

Recycling of Styrene Polymers from Shredded Screen Housings Containing Brominated Flame Retardants

Martin Schlummer, Andreas Mäurer

Fraunhofer-Institute for Process Engineering and Packaging, Giggenhauser Str. 35, D-85354 Freising, Germany

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ABSTRACT: Recycling of plastics from screen housing polymers is considered to be helpful to fulfill the requirements of the European waste of electric and electronic equipment directive. However, brominated flame retardants (BFR) and polybrominated dioxins and furans, which are partly limited in marketable products by European and German legislation, have been identified in waste screen housings and need to be eliminated. On application to housing shredder, sink and float was investigated as sorting technology, since BFR-equipped styrene polymers exhibit higher densities compared to corresponding non-BFR types. The feasibility of this concept was proven by database studies and density monitoring of waste screen housing. Laboratory and small-technical scale trials with different mixtures of TV-sets and PC monitor housings revealed that only 5–20% of the original bromine load remained in the target fractions, resulting in bromine levels

between 0.18–1.39%. Recycled polymers from fractions rich in HIPS-based TV-set casings did not exceed given threshold limits for PBDD/F and octabromodiphenylether. They were recovered with yields of 52–63% and exhibited mostly virgin-like mechanical properties. In contrast, PC monitor housing fractions were characterized by low yield, high bromine levels in recycled products and brittle recycled polymers. Furthermore, pilot application of another separation approach, the specific swell and float technology, allowed the separation of upgraded HIPS qualities from bromine-reduced TV-set fractions. In contrast, this success has not yet been achieved with waste PC monitors. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1262–1273, 2006

Key words: recycling; flame retardance; mechanical properties; WEEE directive; RoHS directive

INTRODUCTION

Recycling of plastics from waste of electric and electronic equipment (WEEE) is considered to be helpful to fulfil the requirements of the European WEEE directive, which defines strict recycling quotas between 50 and 75%.¹ Postconsumer plastics from WEEE, however, may include > 15 different polymer types,² and thus, recycled polymers from WEEE often contain material impurities. These reduce both material properties and market value, and consequently put the economy of recycling approaches in question.

In this regard, screen housing polymers are of special interest, which are separated from their devices during cathode-ray tube glass recycling in existing dismantling plants. These polymers are available without changing the current treatment of WEEE materials^{3,4} and they have been shown to contain only a limited number of different high-value engineering plastics, i.e., acrylonitrile–butadiene–styrene

(ABS), high impact polystyrene (HIPS), blends of polyphenyloxide and polystyrene (PPO/PS), and blends of ABS and polycarbonate (ABS/PC).^{4–6} However, even if all these materials are styrene-based, a recycling approach without material separation is assumed to result in low quality products. Thus, Brennan et al.⁷ report that the incompatibility of ABS and HIPS may result in reduced impact strength of ABS and HIPS containing compounds.

But recycling of screen housing polymers is not only an issue of sorting plastic types. A significant percentage of these materials contain brominated flame retardant additives (BFR), including polybrominated diphenyl ethers (PBDE) and biphenyls (PBB).^{4–6} Congeners of these substance groups have been shown to be persistent, bio-accumulative, and toxic.^{8,9} Furthermore, several authors proved the potential of PBB and PBDE to form polybrominated dioxins and furans (PBDD/F) during processing.^{10,11} Thus, recent European directives^{12,13} prohibit or limit the use of PBB and PBDE in new products, and consequently, in recycled polymers. In addition, the German Chemikalienverbotsverordnung¹⁴ restricts the distribution of products exceeding strict PBDD/F limits in the lower ppb range and hinders the recycling of polymers containing PBDD/F precursors at least in Germany. In consequence, bromine-free (recycled) polymers are preferred these days, even

Correspondence to: M. Schlummer (martin.schlummer@ivv.fraunhofer.de).

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when the PBDD/F building potential of modern BFR alternatives is reduced.¹⁵

Elimination of BFR polymers by sorting appears to be reasonable.^{3,5} However, manual bromine and polymer identification at dismantling lines is time and man-power consuming and hence automated sorting systems are preferred, which allow the treatment of shredded materials.¹⁶ Since current high-throughput spectroscopic sorting systems are restricted to particle sizes larger than typical shredder material and cannot treat black polymers, nonspectroscopic means are required for shredder separation at present.

Density-based technologies fail to separate ABS and HIPS because of almost equal densities of both materials. Dodbiba et al.¹⁷ report successful separations on the basis of electrostatic properties. However, this method is limited to well-defined mixtures and fails when treating heterogeneous mixtures of variable composition. To our knowledge no nonspectroscopic separation of BFR and BFR-free polymers has yet been reported. Instead extractive material recycling technologies^{18,19} or pyrolysis-based recovery options^{20–22} were proposed. However, these high-technological approaches have turned out to be out of the scope of WEEE dismantling companies, since they are normally run by small- and medium-size enterprises.

Hence, the authors aimed to apply sink and float as an inexpensive, nonspectroscopic separation technique, which might allow performing both separation issues discussed. The approach is based on the fact that BFR exhibit densities greater than 2 g/cm³.^{3,23} Consequently, housing polymers, which are usually equipped with BFR in the 10–20% range,⁴ exhibit densities significantly higher than corresponding non-BFR styrenes. Furthermore, density separation might segregate ABS and HIPS after treatment of the polymer mixture with a selective swelling agent, which decreases the density of one polymer significantly.

This case study presents monitoring data maintaining the feasibility of a density-based separation of BFR and non-BFR styrenics. Laboratory scale separation trials and a small technical scale production are reported. In addition, separation trials for ABS and HIPS are shown. Finally, material properties as well as BFR and PBDD/F levels of these pilot trial products are presented and discussed.

EXPERIMENTAL

Initial evaluation of the study concept

Density screening of postconsumer screen housing polymers

Monitoring of densities was performed in graduated cylinders filled with distilled water and placed on an analytical balance. Polymer parts of 40 PC monitors and TV-sets were sampled from postconsumer

WEEE and were put into the cylinder. The increase in weight and volume was monitored, respectively, and used for density calculation. The presence of BFR was investigated by energy dispersive X-ray fluorescence (EDXRF). For comparison, density ranges were derived from styrenics listed in the comprehensive materials database of the Plastics Technology website (<http://www.ptonline.com>).

