USING THE CREASOLV® PROCESS TO RECYCLE POLYMERS FROM CANADIAN WASTE PLASTICS CONTAINING BROMINATED FLAME RETARDANTS

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Introduction

End-of-life management of polymers from waste of electric and electronic equipment (WEEE) is challenging due to the presence of PBBs and PBDEs, two types of dominating brominated flame retardants (BFR) in older polymeric casing applications. In particular, technical OctaBDE and DecaBDE were identified in shredded waste casings, ranging from 0.2-2.1 weight %[1]. Additionally, it has been shown that WEEE plastics may contain polybrominated dioxins and furans (PBDD/F) in the lower ppb range[1], which are the result of thermal stress on BFR-equipped materials.[2]

In Canada, new legislation supports a zero waste approach for the treatment of WEEE. With respect to WEEE plastics this implies a material recovery approach. Due to product threshold values for OctaBDE of 0.1 weight% on the European market[3] and equivalent initiatives in China and North America, a recovery technology will have to include an elimination of OctaBDE itself or of polymers equipped with OctaBDE.

A Canadian company, 36ZeroWaste Group Inc., has identified the CreaSolv® process as the most promising technological approach to treat WEEE plastics in Canada. In a recent study of the British Waste & Resources Action Program (WRAP), which investigated technologies for BFR containing polymers, this processes was also found to be the most promising approach from both an economical and ecological point of view. The patented technology developed by the Fraunhofer-Institute for Process Engineering and Packaging IVV, Germany, removes BFRs from polystyrene-based plastics efficiently[4]. The technology involves three main steps:
a) dissolving target plastics with a selective solvent while other components of the waste remain undissolved;
b) separation of contaminants from the polymer solution; and
c) precipitation of the target plastic from the purified polymer solution (Figure 1).
Products have been shown to comply with European RoHS directive and the German Chemikalienverbotsverordnung.[4]

Previous CreaSolv® trials have been based on European polystyrene rich polymer fractions but only little is known about its comparability to Canadian WEEE plastics, which may contain different types and levels of BFR. Additionally, material application for casings may be different and negatively affect the BFR elimination of the CreaSolv® process.

Therefore, Fraunhofer IVV and 36ZeroWaste began a small-scale feasibility study in order to investigate the applicability of the CreaSolv® process to plastics from Canadian WEEE dismantling plants. For process evaluation, input and CreaSolv® products were analysed for BFR, chlorine and cadmium in detail.

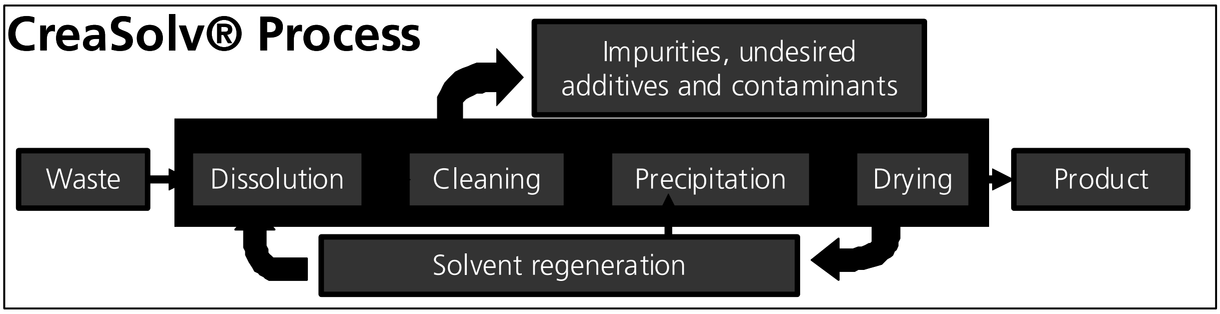

Figure 1: Process scheme of the CreaSolv® process

Materials and Methods

36ZeroWaste Group Inc. (Vancouver, Canada) provided samples of plastics gained from dismantling of waste IT equipment (monitors, hard drives, printers) which were assigned to following five time periods: 1980-1984, 1985-1989, 1990-1994, 1995-1999 and 2000-2005. For each time period samples contained plastic chips with 20-40mm width as well as 250 g portions of mixed casing material ground to a particle size of < 2mm. Ground samples were produced from casings of 60 monitors, 30 printers, and 10 keyboards, each. According to collection records of 36ZeroWaste Group Inc., in 2007 the mentioned periods of production of electronic goods contribute to the overall waste stream as displayed in Figure 2.

