Report: Recycling of flame-retarded plastics from waste electric and electronic equipment (WEEE)

Martin Schlummer, Andreas Mäurer, Thomas Leitner and Walter Spruzina

Waste Management Research 2006; 24; 573
DOI: 10.1177/0734242X06068520

Waste Manage Res 2006: 24: 573–583
Printed in UK – all right reserved

Waste Management & Research
ISSN 0734–242X

Report: Recycling of flame-retarded plastics from waste electric and electronic equipment (WEEE)

Shredder residues produced in plants processing waste electric and electronic equipment are excluded from material recycling due to a variety of polymeric materials and the presence of brominated flame retardants (BFR), which might contain banned polybrominated diphenyl ethers or toxic polybrominated dioxins and furans (PBDD/F). Herein we present a technological approach to transfer a significant portion of the shredder residue into recycled polymers. The technological approach consists of a density-based enrichment of styrenics, which are subjected to a solvolysis process (CreaSolv® process) in a second stage. This stage allows the elimination of non-target polymers and extraction of BFR and PBDD/F. Pilot processing of 11.5 and 50 kg shredder residues indicated a material yield of about 50% in the density stage and 70–80% in the CreaSolv® process, and an effective removal of BFR additives. The recycled products were proved to comply with threshold values defined by the European directive on the restriction of hazardous substances (RoHS) and the German Chemikalienverbotsverordnung. Mechanical material properties exhibited high tensile and flexural modules as well as slight impact strength, which qualify the products for applications in new electronic equipment.

Martin Schlummer
Andreas Mäurer
Department Polymer Recycling, Fraunhofer-Institute for Process Engineering and Packaging, Giggenhauser Str. 35, D-85354 Freising, Germany

Thomas Leitner
Walter Spruzina
KERP - Centre of Excellence on Electronic Scrap Recycling and Sustainable Design, Meldemannstr. 18/4, A - 1200 Vienna, Austria

Keywords: WEEE, CreaSolv® process, polymer recycling, density separation, brominated flame retardants, PBDD/F, RoHS compliance, wmr 966–3

Corresponding author: Martin Schlummer, Department of Polymer Recycling, Fraunhofer-Institute for Process Engineering and Packaging, Giggenhauser Str. 35, D-85354 Freising, Germany.
Tel: ++49 (0) 8161 491-750; fax: ++49 (0) 8161 491-777;
e-mail: martin.schlummer@ivv.fraunhofer.de

DOI: 10.1177/0734242X06068520

Received 9 January 2006; accepted in revised form 13 June 2006

Figure 5 appears in color online: http://wmr.sagepub.com

Introduction

In Europe, more than 6 million tonnes of waste electric and electronic equipment (WEEE) are produced annually, containing more than 1 million tonnes of plastics. Aiming at a responsible waste treatment of this amount, the European WEEE directive defines strict recycling and recovery quotas (EC 2003a), namely 70–80% for recovery and 50–75% for recycling strategies. With respect to typical WEEE plastic weight percentages of 15–30%, it is obvious, that these quotas cannot be fulfilled by state-of-the-art metal and glass recycling, only. Therefore, it is imperative to provide and develop economic recovery systems for plastics.

However, the main source of WEEE plastics are shredder residues from WEEE treatment plants, which are produced by a combination of shredding and metal-removal techniques. Material recycling of these shredder residues is challenging for two main reasons. Firstly, the plastic waste fraction of WEEE consists of more than 15 different polymer types, which provides a maximum share of about 20% per type (APME

2001). Thus, the economy of material recycling approaches is questionable. Secondly, a large part of the WEEE plastics contains brominated flame retardants (BFR), including polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) (Riess *et al.* 2000, Schlummer *et al.* 2005a, Morf *et al.* 2005). Due to their potential to form brominated dioxins and furans (PBDD/F) during processing, these substances are restricted or limited by the European directive on the restriction of hazardous substances (RoHS) (EC 2003b) and by the 'Penta' directive (EC 2003c). Thus, the presence of PBB and PBDE in WEEE shredder residues hinders the distribution of recycled polymers. In addition, the German Chemikalienverbotsverordnung (ChemVerbotsV 1996) defines strict PBDD/F limits and therefore provides another regional distribution hindrance for PBB and PBDE-containing materials. Consequently, up-to-date thermal recovery options such as pyrolysis are discussed (Bockhorn 1998, Uddin *et al.* 2002), whereas material recycling is practically limited to manual-sorted polymers that are free of BFR (Schwarz & Schultheiss 2000, Hornberger 2002).