Initial trials on separation of HIPS and ABS using "swell and float" technology

Material separation trials of ABS and HIPS were performed with colored granulates of virgin materials. Green HIPS was prepared on the basis of Atofina Lacqrene 7240, and Novodur P2H-AT was applied as noncolored ABS. CreaSolv[®] Separation Fluid ABS/HIPS (CreaCycle GmbH, Grevenbroich, Germany) was used as swelling agent. Laboratory tests were performed by mixing 20 g of colored ABS and HIPS, respectively, 200 g of water, and 10 g of CreaSolv Separation Fluid ABS/HIPS in a stirred batch reactor at 60°C. After 1 h of treatment, the solution was cooled down to ambient temperature, stirring was stopped, and the separation of polymers was observed. Percentage of false material was determined in sink and float fractions, respectively, by color-based identification and weighing of "false" particles.

Alternatively, a polymer mixture was placed in a sealed drum, covered with CreaSolv Separation Fluid ABS/HIPS, and stored at ambient temperature for 24 h. After removing the fluid, polymers were separated by sink/float in water.

Production of recycled materials

Input materials

Twenty to fifty kilograms of samples of shredded screen housings were provided by several European WEEE dismantling plants for laboratory material screening tests (Table I). Samples 1–3 were obtained from three different sources and were used for material balances only. Samples 4–7 were from a local dismantling plant, which provided selected housing shredder materials from cathode-ray tube glass recycling lines. Careful material flow management allowed separating gray PC monitor housings (Sample 4), black TV-set casings (Sample 5), and two mixtures of both, whereas TV-set casings dominated Sample 6 and to a lower extent Sample 7. All materials were shredded to particle sizes below 20 mm. For small technical-scale and a 200-kg pilot production the dismantling plant provided larger quantities of Samples 4 and 5.

To evaluate the material composition at the local dismantling plant, almost 900 kg of housing materi-

TABLE I
Waste Polymers Samples from WEEE Dismantling Plants Investigated in This Study

Sample	Main colour(s)	Description	Sample treatment in this study	Parameters studied in treated samples
Sample 1	Grey/black	TV set and monitor housings	Lab scale density fractionation	None
Sample 2	Varicoloured	Mainly ABS housings, selected manual sorting	Lab scale density fractionation	None
Sample 3	Grey	Monitor housings	Lab scale density fractionation	None
Sample 4	Grey	Monitor housings	Small-tech. scale density fractionation, regranulation and injection moulding	Halogens, BFR, PBDD/F
Sample 5	Black	TV set housings	Tech. scale density fractionation, regranulation and injection moulding	Halogens, BFR
Sample 6	Grey/black	Mainly TV set and monitor housings	Small-tech. scale density fractionation, regranulation and injection moulding	Halogens, BFR, PBDD/F
Sample 7	Varicoloured	TV set and monitor casings, other coloured housings	Small-tech. scale density fractionation, regranulation and injection moulding	Halogens, BFR

als was examined by means of two hand-held items, a sliding spark spectrometer (SSS3-FR, IoSys; Dr. Timur Seidel E. K., Ratingen, Germany) and a X-ray fluorescence analyzer XRF XLt-797WZ (AnalytiCON Instruments GmbH, Rosbach, Germany). The first is able to identify the polymer type as well as the presence of bromine, chlorine, or phosphorous, which indicate the use of flame retardants. The second is able to detect bromine even in the lower ppm range. According to the results obtained by these hand-helds, the material was separated into the following fractions: ABS, ABS/BFR, HIPS, HIPS/BFR, ABS/PC, PPO/PS, PBT, and refuse. The latter contained housings with uncertain polymer identification as well as poorly dismantled housing parts with obvious high content of metals or foreign polymers.

Laboratory scale production

A defined mixture of CreaSolv Separation Fluid WEEE (CreaCycle GmbH, Grevenbroich, Germany) and water was titled "Separation Fluid 1" and filled in a stirred 10-L laboratory reactor. WEEE polymer Samples 1–7 were added applying a solid to liquid ratio of 0.2. After 30 min of stirring, the samples were allowed to separate for another 30 min. Sink and float fractions were sieved out separately. Subsequently, both fractions were washed with water and the float fraction was again treated with pure water in the stirred 10 L reactor. The sink fraction of the first separation step was called "heavy fraction" and the float fraction of the second stage "light fraction." Finally, the "target fraction," the sink fraction of the second stage, was intended to contain bromine-free styrene polymers. All fractions were dried overnight in an oven at 50°C. Dry masses of the three fractions were used to calculate mass balances, and samples of the three fractions were analyzed chemically (see Chemical Analysis section).

Small-technical scale production

Separation Fluid 1 was filled into a 200-L barrel. About 40 kg of Sample 4 waste was added and wetted with the solution by slow manual stirring. After that, the sample was separated in a sink and a float fraction. The latter was sieved out and washed with water in another 200-L barrel. Polymer particles, floated in this second stage, were removed and only the sink fraction, the target fraction, was sieved out and dried in a centrifugal dryer (Neue Herbold, Sinzheim, Germany), before residual water was removed in an oven at 50°C.

The same procedure was performed with 10–15 kg of Samples 6 and 7.

Two hundred kilograms of Sample 5 was processed in an open 1 m³ tub filled with Separation Fluid 1. The float fraction was washed with water in a 400-L tub and dried by a centrifugal dryer.

Products of Samples 4 and 5 were granulated and test plates were prepared by injection molding for further material testing (see Material Characterization section).

Optimized density separations

Another portion of Sample 4 and the target fraction of Sample 5 were ground to particles of about 5 mm and subjected to two different laboratory scale experiments to optimize the separation of BFR materials.

Sample 4 was treated with Separation Fluid 1, which was applied in two consecutive separation stages, i.e., the float fraction of the first stage was treated with the same separation fluid again. The float fraction of the second stage was dried, ground, and analyzed chemically (see later). The masses of that trial were balanced.

Sample 5 was treated with two further mixtures of CreaSolv Separation Fluid WEEE and water, which allowed performing sink/float separations at two

lower density values. The mixtures were called Separation Fluids 2 and 3, whereas the densities of Separation Fluids 1, 2, and 3 decrease with increase in fluid number. About 1 kg of polymers was placed in Separation Fluid 2. The float fraction was removed by means of a laboratory sieve and put into Separation Fluid 3 with further reduced density. Float fraction of the second stage and both sink fractions were separated, dried, balanced, and chemically analyzed.