Samples provided by 36ZeroWaste were subjected to a detailed screening via energy dispersive x-ray fluorescence analysis (EDXRF, Spectro X-LAB 2000) applying a standard method for WEEE plastics.
The CreaSolv® process: A small technical scale production was performed in order to check the general suitability of the input material in terms of solubility and bromine elimination. It was carried out in three consecutive trials with 1 kg of input each. Input samples were prepared by mixing samples from the 5 sampling periods according to their fractions given in Fig. 2. Input was dissolved in a CreaSolv® solvent and subsequently filtered through a 0.71 mm sieve in order to remove non-dissolved plastic chips. Co-dissolved contaminants as PBDD/F, PBDE, and other BFR were eliminated by a cleaning step using a proprietary CreaSolv® precipitation formulation. Cleaned intermediate products were dried in an oven overnight. Product yield and bromine elimination were calculated from masses and bromine levels in both the input and product.

Product characterization: An FT-IR screening using diamante ATR was performed as well as a RoHS compatibility check applying EDXRF, GC-ECD and GC-MS (quantification with ^{13}C-labelled internal standards).

Results and Discussion

Results of EDXRF screening of ground casing mixtures assigned to 5 productions periods from 1980-2005 are displayed in Figure 3. They show percent levels of bromine from 1980-1994, but significant lower levels below 50 mg/kg since 1995. In analogy, chlorine concentrations were in the per mille range until 1994 and dropped below 100 mg/kg afterwards. Cadmium levels decreased consistently and are below 10 mg/kg since 1994. However, measurements of plastic chips from 62 single casings revealed high bromine levels in the percent range in materials from all 5 different time periods, i.e. in samples from 1985-2005 (Figure 4). Therefore, it remains unclear whether these data indicate a significant phasing out of BFR application or not. It was found that the older the plastic casings, the prevalence of high Br levels increased. Additionally, high chlorine levels were obtained in a number of plastic chips. Most notable are two samples in which percent levels of both halogens were detected. Casings made of PVC or ABS/PVC blends are discussed as a source of these elevated chlorine levels.

Small technical scale recycling trials with the CreaSolv process were promising with regard to applicability of the Canadian WEEE plastics. Compared to previous trials with European WEEE plastics, differences in polymer compositions were identified. As a result, relatively high chlorine levels of the product were obtained, probably due to larger amounts of PVC or ABS/PVC blends in the input. Furthermore, process parameters had to be adjusted to the investigated material.

Recycling trials were successful with regard to elimination of BFR, including PBDEs. However, the observed bromine elimination (90-94% of absolute bromine input) was a bit lower than expected from former trials.[4] As displayed in Table 1, product levels of the dominating PBDE congeners, cadmium, chromium, mercury and lead are well below the threshold values of the European RoHS directive. Lower concentrated tetra- to hexabrominated BDE were below 100 mg/kg. A detailed mass balance of single PBDE congeners was out of scope of this pilot study.

Calculated bromine levels in the products were computed from measured BFR levels and their specific bromine content. Measured bromine concentrations exceeded the calculated levels by ~1070 ppm. Since this amount of bromine could not be attributed to a signal in the ECD-chromatogram, it indicates the presence of oligomeric BFR. These cannot be extracted with this technology but neither are they expected to form PBDD/F in polymer processing.

References

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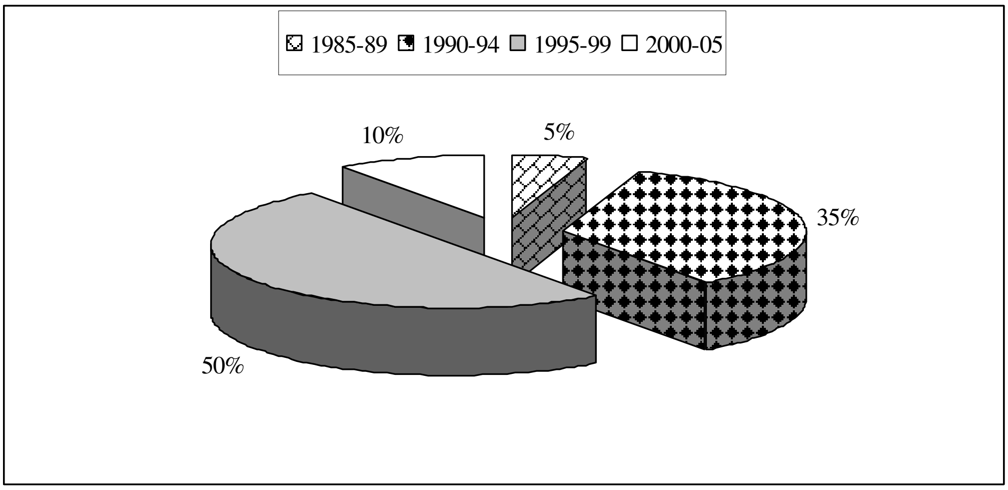

Figure 2: Distribution of production times in waste IT equipment recorded by 36ZeroWaste Group Inc. (Calgary facility) in 2007

