RECYCLING OF TECHNICAL POYMERS FROM ELECTRONIC WASTE WHILE ELIMINATING BROMINATED FLAME RETARDADANTS AND PBDD/F

Martin Schlummer, Fritz Brandl, Ludwig Gruber, Andreas Mäurer, Angela Möller, Gerd Wolz

Fraunhofer Institute for Process Engineering and Packaging, Dept. Product Safety and Analysis, Giggenhauser Str. 35, 85354 Freising, Germany

Introduction

In the past decades special polymer parts of electronic articles were equipped with brominated flame retardants including polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE). After PBB and PBDE have been recognised as a possible source of polybrominated dioxins and furans (PBDD/F),[1,2] producers of electronic equipment started to fade out the use of these flame retardants.

However, due to the expanded life time of at least some electronic articles, polymers in today´s electronic waste may still contain PBB and PBDE but also PBDD/F in the ppb range[3]. Besides technical problems it is mainly the probable existence of high PBDD/F levels in electronic waste polymers which hinders any mechanical recycling approaches to treat this waste fraction[4], even if waste amounts and polymer properties would favour a recycling from the economic point of view.

A new solvent based polymer recycling process developed in our institute might serve as a solution to this problem[5]. The technique involves a dissolution step in which polymer containing waste fractions are dissolved, a cleaning step and a re-precipitation of the polymers by adding a different solvent. Finally, the precipitated polymer is dried and regranulated (Fig. 1). Treating PVC and ABS polymer fractions the general ability of this process has been demonstrated to substantially eliminate additives and contaminants from the polymer phase including phthalates and PBDD/F [5].

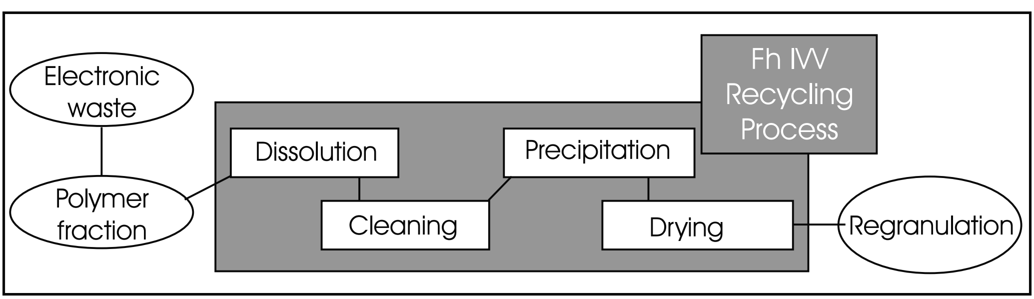

Figure 1. Recycling of polymers from electronic waste with the Fh IVV Process

In order to further optimise the reduction potential and to adjust the single process steps to the polymer types present in electronic waste plastic fractions we built up the following project cluster:

Project 1) Screening of typical waste fractions for polymer types and levels of PBDD/F and flame retardants

Project 2) Process optimisation driven by polymer types to handle and mass balances for brominated flame retardants and PBDD/F

Project 3) Tests of different toxic waste treatment approaches to decontaminate the separated waste fraction containing brominated flame retardants and PBDD/F

Project 4) Development of analytical tools for an efficient and inexpensive quality assurance

Here we present first results of the projects 1 and 2 focussing on waste fractions containing high amounts of TV set and monitor housings gained from a local disassembling plant. It should be stated that the mass balance results shown summarise the reduction potential of the initial state of the FhIVV recycling process. All future process optimisation approaches will be mass balanced and compared with the current state.

Methods and Material

Characterisation of waste input, intermediate products and regranulated samples

FT-IR: Types of polymers and polymer blends were identified in ground samples by Fourier transform infrared spectroscopy applying the *golden gate* technique.

X-ray fluorescence analysis: The existence of brominated flame retardants was screened via bromine determination with energy dispersive x-ray fluorescence analysis (EDXRF). Since the surfaces of the samples potentially affect the precision of the results and since they were quite different for the investigated materials, the samples were dissolved in suitable solvents and the solution were analysed for bromine.