Small-technical material separation

Laboratory scale products of Samples 4, 5, and 7 were filled into tubs containing CreaSolv Separation Fluid ABS/HIPS and the mixtures were exposed to 40°C overnight. After decanting the separation fluid, the mixture was treated with water, where swollen polymers were floated from nonswollen particles and separated using a laboratory sieve.

Chemical analysis

Materials

Analytical grade tetrahydrofuran, 2-propanol, dichloromethane, cyclohexane, heptane, toluene, and diethyl ether were purchased from Fluka. Silica gel and florasil[®] were purchased from Roth, and alumina oxide for the dioxin analysis from ICN.

BFR analysis

Element concentration, viz. bromine, chlorine, mercury, cadmium, chromium, and lead were analyzed by means of EDXRF analysis (Spectrolab 2000, Spectro, Germany). To acquire representative element concentrations, 500–1000 g of coarsely shredded polymers were ground to 1 mm, and 5 subsamples of this powder were subjected to EDXRF.

For specific BFR analysis, flame retardants were extracted from the polymers by dissolution of the polymers in tetrahydrofuran and precipitation of the polymer in the 5- to 10-fold amount of 2-propanol. Identification and quantification was performed by GC-ECD using a 10 m DB5 (0.18 μm \times 0.18 mm, J and W) as stationary phase. Four specific BFR were quantified, viz. tetrabromobisphenol A (TBBPA), 1,2-bis(tribromophenoxy)ethane (TBPE), deca- and octa-brominated diphenyl ethers (DecaBDE and OctaBDE).

PBDD/F analysis

For PBDD/F analysis, samples were dissolved in tetrahydrofuran, spiked with a mixture of four ¹³C-PBDD/F standards, and the polymers were precipitated with 2-propanol. The extract was filtered and evaporated. Extracts were treated with a four column clean-up

using acid/basic silica, alumina, and twice florasil as adsorbent materials and mixtures of dichloromethane and cyclohexane, as well as heptane and a mixture of toluene and diethyl ether as eluents. After clean-up, the extracts were reduced to 30 μL , analyzed by GC-HRMS (MAT 90, Thermofinnigan), and quantified by the isotope dilution method. Chromatographic separation was performed on a DB-5MS phase (60 m \times 0.25 μm \times 0.25 m, J and W).

The method was calibrated for the measurement of eight 2,3,7,8-substituted PBDD/F isomers listed in the German Chemikalienverbotsverordnung (Chem-VerbotsV, 1999). Results are reported in terms of "Sum 4", reflecting the sum of 2,3,7,8-TeBDF; 2,3,7,8-TeBDD; 2,3,4,7,8-PeBDF; and 1,2,3,7,8-PeBDD, as well as in terms of "Sum 5", which is the sum of 1,2,3,7,8-PeBDF; 1,2,3,6,7,8-HxBDD; 1,2,3,4,7,8-HxBDD; 1,2,3,7,8,9-HxBDD; and Sum 4.

Material characterization

Tensile and flexural testing was done according to EN ISO 527-1 and EN ISO 178, respectively; Charpy impact stress was measured according to EN ISO 179.

Erichsen indentation was analyzed according to DIN 53 156, which is the standard procedure for fast routine testing at JVK Plastic Systems GmbH, Nuremberg (Germany), who performed these tests during pilot production.

Products of the described material separation process were characterized by means of FTIR (Spectrum One, Perkin-Elmer), using diamant attenuated total reflectance (ATR). Polymer identification was based on the Perkin-Elmer ATR library of polymers.

RESULTS

Density separation was investigated as recycling strategy for postconsumer styrene polymers obtained from screen housing dismantling lines: first, as a single process for sorting non-BFR materials from BFR qualities; second, in combination with material-selective swelling agents, as a means of separating non-BFR grades of ABS and HIPS. The approaches were examined with regard to concept feasibility, yield of recycled material, efficiency of BFR elimination, and properties of recycled materials in relation to legal thresholds and engineering demands.

Investigation of concept feasibility

Density screening of BFR and non-BFR materials

In Figure 1, results of a screen housing density monitoring are compared with literature data and a database review. Density monitoring of 40 single monitor and TV-set housings revealed that non-BFR HIPS

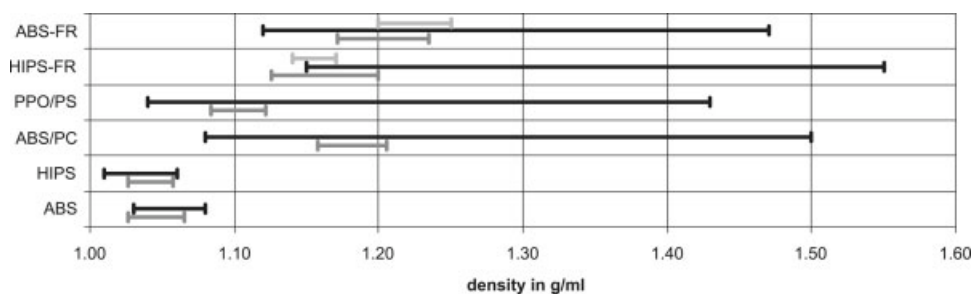


Figure 1 Density ranges of BFR and non-BFR styrenics obtained from own measurements (dark gray) and from Plastics Technology Material Database²⁴ (black) as well as data by Song²⁵ (light gray).

and non-BFR ABS show densities below 1.07 g/mL, whereas densities of BFR-containing ABS and HIPS were higher than 1.13 g/mL. ABS/PC and PPO/PS did not contain brominated BFRs and their specific weights were higher than 1.15 and 1.08 g/mL, respectively. Equivocally, Song²⁵ reports densities of BFR-equipped engineering plastics, which are higher than 1.2 g/mL for ABS and higher than 1.14 g/mL for HIPS. Densities listed in the materials database of the Plastics Technology²⁴ state maximal densities of non-BFR HIPS and ABS of 1.08 g/mL (neglecting glass fiber reinforced qualities), whereas BFR containing HIPS and ABS had minimal densities of 1.15 and 1.12 g/mL, respectively. The database also gives density ranges for PPO/PS qualities between 1.04 and 1.43 g/mL, and for ABS/PC a minimal density of 1.08 g/mL.

Material separation by means of swelling agents

In a laboratory scale feasibility study we subjected a mixture of the same amounts of green-colored virgin HIPS and white virgin ABS to CreaSolv Separation Fluid ABS/HIPS. The fluid was able to swell HIPS whereas ABS was not affected. Furthermore, on swelling, the fluid was incorporated in the HIPS, lowering the density of non-BFR HIPS below 1.0 g/mL. Consequently, a floating in water led to an almost complete separation of both materials. Manual counting of green and white granulates present in the float (HIPS) and sink fractions (ABS) revealed ABS or HIPS impurities of 1%, respectively.