A closer look at the material diversity allows the identification of styrenics (PS, HIPS, ASA, SAN, ABS; definitions are given in the Appendix) as a main fraction of WEEE plastics, which roughly account for 50 wt.% (APME 2001). As recyclates of technical styrenics are comparatively valuable, recycling concepts for WEEE plastics may focus on their isolation, for instance, by density or electrostatic separation. However, styrenics exhibit incompatibilities among themselves, which have been shown to result in reduced impact strength or decreased strains to failure (Brennan *et al.* 2002). Thus, the production of recycled polymers of high quality requires a separation of incompatible polymers or an application of special additives (compatibilizers and impact modifiers).

With regard to brominated flame retardants, two strategies are discussed: (1) the identification of bromine-containing materials by means of near infrared (NIR) or X-ray fluorescence (XRF) spectroscopy and their disposal (Meyer *et al.* 1993, Riess *et al.* 2000); or (2) an extractive elimination from polymeric material (Marioth *et al.* 1998, Altwaiq *et al.* 2003, Mäurer & Schlummer 2004). The first approach, however, is at present not available for shredded input materials, since automatic systems require larger particle sizes. The second requires high-technology production plants and – in order to achieve economic viability – a high percentage of the target polymers in the process feed. Therefore, WEEE shredder residues cannot be directly subjected to these technologies.

In summary, there is no single recycling technology available, which would provide a solution to both issues discussed: material diversity and elimination of PBB and PBDE. Thus, Fraunhofer IVV and KERP performed a feasibility study, which aimed to combine two recycling techniques in order to recover recycled HIPS and ABS from mixed WEEE shredder. The products were intended to comply with the material properties required for technical polymers and with legal European restrictions and thresholds. The applied process included a two-stage wet density separation as well as the extractive CreaSolv® process.

Case study concept

This case study is based on the assumption that two polymer properties, namely density and solubility, are decisive for the isolation of styrenics from bulk mixtures of WEEE polymers. In addition, a solubility-based technology allows the extraction of flame retardants and separating incompatible styrenics.

As shown in Figure 1, density separation allows the separation of styrenics from other polymers identified in WEEE (e.g. PE, EP, UP, POM, PC, definitions are given in the Appendix), but the corresponding density window overlaps with polyamide (PA), glass fibre-reinforced or talcum-filled polypropylene (PP–GF, PP–T), rigid polyurethane (PU) or with plasticized polyvinylchloride (PVC). Consequently, density-based polymer separation alone will not permit pure recycled polymers to be obtained.

However, residual non-styrenic polymers can be eliminated by the CreaSolv® process, a solvent-based technology. In addition, this process allows for removing non-polymeric materials such as dust, metals and glass splinters as well as unwanted additives and contaminants such as BFR and PBDD/F from the polymer solution (Mäurer & Schlummer 2004).

Thus the case study presented herein included density separation as well as the solvent-based CreaSolv® process (Figure 2): polymers, derived from state-of-the-art WEEE processing were separated by two-stage liquid density separation, which allows the isolation of a medium styrene-enriched fraction defined by an upper and a lower density limit. This fraction was subjected to the CreaSolv® process, in which styrenics are dissolved and separated from insoluble non-polymers and non-styrenic polymers in the first stage and from unwanted flame retardants and contaminants in the second stage. After the cleaning step, the solution was precipitated and dried. As the incompatible styrenics exhibit different precipitation behaviour, this allowed two separate product fractions to be obtained, each of them intended to contain compatible styrenics only.

