer flame retardant formulations.

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A positive linear relationship was found between the percentage leaching and the impact strength and strain at break. The harder the material, and maybe therefore also more brittle, the higher the leaching.

In addition, the surface structures of the PA, EPR and PBT moulded plates were studied, using 3D laser microscopy. Although structural differences were observed for PA5, EPR3 and PBT4 (Fig. 5) the differences in leaching found for AlPi could not be explained.
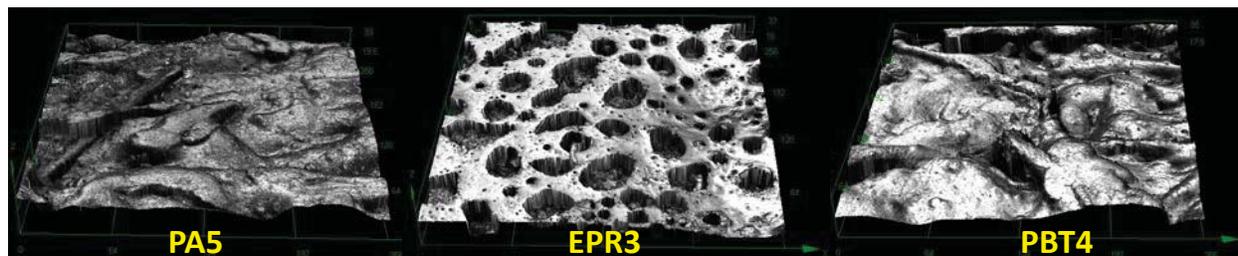

Figure 5. 3D laser microscopic pictures of PA5, EPR3 and PBT4 using a 50x zoom on 258 x 258 µm of each plate.

Variation in leaching behaviour was also observed for BDE209 between PCA, PHB and EPR (Fig 6). No BDE209 was detected in the leachates from PHB and only in the 30 days leachates from PCA BDE209 was detected at a very low concentration (0.8 ng/cm^2). Highest concentrations were observed in the leachates from EPR with a C_{max} of 27 ng/cm^2. In all polymers, BDE209 is used as an additive flame retardant and thus not covalently bound to the polymeric materials, so this cannot explain the differences. Compared to PHB2 (14%) and EPR2 (20%), a lower amount of BDE209 was added to PCA2 (10%), which could have influenced the results to some extent. However, it is more likely that the leaching behaviour is influenced by the polymer type. The surface structures of the PCA, PHB and EPR containing BDE209 are shown in figure 6. The surface of PCA and PHB were smooth compared to the rough surface of EPR (Fig. 6). The rougher structure may have contributed to the higher leaching of BDE209 from EPR than from PCA and PHB plates.

PBDPP and BPA-BDPP were not detected in the leachates from PHB and PCA moulded plates. No explanation could be given. Probably the polymer type in combination with the smooth surface of the PHB and PCA plates reduced the leaching of PBDPP and BPA-BDPP from the plates.