Material composition at local dismantling plant

The local WEEE recycling company, which provided screen housing Samples 4–7, was examined to get an estimate of usual polymeric material composition at the end of its screen housing dismantling lines. Therefore, 880 kg polymer waste was tested for polymer types by sliding spark near infrared spectroscopy (NIR) and the presence of BFR by sliding spark NIR and X-ray fluorescence. The share of five different polymer types and a residue fraction is dis-

played in Figure 2 and present the four major fractions at this plant: BFR-ABS (16 wt %), BFR-HIPS (24 wt %), non-BFR HIPS (18 wt %), and ABS/PC (14 wt %). Both, PPO/PS and polybutadiene-terephthalat (PBT), accounted for 2%, whereas the refuse fraction accounted for 20%. This high value is due to the strict elimination of poorly dismantled housing parts containing significant amounts of metals (screws, rivets, etc.) and foreign polymers.

Material yield of separation trials

Two-stage sink and float processing of Samples 1–7 with Separation Fluid 1 and water produced light, target, and heavy fractions, respectively. Their mass percentages are shown in Figure 3.

The light fractions account only for small weight percentages. The target fractions, however, accounted for 26–90 wt %, whereas 5 of 7 materials had more than 50% in the target fraction. Significantly lower percentages of target fractions were obtained for Samples 3

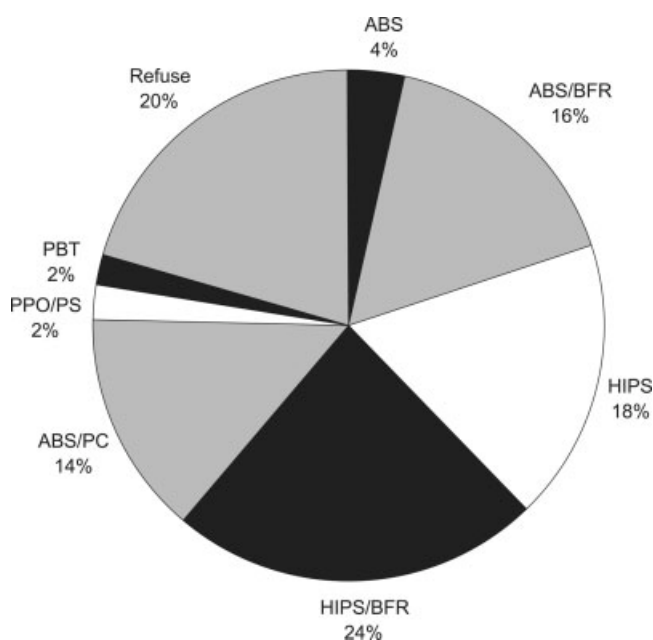


Figure 2 Exemplary material composition of screen housings obtained at a local dismantling plant.

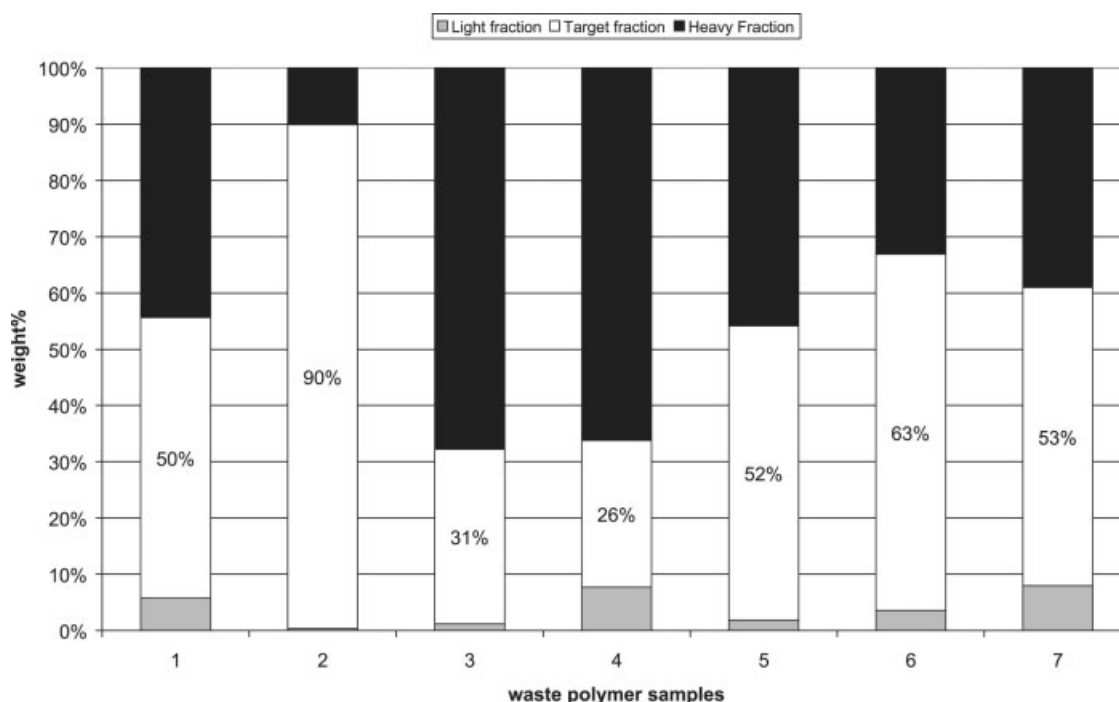


Figure 3 Material balances of investigated housing fractions.

and 4, which contained gray monitor materials only. Samples containing both, monitors and TV-sets, were characterized by about 50 wt % of target material. In contrast, Sample 2, which was delivered by a dismantler specifically trained on sorting non-BFR-ABS, contained 90% of the target fraction. In this case, the residual 10% of heavy fraction are attributed to glass fiber-reinforced ABS or nonsorted BFR containing qualities.

Halogen elimination and residual BFR and PBDD/F levels in recycled polymers

First laboratory and technical scale density fractionation trials were performed using Separation Fluid 1. Masses of the target fraction as well as their halogen concentrations, obtained by EDXRF, allowed calculating halogen mass balances. Results are presented in Figure 3, where bromine and chlorine mass percentages of light, target, and heavy fractions are superimposed.