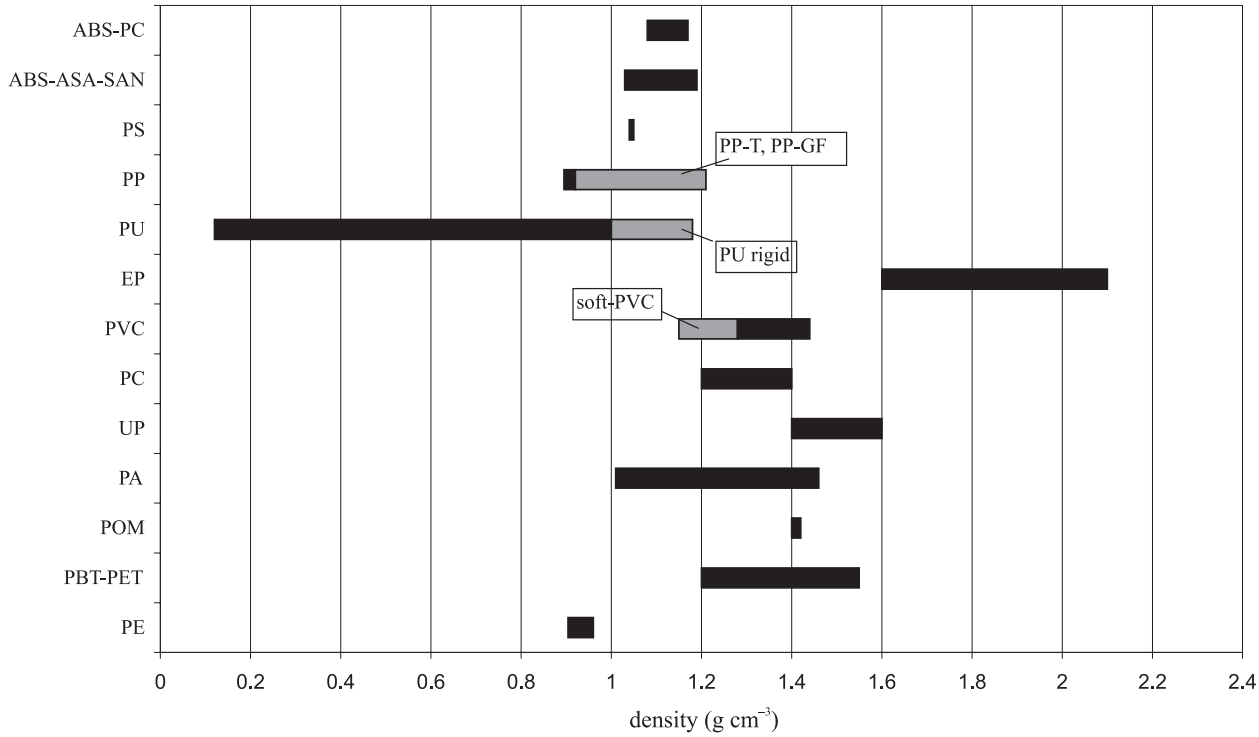

Fig. 1: Densities of typical polymers found in WEEE plastic fractions. The density range of PS refers to both, general purpose and high impact polystyrene (HIPS).