In conclusion, substantial variation in leaching behavior of FRs are found between polymer types. One of the main factors effecting the leaching behavior is the polymer type as has been seen for AlPi and BDE209. Factors as porosity, surface and hardness of the polymer are probably important factors.
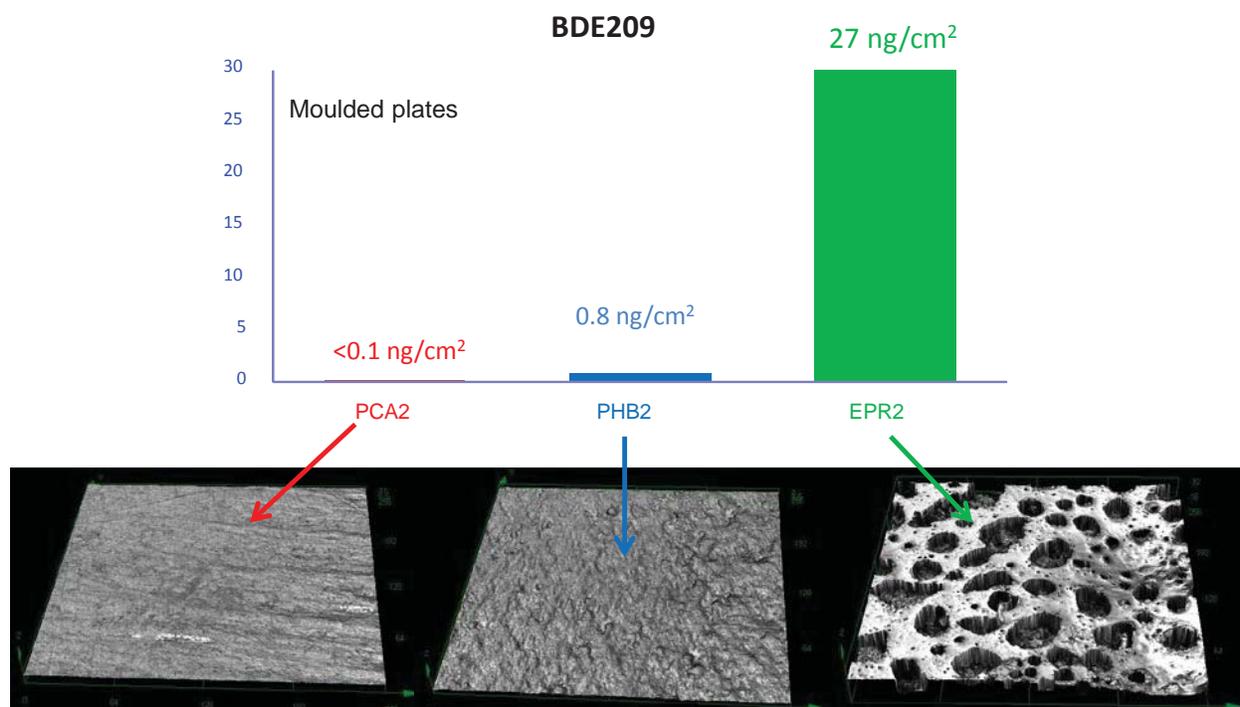
Figure 6. Concentrations of BDE209 (ng/cm^2) leaching from three different polymer plates. PCA2; PCA + 10% BDE209 + 5% ATO, PHB2: PHB + 14% BDE209 + 6% ATO, EPR2A1: ERP + 20% BDE209 + 20% ATO. Included are the *3D laser microscopic pictures using a 50x zoom on 258 x 258 µm of each plate.*

Particle size: Pellets versus moulded plates

The influence of the particle size on the leaching behaviour of FR were studied in a leaching experiment with PBT and PA pellets and moulded plates containing AlPi. The leachabilty of AlPi from the PBT pellets was 80-100 times higher than from the PBT moulded plates. Also PA pellets leach more (20-50 times) than the plates. Keith et al. (2008) also observed that a decrease in particle size of printed circuit boards (PCBs), from 10-20mm to <2mm, increased the amount of lead leaching from PCBs by a factor of 10. This was also observed for BFRs (PBDEs) by Kim et al. (2006) and Zhou et al. (2013).

In the leachates from the pellets containing a synergist (ZS or nanoclay) the AlPi concentrations was significantly higher, up to 2.5 times higher for PBT and 1.4 times higher for PA. We assume that this increase in leaching is related to the porosity of the polymer pellets, as the pellets containing a synergist (nanoclay) were more porous. The results observed for the PBT pellets were consistent with the PBT moulded plates. However, for PA the higher AlPi levels observed in the pellets was not observed in the PA moulded plates.

To investigate the influence of the pH on the leaching behaviour we compared the TCLP method with the DIN 38414-S4. TCLP uses a buffered leaching solution with a pH of 4.93, and the DIN 38414 use only deionized water. The experiment was performed with the PBT pellets and the PA moulded plates containing AlPi. We observed for the PBT pellets (PBT3 and PBT4) no significant differences in C_{max} of AlPi between the TCLP or the DIN 38414 methods. Only the rate constant (k) was up to 2 times higher using the TCLP method. This indicates that equilibrium is reached faster by using the TCLP leaching solvent, however after 30 days the same amount of AlPi leached were found. Comparable results were observed for the PA moulded plates. Similar C_{max} and a 2 times higher rate constant using the TCLP protocol.

Environmental relevance

The leaching experiments show that, using the modified TCLP protocol, AlPi is able to leach from PBT, PA and EPR polymers (Table 3, Fig. 4). C_{max} for Al ranges from 1.7 µg/cm^2 from PBT to 25 µg/cm^2 for PA. The addition of a synergist such as ZS changed the leaching behaviour of AlPi from PA . When an inorganic FR such as AlPi and the synergist ZS end up in the environment they may easily dissociate. Monitoring the occurrence and fate of AlPi and ZS in the environment by measuring the elements Al and Zn is not possible because of the natural occurrence of the elements. Aluminum is one of the most abundant metals observed in the earth crust. Typically Al levels in soil range from 10,000-300,000 mg/kg and Zn levels from 10-300 mg/kg (McLean and Bledsoe, 1992). The value of the leaching experiment for the inorganic flame retardants is therefore mainly for use in life cycle assessment studies.