Obviously, the major part of halogens is transferred into the heavy fraction and the mass percentages in the light fraction can be neglected. However, 2–20 wt % of bromine and chlorine remain in the target fraction, which is higher than expected from the findings in the feasibility study. In addition, bromine concentrations (Table II) are surprisingly high and exceed 1000 ppm in all cases.

Optimized lab scale separation trials were performed with the target fraction of Sample 5 and Separation Fluids 2 and 3, fluids of reduced densities, on the one hand, and by accurate two stage treat-

ment of a new portion of Sample 4 with Separation Fluid 1 on the other hand. Results of these trials are summarized in Table III. With respect to Sample 4, material yield was below 9%, but residual bromine accounted for 0.1% of total bromine only. EDXRF analyses revealed a bromine level of (563 ± 155) ppm. The two optimized treatments of Sample 5 reduced the material yield to 47 and 37%, respectively, whereas the residual bromine percentage was reduced from 20% to 15 and 6%, respectively.

Using EDXRF and GC-ECD, recycled materials of Samples 5–7 were tested for halogens, specific BFR, and heavy metals listed in the RoHS directive. In addition, Samples 4 and 6, representing the samples with the highest bromine content and with the highest yield of target fraction, were tested for PBDD/F. Two sieve fractions of each sample were analyzed, a coarse fraction (> 2 mm) and a fine fraction (< 2 mm). Results of halogen levels, specific BFR and PBDD/F are summarized in Table II and compared to threshold values of the European RoHS directive^{12,13} as well as the German Chemikalienverbotsverordnung.¹⁴ PBB and PentabDE, specific BFR controlled by the RoHS, were not identified in the samples.

Recycled polymers of Samples 5–7 are in compliance with legal thresholds. In spite of bromine levels up to almost 10,000 ppm, OctaBDE levels were far below 1000 ppm as requested by European law.¹³ Sample 4, however, contained almost 14,000 ppm bromine and exceeded the OctaBDE level with 1348 ppm. With regard to PBDD/F and both investigated particle sizes, Sample 6 passed the requirements of the

TABLE II
Selected Analytical Parameters Obtained in Granulated and Moulded Target Density Fractions of Samples 4–7^a

	Dimension	Sample 4	Sample 5	Sample 6	Sample 7	Threshold limits
Bromine	µg/g	13,880	9,850	3,030	1,797	–
Octabromodiphenyl ether	µg/g	1,348	191	40	53	1,000
Decabromodiphenyl ether	µg/g	2,192	1,096	368	301	–
Tetrabromobisphenol A	µg/g	2,756	145	166	245	–
1,2-bis(tribromophenoxy)ethane	µg/g	1,394	765	43	480	–
Cadmium	µg/g	23	31	76	79	100
Mercury	µg/g	< 10	< 10	< 10	< 10	1,000
Chromium	µg/g	37	28	46	47	1,000
Lead	µg/g	41	53	142	34	1,000
PBDD/F, Sum 4 ^b (particles > 2 mm)	ng/g	1.89	na	0.03	na	1
PBDD/F, Sum 4 ^b (particles < 2 mm)	ng/g	4.96	na	0.87	na	1
PBDD/F, Sum 5 ^b (particles > 2 mm)	ng/g	3.46	na	0.59	na	5
PBDD/F, Sum 5 ^b (particles < 2 mm)	ng/g	7.84	na	1.59	na	5

na, not analysed.

^a Analytical results are compared with threshold limits given by the European RoHS directive and the German Chemikalienverbotsverordnung.

^b According to Ref. 14.

German Chemikalienverbotsverordnung¹⁴ but Sample 4 did not.

Mechanical properties of recycled materials

Not separated materials

Table IV compares values obtained for small technical scale products of Samples 4 and 5 with data of virgin ABS and HIPS types, both typically applied to screen housing production. Most processing and mechanical properties are in agreement with virgin material data. Obviously worse results were obtained for the Charpy impact strength of Sample 4.

Separated materials

Processing Samples 4, 5, and 7 with the described specific swell and float technique, we obtained sink and float fractions for each sample. Whereas the sink fraction is assumed to be ABS, mainly, the float fraction is accounted to HIPS. Comparing the sink and float masses, we deduced ABS to HIPS ratios of 70/30 for Sample 4, 10/90 for Sample 5, and 30/70 for Sample 7.

FTIR spectra of the sink and float fractions of Sample 4 were recorded. Using the Perkin–Elmer ATR Polymer database the spectra could be assigned to ABS and HIPS, respectively. As the most visible difference the nitrile band at 2200 cm⁻¹ in the sink (ABS) spectrum hints to the presence of acrylonitrile, which was not identified in the float (HIPS) spectrum.

To investigate whether the material separation increased the mechanical properties of both resulting fractions, the Erichsen indentation was measured for the initial target fraction as well as for the ABS and the HIPS fractions. This test protocol has been estab-

lished as a fast screening test at JVK Plastic Systems GmbH (Nuremberg, Germany), who performed a pilot application test of the separated materials. For Sample 4 Erichsen indentations could not be obtained for the initial target fraction nor for the sink or float fractions, since the plates broke below 2 mm.

Results obtained for Samples 5 and 7, however, are ambiguous. As depicted in Figure 5, the float (HIPS) fractions have significantly higher values than their corresponding initial target fractions. The sink fractions, however, could not be determined, due to the same behavior as Sample 4.

DISCUSSION

Elimination of BFR containing plastics

The main task of recycling screen housing polymers is the elimination of BFR materials. In this study the separation was performed by means of a sink and float technology.

TABLE III
Results of Optimised Density Separation Trials at Lab Scale

	Sample 4	Sample 5	Sample 5
Separation fluid	Separation fluid 1	Separation fluid 2	Separation fluid 3
Yield of target fraction (%)	8.8	47	37
Br concentration in target fraction ^a (%)	0.056	0.789	0.426
Percentage of total bromine transferred into target fraction (%)	0.1	15	6

^a Obtained by EDXRF.