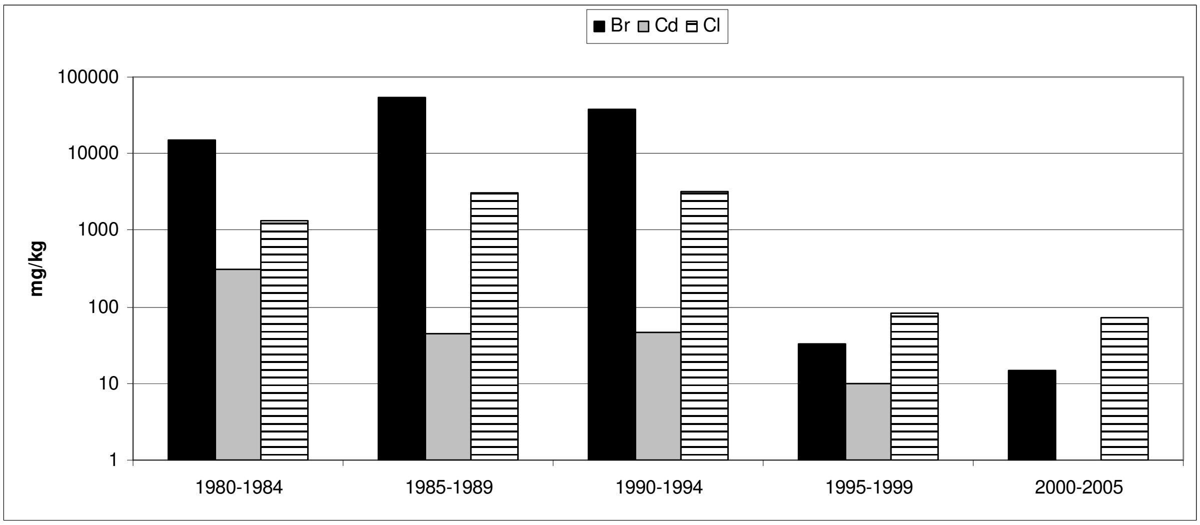

Figure 3: Bromine, cadmium and chlorine levels on a logarithmic scale identified in shredded samples from 5 investigated time periods.

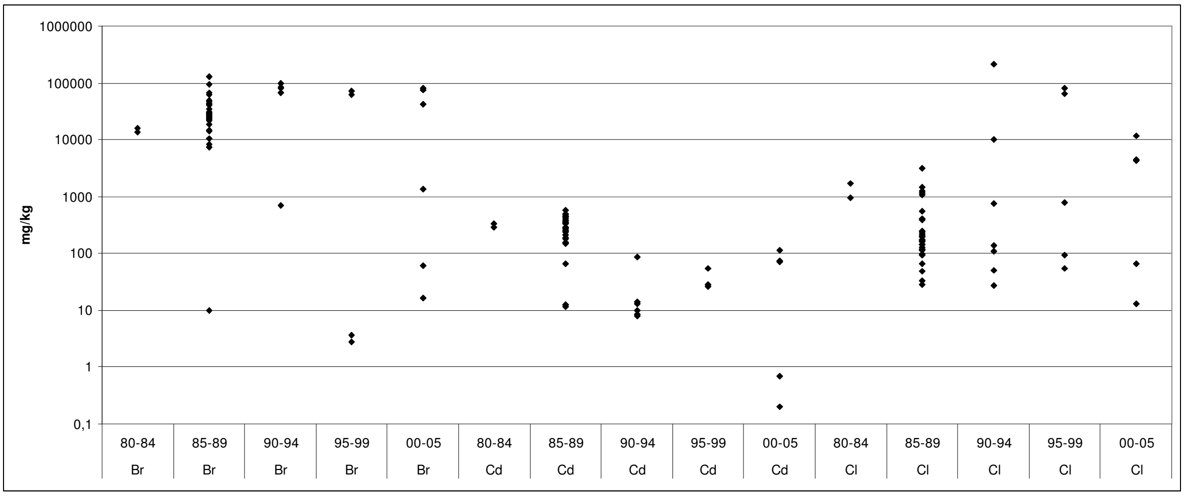

Figure 4: Bromine, cadmium and chlorine levels identified in 62 plastic chips

Table 1: Levels of cadmium, lead, mercury, chromium and PBDE congeners (mg/kg) identified in the CreaSolv® product

Compound	Product	RoHS limit
Cd	80	100
Pb	211	1000
Hg	< 5	1000
Cr	31	1000
Calculated technical OctaBDE*	666	1000
BDE 183	273	-
BDE 197	526	-
BDE 207	232	-
BDE 209	358	-
TBPE	357	-
TBBP A	5581	-
PBB	< 100	1000
Bromine calculated**	4087	-
Bromine (EDXRF)	5155	-

* Technical OctaBDE is calculated on the base of a 41% share of BDE 183.

** Assuming a bromine share of 54%, 70 %, 79% and 83% for TBBPA, TBPE, technical OctaBDE and DecaBDE, respectively.