DIOXIN ASSESSMENT AND RECYCLING ASPECTS OF PLASTICS CONTAINING POLYBROMINATED FLAME RETARDANTS

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Introduction

Flame-retardants are playing a very important role to improve consumer safety. Severe flame retardancy requirements are applied to engineering resins such as poly(butylene terephthalate) (PBT). This plastic is from the polyester family. PBT's crystalline nature contributes good chemical resistance and physical properties. Flame retarding this polyester enables it to meet specifications in building products, automotive, and electrical & electronic applications.

There are several trends in the market regarding the use of flame retarded plastics:

- Miniaturization of component parts in computerized systems.
- Weight reduction by production of thin wall housings implying the need of high melt flow compounds.
- A recent trend, becoming increasingly important, is the safe recycling of used plastics. Recycling is important because it helps improve the environment and conserve resources. Poly(pentabromobenzyl acrylate) was assessed as a flame retardant in PBT matrix for recycling performance. Flame retardancy, physical properties and flow properties were examined. Very importantly, an assessment for dioxin contamination was made following severe thermal and mechanical processing conditions.

Methods and Materials

- Materials

A flame retarded plastic recipe was utilized which simulated commercial formulations. The resin selected was a general purpose molding grade. Antimony trioxide was incorporated as shown in Table 1. Standard stabilization and lubrication additives were employed.

TABLE 1: Compositions

	Amount (% by weight)	
PBT Plastic Resin	99.5	81.5
Poly(pentabromobenzyl acrylate)	0.0	12.0
Antimony trioxide	0.0	6.0
Stabilizers and Lubricants	0.5	0.5
Total Wt. Percent	100	100
Bromine content, %	0	8.4

- Recycling Methodology

Table 2 summarizes the sequence of events used to prepare samples for testing. Although the compounds were continually processed through six thermal cycles, only virgin and 6 pass samples were selected for testing and comparative purposes.

TABLE 2: Recycling Program

Process Step	Description
1. Extrusion History: 0^{th} Pass	Compound recipe as virgin
2. Extrusion History: 1^{st} Pass	Extrude 100% Virgin to produce 100% regrind.
3. Extrusion History: 2^{nd} Pass	Extrude 50:50 blend of Virgin to 1^{st} Pass regrind
4. Continue n^{th} reprocessing history made using 50% virgin and 50% (n-1) pass regrind.	
5. Extrusion History: 6^{th} Pass	Extrude 50:50 blend of Virgin to 5^{th} Pass regrind
6. Make Test Specimen	Injection mold test samples for 0^{th}, 2^{nd}, and 6^{th} pass compounds.
7. Testing	Flame retardancy Melt Flow Rate Tensile Strength Dioxin Levels

- Processing

The compounds in Table 1 were extruded in a twin-screw extruder at melt temperatures of approximately 255 to 275 °C. Compound pellets were then injection molded using standard molding techniques.

- Testing

All physical property testing was conducted using ASTM test specifications. Dioxin testing was made on samples prepared from the final recycling step (6th pass). Analysis for polybrominated p-Dibenzodioxins and Dibenzofurans contamination was made at Fresenius Institute, Germany. High resolution gas chromatography followed by high resolution mass-spectrometry was used for analysis of the polybrominated p-Dibenzodioxins and Dibenzofurans. The method of analysis included several chromatographic extraction and clean-up steps. Quantitation levels (in ppb's) were achieved by spiking the solutions with $^{13}C_{12}$ labeled PBDD/PBDF standards. Recovery rates of ^{13}C-labeled standards are within the EPA guidelines (50-150%).

Results

- Physical Properties

Table 3 summarizes results of physical properties for PBT. Tensile strength, Izod impact strength, heat distortion temperature (HDT) and melt flow index results are shown.

TABLE 3
Physical Properties of Recycled FR PBT

	Neat PBT		FR PBT	
Test Property	Virgin	6thPass	Virgin	6thPass
Tensile Properties				
Stress at Yield (MPa)	54.2	55.7	53.7	57.7
Stress at Break (MPa)	30.1	31.3	35.4	44.7
Elongation at Break (%)	107	34	15	14
Elastic Modulus (MPa)	549	614	616	630
Izod Impact Strength (J/m)	40	44	36	29
Heat Distortion Temp. (°C)	50	50	52	54
Melt Flow Rate (dg/min.) 250°C, 2.16 kg load	19.2	20.3	27.0	31.4
Flame Retardancy (UL 94 V0)	No Rating	No Rating	V0	V0

After recycling through six reprocessing histories, the FR PBT tensile properties demonstrated some improvement. Tensile stress at break increased by 26% and modulus improved by approximately 2.3%. Elongation went down modestly by 6.7%. Properties for the neat PBT demonstrated stable tensile performance over the six recycling histories with one exception. Elongation dropped by about 68%.

Impact strength for both the neat PBT and FR PBT demonstrated relatively stable performance although the neat compound was slightly better. Heat distortion temperature was improved after the six recycling histories as well as melt flow rate. The higher melt flow rate observed in the recycled FR PBT should help enable high quality processing performance. Stable flame retardant

performance was achieved for the FR recipe.

Dioxin Testing

Polybrominated Dibenzodioxins and Dibenzofurans contamination assessments were made.

Analysis was conducted on 6th pass recycled FR PBT samples. Testing was made with respect to conformance assessment of the German Ordinance and also EPA TSCA. Results demonstrated:

(1) The levels of polybrominated p-dibenzodioxins and dibenzofurans found in the samples analyzed are far below the limits specified in the German Ordinance "Chemikalien – Verbotsverordnung". The sum of Group IV isomers (2,3,7,8 TBDD+2,3,7,8 TBDF + 1,2,3,7,8 PeBDD + 2,3,4,7,8 PeBDF) measured was less than 0.04 micrograms per kilogram. The level of Group V isomers (1,2,3,4,7,8 HxBDD + 1,2,3,6,7,8 HxBDD + 1,2,3,7,8,9 HxBDD + 1,2,3,7,8 PeBDF) was measured at 0.31 micrograms per kilogram. This is well below the German requirement of Group IV + Group V less than 5 micrograms per kilogram.

(2) No polybrominated dibenzodioxins and dibenzofurans are present in the samples analyzed at a level higher than the limits of quantitization (LOQs) specified by US EPA Toxic Substance Control Act (TSCA) 40 CFR §766.27.

Conclusions

Poly(pentabromobenzyl acrylate) flame retardant produced by DSBG has been assessed in a recycling process in FR PBT. Testing was conducted on material that contained 50% recycled content. The recycled FR plastic demonstrated:

- Conformance to German Ordinance for dioxins and furans.
- Conformance to TSCA dioxin and furan LOQ requirements.
- Excellent to fairly good retention of physical properties.
- Full preservation of UL 94 V0 rating throughout entire recycling compositions.
- Excellent process stability and color retention.

These new results confirm that brominated flame retardants can serve an important role for better protection of our environment. Brominated flame retardants are contributing significantly to reduce the risk of fires and the associated toxic fume hazard.