TABLE IV
Material Properties of Extruded Samples 4 and 5 in Comparison to Virgin ABS and Virgin HIPS^a

Test	Test norm	Compound of sample 4	Compound of sample 5	VirginABS (Novodur P2X)	Virgin HIPS (Polystyrol 456 M)
Tensile strength (MPa)	EN ISO 527-1	37.70 ± 0.4	24.5 ± 0.2	45	40
Elongation at yield (%)	EN ISO 527-1	2.07 ± 0.03	1.36 ± 0.01	2.3	2.5
Elongation at break (%)	EN ISO 527-1	5.61 ± 2.68	8.95 ± 2.47	–	35
Tensile modulus (MPa)	EN ISO 527-1	2,274 ± 57	2,011 ± 31	2,600	2,450
Flexural modulus (MPa)	DIN EN ISO 178	2,012 ± 117	1,891 ± 112	2,400	2,400
Standard deflection (MPa)	DIN EN ISO 178	58.13 ± 0.28	36.79 ± 2.66	–	–
Charpy impact strength, 23°C (kJ/m ²)	EN ISO 179	15.2 (CB)	32.9 (CB)	NB	65
Charpy notched impact strength, 23°C (kJ/m ²)	EN ISO 179	2.7 (CB)	9.8 (CB)	16	9.5

NB, non break; CB, complete break.

^a From subsequent material separation we assume that sample 4 consists of 70% ABS and 30% HIPS and sample 5 of 10% ABS and 90% HIPS.

Our monitoring data, literature, and the Polymer Technology databases²⁴ show that densities of non-BFR ABS and HIPS are significantly lower than corresponding BFR qualities. Otherwise, ABS/PS and PPO/PS, two further valuable engineering polymer types in shredded screen housings, which normally do not contain BFR,⁶ exhibit a wide density range, whereas only PPO/PS partly overlaps with densities of non-BFR ABS and HIPS. The latter two non-BFR materials can be separated from BFR materials and ABS/PC and a major part of PPO/PS by technical isolation of a density window from 1.00 to 1.08 g/mL. Considering the material composition obtained at two screen housing dismantling lines (see Fig. 2) with a PPO/PS share of 2%, these residues are not intended to be a big drawback.

Consequently, the density-based technology would remove BFR polymers and further reduce the num-

ber of different polymer types. The drawback is that normally BFR-free ABS/PC qualities with high market value would be lost with the BFR fraction, which is intended to be treated as waste or might be subjected to extractive treatment technologies.^{18,19}

This density-based recycling strategy is not completely reflected by our pilot sink and float trials on a laboratory and small technical scale. Indeed, for all samples, the majority of BFR and chlorine containing materials were separated, but 5–20% of the initial bromine remained in the target fraction (Fig. 4). Optimized laboratory scale trials with less dense separation fluids could reduce the maximum residue of 20% of Sample 5 to 6%, and cautious laboratory scale treatment of a small portion of Sample 4 transferred 99.9% of bromine into the waste fraction. Anyway, the target fractions were never free of bromine and chlorine.

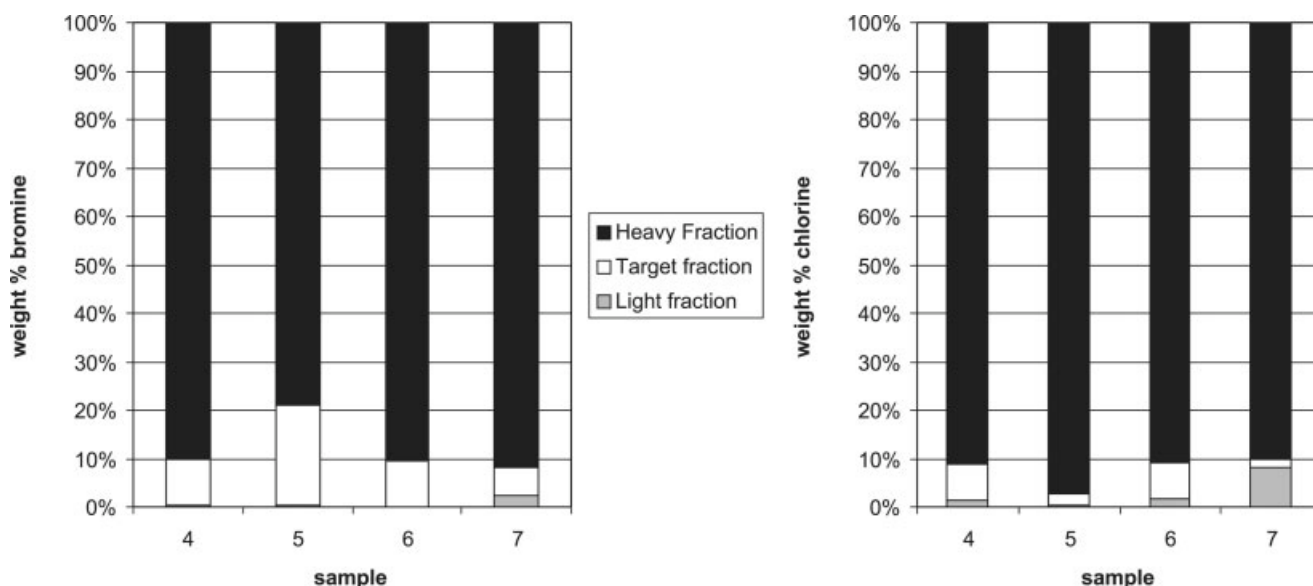


Figure 4 Halogen balances of Samples 4–7.

We assume that two technical problems with the applied density separation in open tubs might have caused these high bromine residues. First, particles may be transferred in the wrong fraction due to the sink and float behavior of neighboring particles, i.e., lifting of sink particles by float particles or concealing of float particles with sink material. Second, air bubbles in the separation fluid adhere to particles and lift them to the surface even if the particle has a higher density compared to the surrounding medium. Because of their high surface to mass ratio the latter effect is crucial especially for small (< 2 mm) particles.

The laboratory scale optimization with Sample 4 using a two-stage treatment in Separation Fluid 1 aimed to overcome this difficulties, since the probability that the same particles is affected twice decreases with increase in treating steps. However, the observed significant reduction in both, residual bromine and material yield (compare Table III), cannot be contributed to the two-stage treatment only. Most of the reduction is assumed to be the result of material inhomogeneity.

Gas bubbles, surface tension effects, and the described adverse particle interactions may be solved by high-technology sink and float systems, which reduce gas bubbles in the separation media and are run continuously, which allows a better separation of single particles during sink and float processing. Considering the positive evaluation of the basic concept and the about 90% removal of bromine achieved so far, further trials in high-tech sink and float plants seem to be promising and are scheduled in the near future.

