Determination of Polychlorinated Biphenyls (PCBs) and Phthalates in Waste Polymer Samples Intended for Mechanical Recycling

Cleres S.[1], Gruber L.[2], Lastennet G.[1], Schlummer M.[2], Wolz G.[2]
[1]Büchi Labortechnik AG, 9230 Flawil, Switzerland; [2]Fraunhofer Institute for Process Engineering and Packaging IVV, 85354 Freising, Germany

Abstract

The purpose of this study was to determine the levels of PCBs and phthalates in homogenized waste polymer samples intended for mechanical recycling using pressurized solvent extraction with two different instruments: SpeedExtractor E-916 (Büchi) and ASE® 200 (Dionex). Both instruments showed similar results, but with the SpeedExtractor E-916 the extraction time per sample was much shorter. Measured PCB levels were in the lower and sub ppm range. They were used to calculate total PCB levels using the German LAGA norm[5]. No sample exceeded the 50 ppm threshold value, however, the margin of safety of one sample was much smaller then expected. DEHP dominated the phthalate pattern as expected. Both samples exceeded the 0.1 % level set by the U.S. Consumer Product Safety Improvement Act for Toys[3]. As a matter of fact, these results show the necessity to monitor the levels of PCBs and phthalates in certain waste polymers for mechanical recycling.

Introduction

PCBs are persistent organic pollutants (POPs) and have been therefore phased out of production in many parts of the world[1,2]. PCBs were widely used in polymer because of their non-flammability, chemical stability, high boiling points and electrical insulating properties. Phthalates are added to plastic to increase flexibility. Recently, health concerns over human exposure to phthalates resulted in regulations regarding the type and the levels of phthalate congeners in consumer products[3]. Today PCBs are not expected to be present in virgin polymers but reclaimed polymers from specific polymer waste streams may contain PCBs and phthalates in such levels that they may not conform to the actual quality standards[4]. The new Büchi's SpeedExtractor E-916 is an innovative instrument especially designed for environmental laboratories (Figure 1). Its unique parallel extraction system prevents cross-contamination, guarantees high reproducibility and high sample processing speed. The purpose of this study was to determine the levels of PCBs and phthalates in homogenized polymer samples from typical shredder residues intended for mechanical recycling using two instruments, the SpeedExtractor E-916 and the ASE® 200.

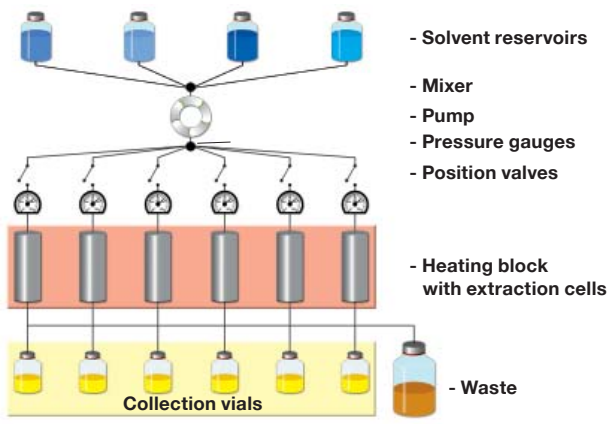

Fig. 1: *Schematic representation of the SpeedExtractor E-916 set-up*

Materials and Methods

PCBs and phthalates in two waste polymer samples intended for mechanical recycling were extracted using the SpeedExtractor E-916 with 6 extraction cells (20 ml) in parallel and the ASE® 200 (22 ml extraction cells) sequentially. Two ground polymer samples (< 0.7 mm) from automotive waste streams containing high polymer content were used as test material.