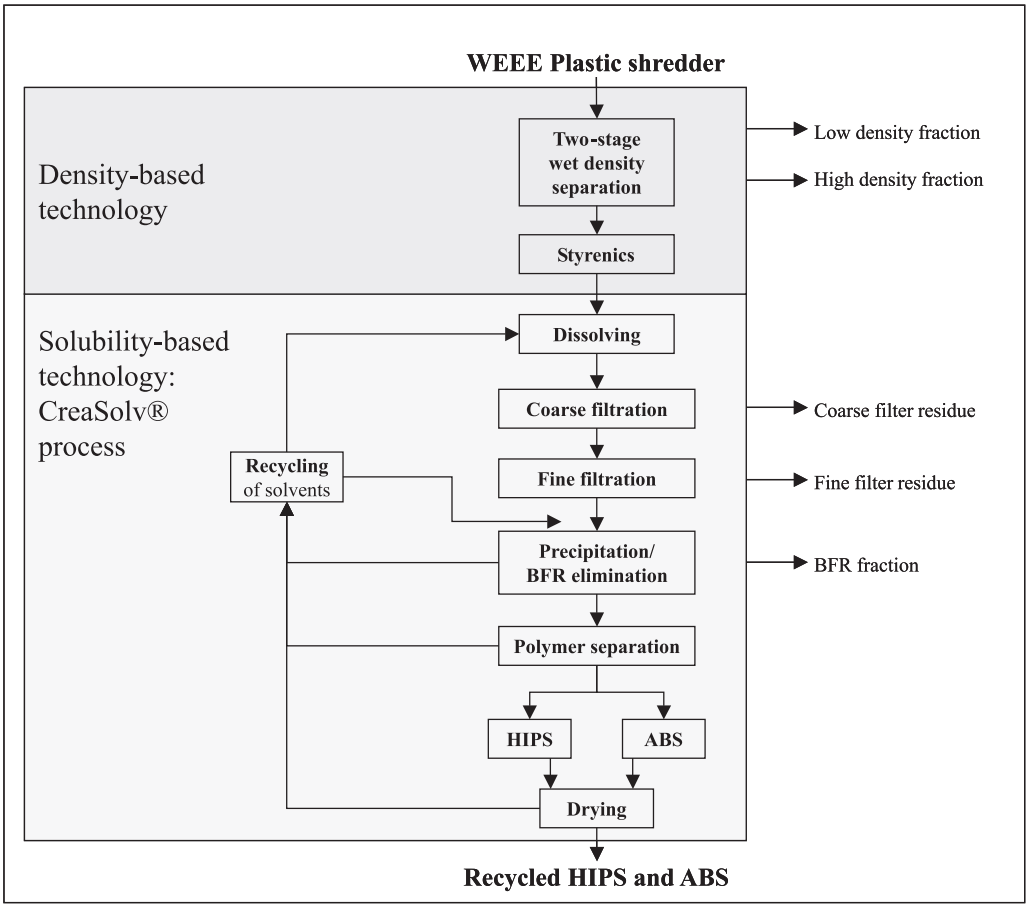

Fig. 2: Process combination applied: two-stage density separation of a medium 'styrenics' fraction followed by the extractive CreaSolv® process. Fine filtration through a 20 µm β-mesh filter is considered as optional step and was only applied to the 11.5 kg sample. Polymer separation is also an optional process step.

Experimental

Materials

Polymer waste

Five WEEE shredder samples were derived from European WEEE processing plants during the past 3 years. One of them was provided by the Austrian centre of excellence for electronic scrap recycling and sustainable product design (KERP). It was derived from the state-of-the-art DIVITEC plant. Materials other than plastics had been separated by flotation, magnetic and non-ferrous separation. The plastic waste was shredded to a particle diameter of roughly 10 mm.

Fluids and solvents

For the density-based isolation of a polystyrene fraction, water and CreaSolv Separation Fluid WEEE® were applied. The CreaSolv® process was realized using two solvent formulations provided by the CreaCycle GmbH (Grevenbroich, Germany): CreaSolv-PS-T® as a solvent and CreaSolv-WEEE-PS-F® as a non-solvent. Both solvents exhibit boiling points below 100°C and can be separated by means of fractional distillation.

Waste treatment

Isolation of polystyrene and copolymers

Five samples of WEEE shredders were subjected to the following procedure, four times in laboratory scale (1 kg) and once in small technical scale (150 kg): Dry polymer shredder materials were filled in a stirred reactor containing a mixture of water and CreaSolv Separation Fluid WEEE®. After a short time of mixing, the stirrer was turned off and the swim fraction was sieved from the surface. This material was twice stirred with water and the sink fraction subjected to mechanical and thermal drying. Additionally, the sink fraction of the first stage and the swim fraction of the second water stage were dried in order to balance the material flow.

CreaSolv® process

Details of the CreaSolv® process are described elsewhere (Mäurer & Schlummer, 2004). In brief, the PS and copolymer fraction was dissolved in CreaSolv-WEEE-PS®, and filtered through a 400 µm sieve, followed by an optional fine filtration (20 µm β-mesh). This procedure allowed dissolving of polystyrene and copolymers on the one hand as well as the separation from non-dissolved materials (polymers, dust and metals) on the other.