Another consequence of our findings is that the density of the separation medium cannot be understood as a strict separation threshold. With regard to particles, with densities close to that threshold, float or sink forces are very small and may be affected by other forces as lifting by adhering gas bubbles, vertical movements of the separation fluid, or impacts of neighboring particles. As a consequence, the density of the separation medium has to be lower than the theoretical density separation threshold. This is supported by the laboratory scale optimization trials with Sample 5, where a stepwise reduction of the density of the separation medium could decrease the percentage of residual bromine and the bromine level in recycled polymers.

However, not only technical issues influence the separation of BFR materials. In a recent EDXRF screening of TV housings, low BFR materials could be identified, which contain bromine in the range from 0.1 to 1%. These levels are too low to be attributed to an intentional BFR equipment of these polymers. Instead, we assume that these low BFR materials are a result of past polymer recycling activities,

which included small portions of BFR containing plastics. Anyway, those low BFR polymers affect the sink and float technology investigated in this study, since low amounts of BFR shift the density of the basic polymer only to a small degree and consequently, these materials will appear in the non-BFR target fractions.

Compliance of recycled materials with legal thresholds

Results presented in Table II indicate that Sample 4 does not pass the RoHS requirements due to residues of OctaBDE above 1000 ppm. In contrast, Samples 5–7 exhibit OctaBDE levels far below that threshold value. Since neither PBB nor PentaBDE were identified, Samples 5–7 pass the BFR requirements of the RoHS directive. However, bromine ascribed to OctaBDE attributes only to 8, 2, 1, and 2% of the total bromine identified in Samples 4, 5, 6, and 7, respectively. This indicates that relatively high bromine values, which were obtained in the recycled products, do not contradict its marketability. However, BFR specific quality assurance measures have to be taken.

Furthermore, the four specific BFR analyzed in this study do not explain half of the measured bromine levels in Samples 4–7. In Samples 5 and 6, they account for 17 and 15%, only. This is a strong indication for the presence of other brominated compounds in the recycled materials and we expect that most of that bromine can be attributed to modern BFR systems. This is supported by two to four not identified peaks in the ECD chromatograms of Samples 5 and 6.

Levels of chromium, lead, mercury, and cadmium are in compliance with the RoHS directive for all investigated Samples 4–7. However, cadmium reaches up to 79 ppm and comes close to the threshold value of 100 ppm. This finding is supported by two of our previous studies. An extensive material screening of post consumer WEEE plastics revealed cadmium levels close to and above the 100 ppm threshold.⁶ In addition, sink and float has been a part of a recycling concept for polymers in mixed WEEE shredders, and we obtained only a weak density-based cadmium elimination.²⁶ Thus, cadmium is a possible contaminant of recycled polymers from post consumer WEEE plastics and would have to be included in a quality assurance program, if the described concept was applied in industrial practice.

With regard to PBDD/F Sums 4 and 5 defined by the German Chemikalienverbotsverordnung¹⁴ have to comply with threshold values of 1 and 5 ppb, respectively. For the coarse and fine particles of Sample 6 (Table II) the compliance with these thresholds could be stated, whereas both particles sizes of Sample 4 exceeded them. However, because of the

applied chromatographic separation on a nonpolar phase (DB-5-MS), a coelution of non-2,3,7,8-substituted PBDD/F cannot be excluded. Thus, reported Sums 4 and 5 have to be interpreted as maximum concentrations. Real levels of both sums may be smaller.

Samples 4 and 6 were split into coarse (> 2 mm) and fine particles (< 2 mm), since we deduced from previous results that the fine fraction of shredded materials might contain increased PBDD/F levels.²⁷ The differences, which we obtained for coarse and fine particles in this study, support our previous findings. The measured Sum 4 levels of the fine fractions exceeded the levels of the coarse particles by factors of 2.6 and 28 for Samples 4 and 6, respectively. With respect to Sum 5 factors of 2.3 and 2.7 were obtained. As explanation we propose that small particles are subjected to high surface energies and temperatures during shredder processes, which might result in radical-driven PBDD/F formation from BFR precursor molecules.

As a conclusion from these results, a removal of small particles from the bulk target fraction is recommended. Technically, this may be managed by effective dust elimination during shredding. Interestingly, the proposed sink and float technology itself reduces the amount of fine particles within the water washing step, since fine particles are extremely susceptible to adhering gas bubbles and are floated in water to a great extent.

The higher PBDD/F levels obtained for Sample 4 can be explained by a high OctaBDE level in this sample, since this BFR is a well known potent PBDD/F precursor.¹¹ The high OctaBDE level in monitor-based Sample 4 can be due to the higher share of ABS in this sample, since with regard to the past application of PBDE-type BFR, OctaBDE was typically used in ABS, whereas HIPS, the main polymer of Samples 5 and 7, was preferentially equipped with DecaBDE.

Applications for recycled polymers

Although most mechanical properties reported in Table IV are comparable to virgin materials, Charpy impact strength is considerably reduced in Sample 4 and with regard to unnotched Charpy impact only in Sample 5. Based on our polymer separation trials, Sample 4 is considered to contain roughly 70% of ABS and 30% of HIPS, and Sample 5 is dominated by HIPS, containing 10% ABS. Thus, it seems that a small portion of ABS in HIPS has a lower impact strength reducing effect compared to a larger HIPS component in ABS.

This is in agreement with data of Brennan et al.⁷ who blended postconsumer ABS and HIPS from WEEE applications. They yielded quite positive ten-

sile and flexural properties but significantly reduced impact strength. In addition, they observed that blending of ABS with 10 and 50% HIPS, respectively, reduced the impact strength to 65 and 50%, whereas blending of HIPS with 10% ABS did not significantly reduce impact properties.

This behavior is reasonable as the ABS component exhibits higher impact strength than the HIPS fraction. Upon injection molding, the different polarities of ABS and HIPS cause a partial phase separation of both polymers, which reduces the impact strength of the overall specimen at least to the lower value of the HIPS phase. If at a given temperature there were significant differences of the melt viscosities of both blended phases, the effects of phase separation and impact reduction might even increase.

Nonetheless, it is assumed that the addition of stabilizers, compatibilizers, or impact modifiers can increase the impact strength significantly.^{7,28}

The loss of impact strength reduces the economic value of the recycled polymers, and thus, we performed pilot trials to separate ABS and HIPS mixtures obtained by sink and float technology. Applying to defined mixtures of virgin granulates, specific swell and float separation obtained high purities of 99%. However, turning to real post consumer plastics, especially coarse shredded screen housing material, this successful separation might be disturbed by inhomogeneous particle size and the presence of more than one quality of ABS and HIPS, respectively.