Tab. 1: *Extraction parameters of the SpeedExtractor and the ASE®*

	SpeedExtractor E-916	ASE®
Solvent	*n*-hexane 90%, 2-propanol 10%	*n*-hexane 90%, 2-propanol 10%
Temperature	80°C	80°C
Pressure	100 bar	100 bar
Cells	20 ml	22 ml
Cycles	3	3
Hold	5 min	5 min
Discharge	2 min	-
Flush with solvent	1 min	40%
Flush with gas	2 min	120 s

Polymer waste samples (approx. 0.6 g) were mixed with pumice stone and filled into the extraction cells. ^{13}C-labeled internal PCB standard and 2 deuterated internal phthalate standards (D4-DBP and D4-DEHP) were added, and the extraction process was performed according to the parameters given in Table 1. 0.5 ml to 1.0 ml of the extract was used for phthalates analysis. The residual extracts were cleaned with a mixed column containing acid and basic modified silica and reduced to 50 µl.

The determination of the PCB congeners was carried out with a GC-MS (HP 5890 Series II coupled to Thermo Finnigan TSQ 7000) operated in single ion monitoring mode. Quantification of 6 indicator PCBs (#28, #52, #101, #138, # 153, #180) was based on isotope dilution. Phthalates were analyzed with GC-MS (Shimadzu QP-5000) in SIM mode. Quantification was based on an internal standard method with deuterated standards.

Results

Two extracts from two waste polymer samples were analyzed. Table 2 displays the mean concentrations obtained for PCB and phthalate congeners in ppb. The concentration values obtained with both instruments were comparable, the SpeedExtractor E-916 however showed a great advantage over the ASE® in terms of sample processing capacity, due to the parallel extraction of 6 samples.

Tab. 2: *Mean concentration in ppb (ng/g) for PCBs and phthalates extracted from two waste polymer samples*

	Sample 1 [ppb]		Sample 2 [ppb]	
PCB & Phthalates	E-916	ASE®	E-916	ASE®
2,4,4'-TriCB (28)	6,192	5,436	1,214	1,051
2,2',5,5'-TetraCB (52)	1,172	1,063	241	230
2,2',4,5,5'-PentaCB (101)	222	217	110	115
2,2',3,4,4',5'-HexaCB (138)	98.0	113	90.3	95.6
2,2',4,4',5,5'-HexaCB (153)	79.4	95.2	82.7	85.3
2,2',3,4,4',5,5'-HeptaCB (180)	18.5	21.7	21.1	19.7
Total PCB (German LAGA norm)	39,907	34,726	8,799	7,986
DiBP Diisobutylphtalate	8,565	7,837	21,369	22,134
DBP Dibutylphtalate	5,716	5,821	22,657	21,408
DEHP Diethylhexylphtalate	1,257,000	1,272,000	1,278,000	1,180,000

Measured PCB levels were found in the lower and sub ppm range. They were used to calculate total PCB levels using the German LAGA norm (5 times the sum of #28, #52, #101, #138, #153 and #180)[5]. Based on this, no sample exceeded the 50 ppm threshold value; however the margin of safety of sample 1 was much smaller than expected. For the phthalates, DEHP dominated the phthalate pattern as expected. Both samples exceeded the 0.1% level set by the U.S. Consumer Product Safety Improvement Act for Toys[3].

Conclusion

These results show the necessity to monitor PCBs and phthalates in waste polymers intended for mechanical recycling. Both techniques delivered comparable results but the SpeedExtractor E-916 has a great advantage over the ASE® 200 , because it allows the user to process a higher number of samples in a definite period of time, due to the parallel extraction set-up.

References

[1] European Commission Council Directive 96/59/EC. *Official Journal* L243, 24/09/1996 P.0031–0035
[2] Chemikalienverbotsverordnung. *BGBl.* I S.1328
[3] U.S. Consumer Product Safety Improvement Act of 2008, *Public Law* 110-314-Aug. 14, 2008
[4] Osada M., Tanigaki N., Takahashi S. and Sakai S. *Journal of Material Cycles and Waste Management* 2008:10:93
[5] Länderarbeitsgemeinschaft Abfall (LAGA) Merkblatt "Entsorgung PCB-haltiger Abfälle", Germany

Acknowledgments

We sincerely thank the analytical team of the Fraunhofer Institute for Processing and Packaging IVV, Freising, Germany.