Determination of PBDD/F and brominated flame retardants: To characterise input materials, intermediates (dried precipitates) and products (regranulates) of the process the representative samples were spiked with ^{13}C-PBDD/F standards and extracted with cyclohexane by accelerated solvent extraction. The extracts were gravimetrically devided in a flame retardants fraction and a PBDD/F fraction. The first fraction was diluted to concentrations of about 50 ppm, and analysed for decabromodiphenyl ether (DeBDE), octabromodiphenyl ether (OcBDE), tetrabromobisphenole A (TBBP A), 1,2-bis-tribromophenoxyethan (TBPA), resorcinol-diphenylphosphat (RDP) and triaryl phosphates (TAP) by HPLC-UV/MS. Method details are described elsewhere [6].

The PBDD/F fraction was treated with a four column clean-up using acid/basic silica, alumina oxide and two times florisil. The second florisil column was necessary to eliminate residual flame retardants which might disturb the analysis of polybrominated furans. After clean-up the samples were analysed by GC-HRMS (MAT 90, ThermoFinnigan) and quantified using an isotope dilution method.

Mass balance approach

Lab scale recycling unit: The lab scale recycling unit consists of a stirred 10 litre solving reactor, a filtration unit, a precipitation unit and a ventilated oven.

Processes tested: According to the process outlined in fig. 1, the input materials were dissolved, sieved and precipitated. The fine precipitated polymer was washed with fresh solvent twice before it was dried at temperatures below 100 °C. The resulting dried powder (intermediate) was finally regranulated by laboratory scale extrusion (Fa. Haake). The maximum extrusion temperature was 240 °C to simulate a worst case extrusion.

Materials tested: 7 Samples containing different types and amounts of polymers and flame retardants were submitted to the Fh IVV process (table 1). The column “FR present” indicates flame retardants identified in the polymers used, “FR added” refers to flame retardants the polymers were fortified with. Input materials C to G were contaminated with PBDD/Fs produced by thermolytic degradation of technical octabromodiphenylether at 600°C for 7 minutes and with a FR mixture of DeBDE, OcBDE, TBPE and TBBPA.

Table 1. Samples subjected to the lab scale process

No	polymers / polymer blends	FR present	FR added	addition of PBDD/F
A	ABS	OcBDE, TBBPA	none	none
B	HIPS	DeBDE	none	none
C	ABS	OcBDE, TBBPA	FR mixture	yes
D	HIPS	DeBDE	FR mixture	yes
E	monitor shredder	n.d.	FR mixture	yes
F	disassembling plant shredder	n.d.	FR mixture	yes
G	ABS, HIPS, PPO/PS, ABS/PC	none	FR mixture	yes

Results and Discussion

Results of the material screening of 34 TV set and monitor housings are displayed in fig. 2 indicating a dominance of HIPS and ABS in these waste fractions. The frequency of brominated flame retardants which have been shown to produce PBDD/F during extrusion (DeBDE, OcBDE and TBPE)[3] accounts for 40 % in the materials tested so far (fig 3) and hints to the increased caution these waste materials have to be handled with.

polymer / polymer blend	frequency (n=34)
ABS	24 %
ABS/PC	9 %
ABS/PVC	9 %
HIPS	34 %
PPO/PS	24 %

Figure 2. Polymers/polymer blends identified

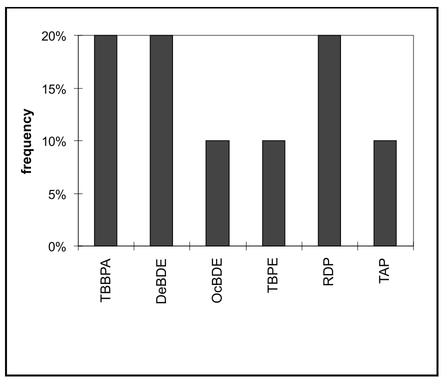

Figure 3. Flame retardants identified

Fig. 4 gives a typical congener pattern of tetra- to hexabrominated PBDD/Fs determined in a typical ABS monitor housing containing OcBDE (sample A). According to the German Chemikalienverbotsverordnung this material has to be excluded from common mechanical recycling processes. However, applying the FhIVV recycling process could significantly reduce the levels of bromine, TBBPA and PBDD/F in the samples A-G (see figures 5-7) even if the process has not been optimised yet. In future the reduction potential will be increased by improving the cleaning and the precipitation step.