Separations performed with WEEE plastics (Samples 4, 5, and 7) seemed to work well. A specific part of the post consumer plastic particles swelled and could easily be floated from the nonswollen particles. The float (HIPS) fractions of Samples 5 and 7 showed increased flexibility (Fig. 5). Test plates of nonswollen particles of both samples were too brittle for the Erichsen indentation test protocol. That means a mechanical improvement was identified for HIPS, which the specific process was designed for. The residual, non specific fraction, however, seemed to be affected by other material residues with low compatibility to ABS, as PPO/PS for example.

With regard to Sample 4, the ABS fraction, the non separated material, and the HIPS phase failed the test. The brittleness of the non-separated material might be due to the higher shares of PPO/PS and ABS/PC, which visibly decrease the low compatibility of ABS and HIPS, and seem to result in a more significant phase separation. However, upon polymer separation non-HIPS components are obviously transferred into the swollen HIPS fraction.

For material recycling purposes, the swelling fluid has to be removed from the swollen HIPS component. This could be performed by vacuum extrusion or thoroughly drying before recompounding. In combination with the aforementioned sink and float

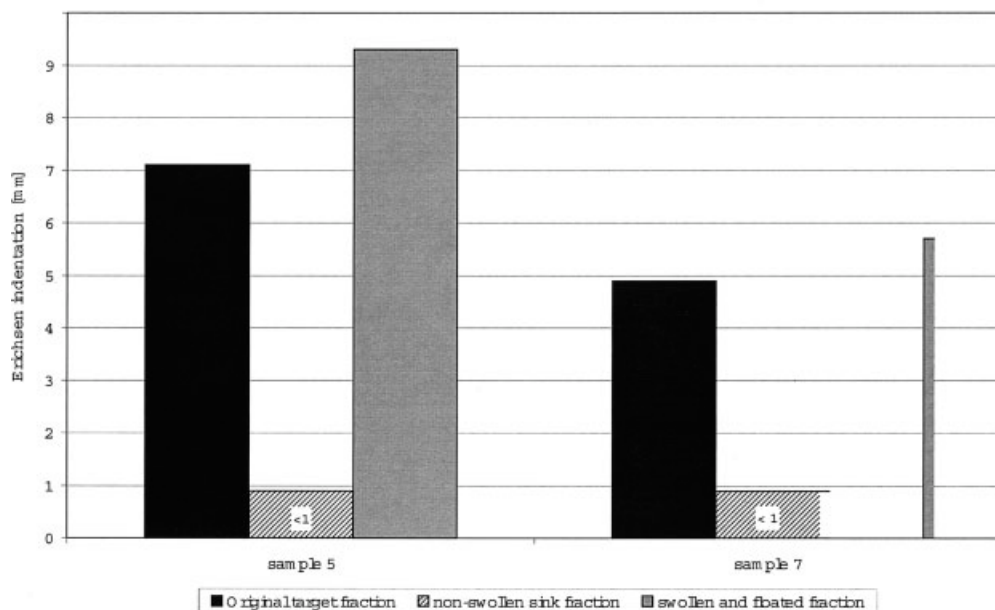


Figure 5 Erichsen indentation obtained in recycled ABS and recycled HIPS obtained polymer separation via specific swelling, followed by sink/float. The Erichsen indentations of the nonswollen sink fractions could not be determined, since these materials broke before a significant indentation could be measured.

separation, a low-cost fractionation of non-BFR qualities of ABS and HIPS seems to be feasible from a technological point of view.

However, the HIPS swelling approach should probably be altered to an ABS specific swelling, since the most positive effects were obtained for HIPS fractions containing 10–30% of ABS and it is preferred to remove the swelling fluid from the minor component. Additionally, if an ABS-specific swelling is able to improve the mechanical properties of that ABS fraction without reducing properties of the HIPS fraction, both fractions might serve as high value polymer recyclates. This is of high economic interest due to the significantly higher market value of ABS.

Material yield and economic demands

Sink and float technology with and without a subsequent swell and float approach for polymer separation, has been shown to produce recycled products from shredded screen housing plastics. Products are in compliance with legal thresholds and a wide range of engineering demands. However, performing the described treatment on industrial scale causes invest and operating cost. These are low compared to alternatives like pyrolysis or extractive polymer recycling technologies,^{18–22} but they have to be covered by market prices of the recycled products.

Since only the non-BFR fraction is assumed to be a marketable product, yield becomes a crucial factor on evaluating the overall economics.

At the beginning of our study, Sample 4 seemed to be the most promising screen housing fraction. How-

ever, the yield of BFR-free ABS and HIPS did not exceed 25%; and for a small portion of Sample 4 the yield was even <math><10\%</math>. Obviously, in monitors, the application of non-BFR ABS or HIPS is rare and has been replaced by PPO/PS and ABS/PC since BFR became an issue of discussion.⁴ Taking into account that products of Sample 4 have not been satisfactory in terms of impact strength and compliance with RoHS and the German Chemikalienverbotsverordnung so far, achievable market prices are not considered to cover costs assumed for a sink and float plant.

Pilot trials with HIPS-rich samples containing TV-set housings mainly (Samples 5–7) were most convincing. Yields of non-BFR materials exceeded 50% in these fractions and in spite of high bromine loads up to 1%, neither RoHS nor German Chemikalienverbotsverordnung were failed by these samples. Anyway, with respect to mechanical properties, screen housings from TV-set dismantling lines (as Sample 5) were most convincing. As material properties of Sample 5 indicate, they meet most of virgin HIPS requirements even without a polymer separation step.

Based on the results of the pilot polymer separation with Sample 7, mixtures from both monitor and TV-set dismantling lines (Samples 6 and 7) may meet engineering demands after a polymer separation step, which—depending on the share of monitors—might reduce the yield significantly. For Sample 7, the yield would be reduced from 53 to about 35%. If higher monitor shares are considered, even stronger yield reduction might occur.

In summary, housings from TV-sets seem to be the most interesting fraction observed, and treatment cost are considered to be covered by achievable market prices based on a first rough economic evaluation. This is supported by the dominance of black materials, which increases the prices for the recycled materials further.

However, for economic demands optimized laboratory scale trials of Sample 5 have to be reviewed. If the market accepts RoHS-conform materials containing up to 1% bromine, there is no need to reduce bromine and yield. However, if total bromine establishes as practical evaluation of recycled materials, a further bromine and yield reduction will be necessary. In this case, lowering the density of the separation fluid seems to be the most promising optimization route.

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