BDE209 and TBBPA also leach from polymers according to the modified TCLP protocol, but at much lower levels. The C_{max} of BDE209 ranged from 0.8 ng/cm^2 in PHB to 27 ng/cm^2 from EPR. TBBPA leached from PCA with a C_{max} of 130 ng/cm^2. PBDEs have been detected worldwide in landfill leachates in highly variable concentrations. For example, Osaka et al. (2004) detected PBDE levels in landfills from Japan ranging from nd - 4 ng/L, which were lower than levels reported for landfills in China (2.5-12 ng/L), South Africa (8.4 - 55 ng/L) and Canada (0.003 - 1020 ng/L) (Huang et al., 2013, Odusanya et al., 2009, Li et al., 2012). Highest PBDE levels were observed by Kwan et al.(2013) in the leachates from eight tropical Asian countries ranges from 3.7 to 133,000 ng/L, with increasing levels towards urban and industrialized Asian countries. BDE209 was not detected in landfill leachates from Japan and South Africa. It was, however, the most dominant PBDE in landfill leachates from China (1.6 - 95 ng/L), Canada (mean 166 ng/L) and in most of the Asian countries (0.77-97,800 ng/L) (Osaka et al., 2004, Odusanya et al., 2009, Haung et al., 2013, Li et al., 2012, Kwan et al., 2013). Many factors such as anaerobic or photolytic debromination, sorption to organic materials influence the leaching behaviour in landfills (Kim, et al. 2006, Odusanya et al., 2009, Haung et al., 2013, Gereche et al. 2005, Watanabe et al. 1987). In addition, to these factors our study showed that the polymer type is an important factor driving the leaching process.

Using the modified TCLP method, the levels of the HFFRs leaching from the polymers were up to three orders of magnitude higher than the BDE209 and TBBPA levels. This can be explained by the higher solubility of some metal based FRs compared to BDE209 and TBBPA in the TCLP leaching solvent. Osaka et al. (2004), Kim et al. (2006), Choi et al. (2009) and Zhou et al. (2013 observed that the leachabilty of PBDEs and TBBPA increased by using dissolved humic matter (DHM). Kim et al., (2006) compared the leaching of BDE209 from a TV containing 21,000 µg/g BDE209 after 5 days of leaching (L/S 100:1) using water and DHM as leaching solution. The BDE209 levels in the leachates in water was 77 ng/L, and 210 ng/L after with DHM. Also Choi et al. (2009) observed 10-fold higher BDE209 levels if DHM was used as leaching solution instead of water. The enhancement in leachabilty in the present of DHM was explained by the complex formations of BFRs and dissolved humic matter (Kim et al., 2006).

Overall AlPi, ZS, BDE209 and TBBPA leach from the polymer material and may, after disposal, end up in landfill leachates. Due to the complexity and variety of the leaching circumstances, comparing the C_{max} of the FRs found in leaching tests with the levels observed in landfills is difficult. Different processes such as waste pre-treatment, anaerobe or photolytic degradation, sorption of the hydrophobic BFRs to the surrounding soil, age of the landfill influence the FR levels in the leachates (Opperhuizen et al., 1985, Huang et al. 2013, Kim et al., 2006, Gereche et al., 2005, Zhou et al., 2013, and Watanabe et al., 1987).

Conclusions

The polymer type is the main determining parameter of leaching behavior. Three polymers (PBT, PA6.6 and epoxy resin) showed the strongest leaching properties. Almost no FR leaches from the PPE/HIPS and PC/ABS polymers. The porosity of the materials has a strong influence on the leaching behavior of the FRs. Differences have been observed between leaching behavior of BFRs compared to that of HFFRs. In the PA6.6 and PBT, the alternative FRs leach stronger than brominated polystyrene, mainly due to the fact that a polymeric-based FR is completely insoluble in water. Compared to BDE209, higher levels of AlPi leached from epoxy resin. There were no differences between leaching of HFFRs and BFRs in PHB and PCA polymers. The leaching methods developed are useful to compare the leaching behavior of BFRs and HFFRs from different types of polymer materials. The data presented can be used in the design of polymer-FR formulations to reducing leaching of FRs.

Acknowledgements

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