References

1. Donnelly JR, Grange AH, Nunn, NJ, Sovocool G, Brumley WC Mitchum RK (1989) Biomed. Environ. Mass Spectrom, 884.

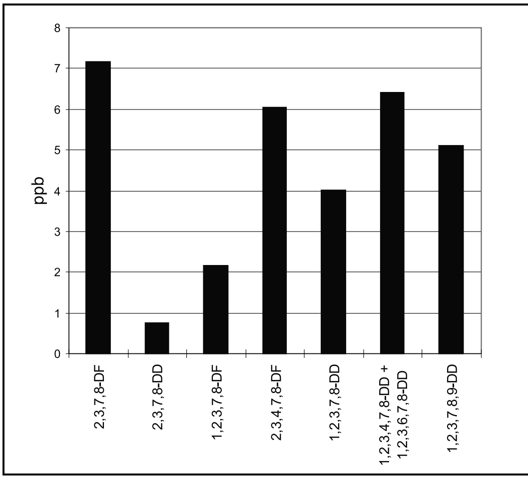

Figure 4. PBDD/F in an ABS/OcBDE monitor housing

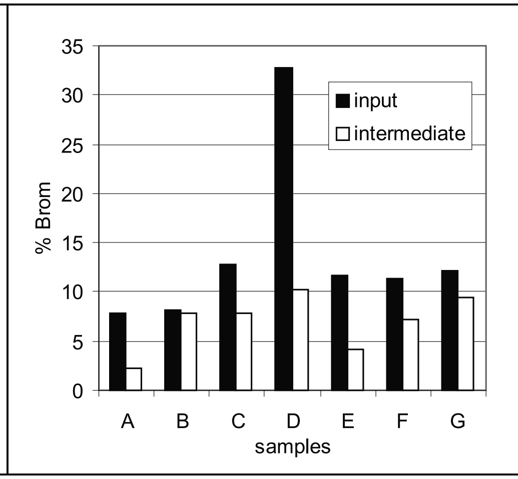

Figure 5. Bromine reduction obtained during the Fh IVV recycling process.

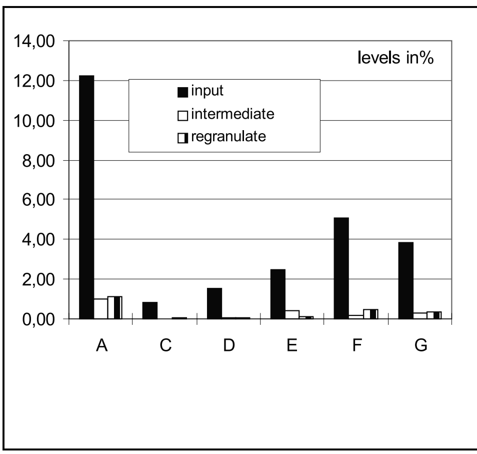

Figure 6. TBBP A reduction obtained during the Fh IVV recycling process.

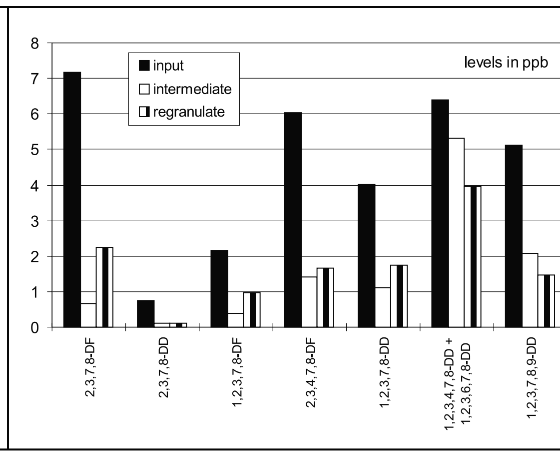

Figure 7. PBDD/F reduction obtained during the Fh IVV recycling process.

2. Brenner K, Knies H (1990) Organohalogen Compounds 2, 319.
3. Riess M, Ernst T, Popp R, Müller B, Thoma H, Vierle O, Wolf M, van Eldik R (2000) Chemosphere 40, 937.
4. Meyer H, Neupert M, Pump W, Willenberg B (1993) Kunststoffe 83, 253.
5. Knauf U, Mahlberg A (2000) Final report, BayForrest Research Project F161.
6. Schlummer M, Brandl F, Mäurer A, Luck T (2001) Müllmagazin 3, 39.