Solutions were precipitated in a stirred reactor by adding a non-solvent, allowing the separation of dissolved contaminants from precipitated polymers. The polymer phase is further processed, whereas the extract is subjected to solvent recovery, concentrating the contaminants in a small amount of solid waste for disposal or bromine recovery.

Solvent residues in the polymer phase were evaporated in a tumbling evaporator, whereas the polymers separate in two different phases. Separating them according to patent application (Mäurer *et al.* 2005) allows the production of two different polymer types. Both were collected and dried, separately. The polymer separation step was conducted for a part of the input material only, since the market value of a mixed ABS-HIPS should also be evaluated.

Initially the CreaSolv process was applied to an 11.5 kg sample of the Styrenics-enriched fraction using a non-technical scale filtration unit. The experiment was repeated with a 50 kg sample of the same input. In this case we used a 100 µm technical scale filtration unit.

Chemical material characterization

With respect to shredder input and density fractions, samples were ground to 0.4 mm by a centrifugal mill (Retsch, Germany) before analysis, in order to gain representative samples. Polymer products were available as homogeneous particles.

Elements and especially the sum parameter bromine were analysed by means of energy dispersive X-ray fluorescence analysis (Spectrolab 2000; Spectro, Germany). Due to expected material inhomogeneity, input and density fractions were analysed fivefold. Percentage standard deviations were below 10% for bromine (Br), lead (Pb), antimony (Sb), zinc (Zn), calcium (Ca), titan (Ti) and tin (Sn), below 20% for chlorine (Cl), cadmium (Cd), chromium (Cr) and silicon (Si) and greater than 20% for copper (Cu) in input and heavy fraction as well as for alumina (Al).

Recycled polymers were characterized by means of Fourier transform infrared spectroscopy (FT-IR), using diamond ATR (attenuated total reflection). Polymer identification based on the Perkin Elmer ATR library of polymers.

Flame retardants were extracted by dissolution in tetrahydrofuran and precipitation in ethanol. The extracts were analysed by high pressure liquid chromatography coupled to an ultraviolet detector followed by an atmospheric pressure chemical ionization mass spectrometer. Method details have been described elsewhere (Schlummer *et al.* 2005).

For PBDD/F analysis, samples were dissolved in tetrahydrofuran, spiked with a mixture of four ^{13}C-PBDD/F standards and the polymers were precipitated with ethanol. The supernatant was filtered and treated with a four-column clean-up using acid/basic silica, alumina, and twice florisil as adsorbent materials, as proposed by Ebert *et al.* (1999). The second florisil column was necessary to eliminate residual flame retardants which might disturb the analysis of polybrominated furans. After clean-up the samples were reduced to 30 µL and subjected to gas chromatography on a DB5-MS column (J&W). PBDD/F were detected by high resolution mass spec-

trometry (MAT 90; Thermofinnigan) and quantified by the isotope dilution method. The method was calibrated for the measurement of eight 2,3,7,8-substituted PBDD/F isomers listed in the German ChemVerbotsV (1999). The results were reported in terms of PBDD/F (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 PBDD/F (sum 5), which is the sum of sum 4 and 1,2,3,7,8-PeBDF, 1,2,3,6,7,8-HxBDD, 1,2,3,4,7,8-HxBDD and 1,2,3,7,8,9-HxBDD. (Compare definitions given in the Appendix.)

Processing and mechanical properties

Mechanical properties

Density, melt flow rate (MFR)and melt volume rate (MVR) were obtained according to ISO 1183, ashing content and Vicat softening temperature according to EN 60 (650°C) and ISO 306, respectively. 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.

Results and discussion

Enrichment of Polystyrene and copolymers from WEEE plastics

The enrichment of a styrenics fraction by two-stage density separation was performed at both laboratory and small technical scale. Treated polymer fractions were supplied from WEEE treatment plants throughout Europe. The results are presented in Figure 3, expressed in terms of percentage shares of the three fractions derived by two-stage density separation. In four of five samples the share of the medium fraction was greater than 50%. Sample 3 contained only 32% of the medium fraction, which could be attributed to a comparably low metal separation in the preceding shredder process.

