

Analysis of flame retarded polymers and recycling materials

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Abstract

Polymer samples were analysed as received from a recycling company. Recycling of the material was tested for the flame retarded polymers identified to occur most frequently. The concentrations of polybrominated dioxins and furans (PBDD/F), as well as of selected flame retardants, were monitored during the recycling process in order to characterize the reaction behaviour of the flame retardants. The results demonstrate that flame retarded polymers can be recycled under certain experimental conditions.

1. Introduction

Recycling activities on polymeric materials are increasing and becoming more and more important in recent years. For certain polymers, suitable recycling strategies already exist [1]. A number of samples were analysed in order to investigate the recyclability of flame retarded plastics that often contain brominated flame retardants. Due to the variety of flame retarded plastics, new rapid analytical methods such as pyrolysis gas chromatography with mass spectrometric detection (py-GC/MS) [2], together with infrared spectroscopy (FT-IR) were employed. Following the identification and sorting of the samples according to type of polymer and flame retardants, material recycling was tested for each fraction. The reactivity of the flame retardants during the recycling procedure was studied by analysing for brominated dioxins and furans.

2. Experimental

Pyrolysis gas chromatography (py-GC/MS) with mass spectrometric detection was employed for the determination of the flame retardancy class of the samples [2]. In addition, the polymer was identified by infrared spectroscopy (FT-IR) in combination with thermogravimetric methods. Energy dispersive x-ray fluorescence (ED-XRF) was used to identify the halogen containing samples [3]. High resolution gas chromatography with mass spectrometric detection (HRGC/MS) was used to quantify the polybrominated dioxins and furans (PBDD/F) in the samples [4]. A suitable clean up method had to be developed for the quantification of the PBDD/PBDF content in polymer extracts containing high concentrations of polybrominated diphenylethers. The sample purification procedure adopted is shown in Figure 1. The HRGC/MS-analysis of the flame retardants was carried out following the H₂SO₄/silica column procedure. For the quantification of PBDD/F, two further Al₂O₃ clean up steps had to be included. The analysis

of these compounds was carried out in the single ion modus (SIM) using internal and external standards, respectively.

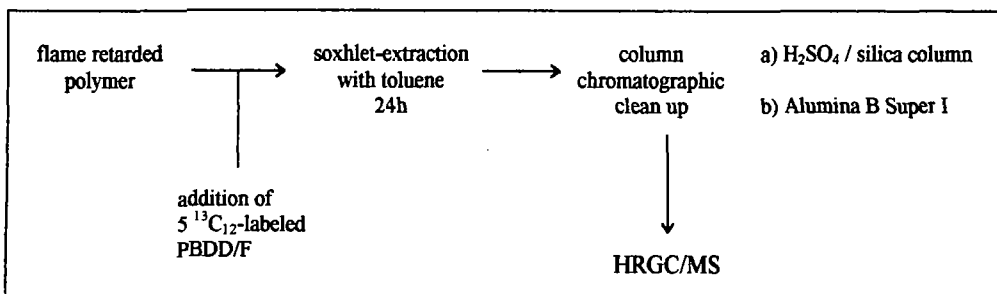


Figure 1: Isolation and purification for PBDD/F

Following chemical characterisation, the polymer samples were recycled. For this purpose the material was grinded to a size of 4 mm. A Leistritz 30.34 twin screw extruder was used. For the high impact polystyrene (SB) materials, the processing temperature was 190°C.

3. Results and Discussion

The materials were analysed as received from a recycling company. A total of 78 TV housings and 34 personal computer housings were analysed. Figure 2 presents an overview of the polymers identified in the samples analysed by FT-IR and py-GC/MS:

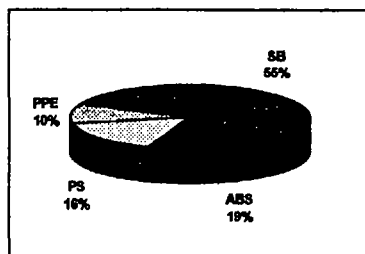


Figure 2: Polymers identified in the samples

The identified flame retardants are listed in Table 1. It shows that polybrominated diphenyloxides (PBDE) are commonly used in such materials. The samples were sorted according to the class of flame retardant and main polymer component. Two samples were composed that represent the most often occurring flame retardant-polymer combinations identified.

Flame retardant	Abbreviation	Occurrence in [%]
Polybrominated diphenyl oxides	PBDE	78
Polybrominated biphenyls	PBB	16
1,2-Bis-(tribromophenoxy)ethane	TBPE	3
Others		3

Table 1: Flame retardants identified in the samples

Polymer	Flame retardant	Sample
Impact modified polystyrene (SB)	PBDE	I
Impact modified polystyrene (SB)	PBB	II

Table 2: Groups of polymers formed

The samples I and II were recycled as a material. In Table 3 the concentrations before (samples I and II) and after the recycling procedure (samples I_R and II_R) are reported. The contents of those PBDD/PBDF-congeners referred to in the German legislation („Dioxinverordnung“) [5], were determined. The analysis was carried out according to the procedure outlined in Figure 1.