The results state experimentally a 50%-share of styrenics in WEEE polymers, which was deduced by APME on the basis of application data in the electric and electronic sector (APME 2001). With regard to the subsequent treatment, the technologically robust and price-worthy enrichment step by modified density separation transformed WEEE shredder residues into valuable input materials for sophisticated extractive processes, such as the CreaSolv® process.

The elimination of non-styrenics may be performed by alternative techniques. Spectroscopic technologies would allow even better elimination rates, but they require larger particles sizes, which are greater than that of typical WEEE shredders. In principle, highly selective solvent-based processes or electrostatic technologies would provide further alternatives; however, both techniques fail in processing complex polymer mixtures with variable material compositions.

Distribution of elements and related materials

Density fractions of sample 1 were analysed for a series of elements by XRF. Applying corresponding fraction masses (compare Figure 3) the percentages of element masses in the three density fractions were calculated and the results are displayed in Figure 4. In addition, the sum of element masses in the density fractions was related to the element amount in the input fraction. In spite of the material inhomogeneity most element masses in the density fractions accounted for 80–120% of the corresponding input masses. Higher deviations were obtained for Cl (178%), Pb (158%) and Sn (138%).

This approach reveals a 95% transfer of Cu, Sn and Cl into the heavy fraction, which is interpreted as the separation of PVC cables including their organotin stabilizers. Printed circuit boards, which are equipped with BFR and lead plumbs, were concentrated in the heavy fraction, as indicated by a

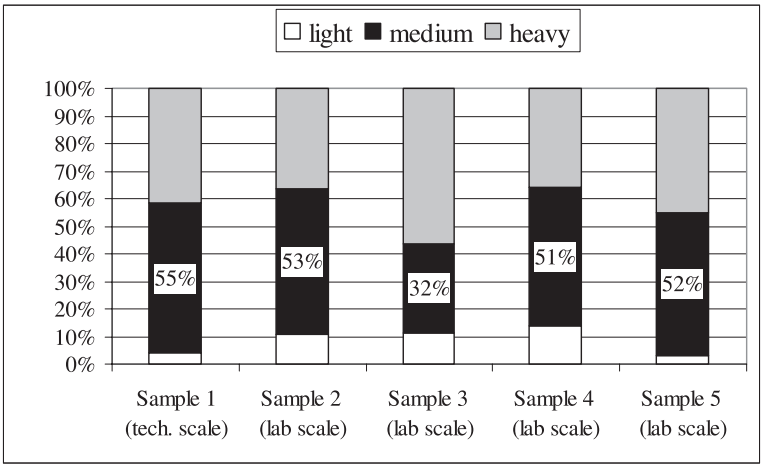

Fig. 3: Mass shares of light, medium and heavy density fractions obtained for five different WEEE polymer fractions. Sample 1 has been exposed to the complete recycling process of the presented case study.