No	Compound	Sample I c [µg/kg]	Sample I _R c [µg/kg]	Sample II c [µg/kg]	Sample II _R c [µg/kg]
1.	2,3,7,8- tetra-BDD	<0,009	<0,016	<0,015	<0,108
2.	1,2,3,7,8-penta-BDD	<0,027	<0,032	<0,051	<0,051
3.	2,3,7,8-tetra-BDF	0,407	0,431	<0,009	0,082
4.	2,3,4,7,8-penta-BDF	5,453	4,048	<0,016	0,881
	SUM 1 (No. 1 to 4)	5,896	4,527	<0,091	1,122
5.	1,2,3,4,7,8-hexa-BDD + 1,2,3,6,7,8-hexa-BDD	<0,111	<0,023	<0,070	<0,086
6.	1,2,3,7,8,9-hexa-BDD	<0,111	<0,023	<0,070	0,086
7.	1,2,3,7,8-penta-BDF	<0,019	<0,021	<0,016	<0,017
	SUM 2 (No. 1 to 7)	6,137	4,594	0,247	1,311

Table 3: Concentration of PBDD/F congeners in the samples

According to this law there is a limit of 1 µg/kg for the sum of the concentrations of the congeners 1 to 4 (SUM 1 in Table 3) and 5 µg/kg for the congeners 1 to 7 (SUM 2 in Table 3).

In the case of sample II, Table 3 shows that all relevant congeners show concentrations below the detection limits. In the reprocessed material (sample II_R) the limits given are reached, but not exceeded too far. In terms of only this legislation, the recycling of high impact polystyrene containing polybrominated biphenyls as flame retardants would in principle be possible.

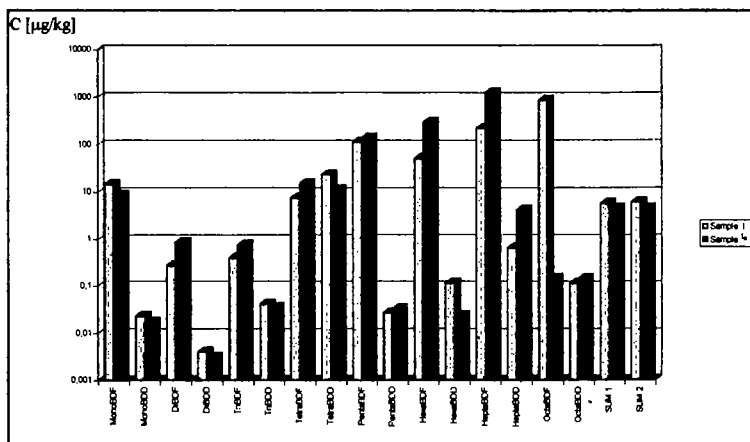


Figure 4: Influence of material recycling on the PBDD/F concentrations

In contrast, the limits given by the „Dioxinverordnung“ are exceeded five times in sample I. In Figure 4, SUM 1 and 2 together with the PBDD/F concentrations for all degrees of bromination, determined in the samples I and I_R, are presented in a logarithmic plot. In sample I_R the concentration indicated by the parameters SUM 1 and SUM 2 is significantly lower. As Figure 4 shows, the concentration of the higher brominated congeners such as OctaBDF decreases during the recycling procedure. On the other hand, the concentrations of the lower brominated congeners (HexaBDF, HeptaBDF) increase during the recycling procedure. The concentrations given by the parameters SUM 1 and SUM 2 in the reprocessed material are lower than in sample I. It follows that the recycling as a material might be practicable if a certain amount of new material (75%) is added.

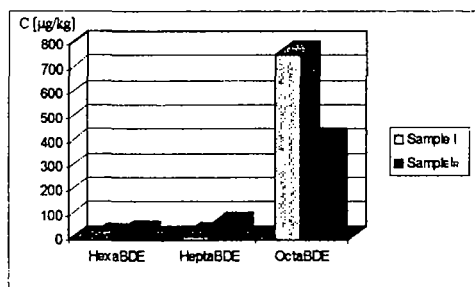


Figure 5: Influence of material recycling on the PBDE concentrations

Finally, Figure 5 represents the concentrations for the PBDE's in sample I and the reprocessed material sample I_R. For this flame retardant class, the concentration of higher substituted compounds decreases, whereas that for lower brominated compounds increases during recycling. Other flame retarded polymers will be investigated in further work.

4. Conclusion

It has been shown that polybrominated diphenylethers (PBDE) are still frequently found in polymers originating from electrotechnical applications. During recycling processes flame retardants as well as PBDD/F tend to form lower brominated products. The recycling as a material is feasible for certain groups of materials.

5. Acknowledgement

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6. Literature

- (1) T. Schubert, J. Schiebisch, G. W. Ehrenstein, Recycling von Kunststoffen der Elektrotechnik, in A. Wilderer, 4. BayFORREST Statusseminar, Munich 24.-25. October 1996, p.123 - 128.
- (2) B. Danzer, M. Riess, H. Thoma, O. Vierle, R. van Eldik, Organohalogen Compounds 31, 1997, 108-113.
- (3) B. Danzer, K. Brodersen, R. van Eldik, Chemical Analysis of Electronic Materials, International Conference and Exhibition Micro Materials, Berlin 16.-18. April 1997.
- (4) R. Dumler-Gradl, W. Miekisch, D. Tartler, H. Thoma, O. Vierle, 26th Symposium on Environmental Analytical Chemistry, Wien 9.-12. April 1996.
- (5) 1. Verordnung zur Änderung der Chemikalienverbotsverordnung, Bundesgesetzblatt Bonn 1994.