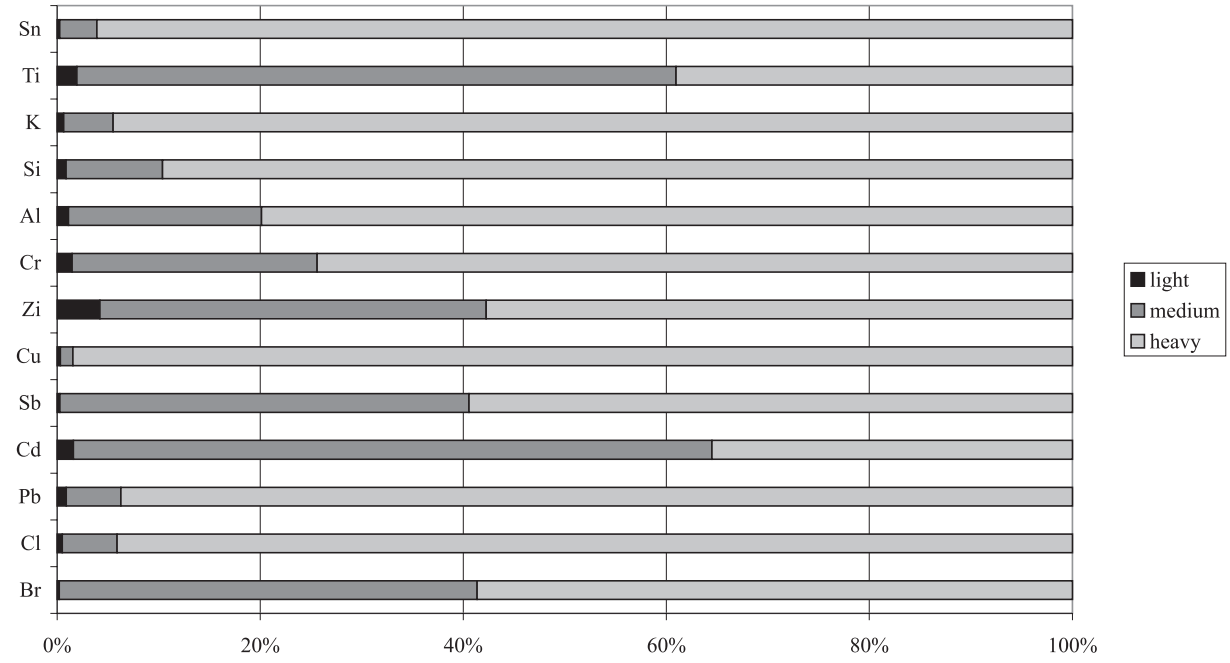

Fig. 4: Element distribution of sample 1.

more than 95% transfer of Pb into the heavy fraction. Br elimination from the medium target fraction is smaller (40%) due to the expected presence of BFR in styrenics. Ti and Sb refer to typical styrenics additives. TiO_2 is used as a white pigment and Sb_2O_3 as a synergist for BFR. Thus their removal from the medium density fraction is poor (< 40%).

Al, Si and K may indicate the presence of dust or of polymer fillers (e.g. glass fibre reinforced PP). Thus, an 80–95% transfer of these elements into the heavy fraction points to a convincing washing effect and or an effective removal of glass fibre-reinforced polymers.

About 24, 38 and 64% of Cr, Zn and Cd, respectively, remain in the medium density fractions. However, their absolute concentrations are rather low, and remain far below legal thresholds.

In summary, by means of density separation only the target fraction has been eliminated from the major part of non-styrenic polymers and other disturbing materials. However, from the economic point of view, costs for the subsequent treatment of light and the heavy fractions must not differ from treatment cost of the input material. Based on our XRF results, we propose to use the light fraction for the production of refuse-derived fuels whereas the heavy fraction exhibits still typical concentration ranges for WEEE shredder residues (compare Schlummer *et al.* 2006).

Material separation achieved by CreaSolv® process

The CreaSolv® process applied in this study is depicted in Figure 2. Applied to an 11.5 kg sample, dissolution, coarse and fine filtration of the input material achieved a material yield of 85%. While processing a 50 kg sample including dissolution and 100 µm filtration a yield of 90% was obtained. Thus, 10–15% of the CreaSolv® process input was rejected due to insolubility in a styrenics-specific solvent. This underlines the benefit of the application of two combined enrichment principles, density and solubility.

The elimination of co-dissolved BFR had to be performed by extraction. The material balance of this process step reveals a yield of 80% for the 11.5 kg sample and an 85% yield for the 50 kg experiment, reflecting roughly the percentage of brominated flame retardants in BFR-equipped materials. However, since not only BFR-containing materials were processed, the loss of 15–20% hints to an elimination of BFR but reveals the co-extraction of other additives and plastic oligomers, too. In sum, the CreaSolv process reaches a total yield of 70% (11.5 kg sample) to 77% (50 kg sample), which indicates good economic conditions for an industrial realization.

During the polymer separation step we obtained two different polymer phases. This effect is illustrated in Figure 5. FT-IR analysis of both polymers revealed that the phases refer to pure ABS and HIPS, respectively. Thus, the applied processing of the precipitated polymers allows the recovering of both materials separately from a bulk mixture. This approach is favoured since pure ABS or HIPS, respectively, is expected to exhibit better material properties than blends (Brennan *et al.* 2002). With regard to the applied input material, ABS and HIPS were almost equally distributed. However, the share of both material fractions has to be validated by processing much larger polymer waste streams.

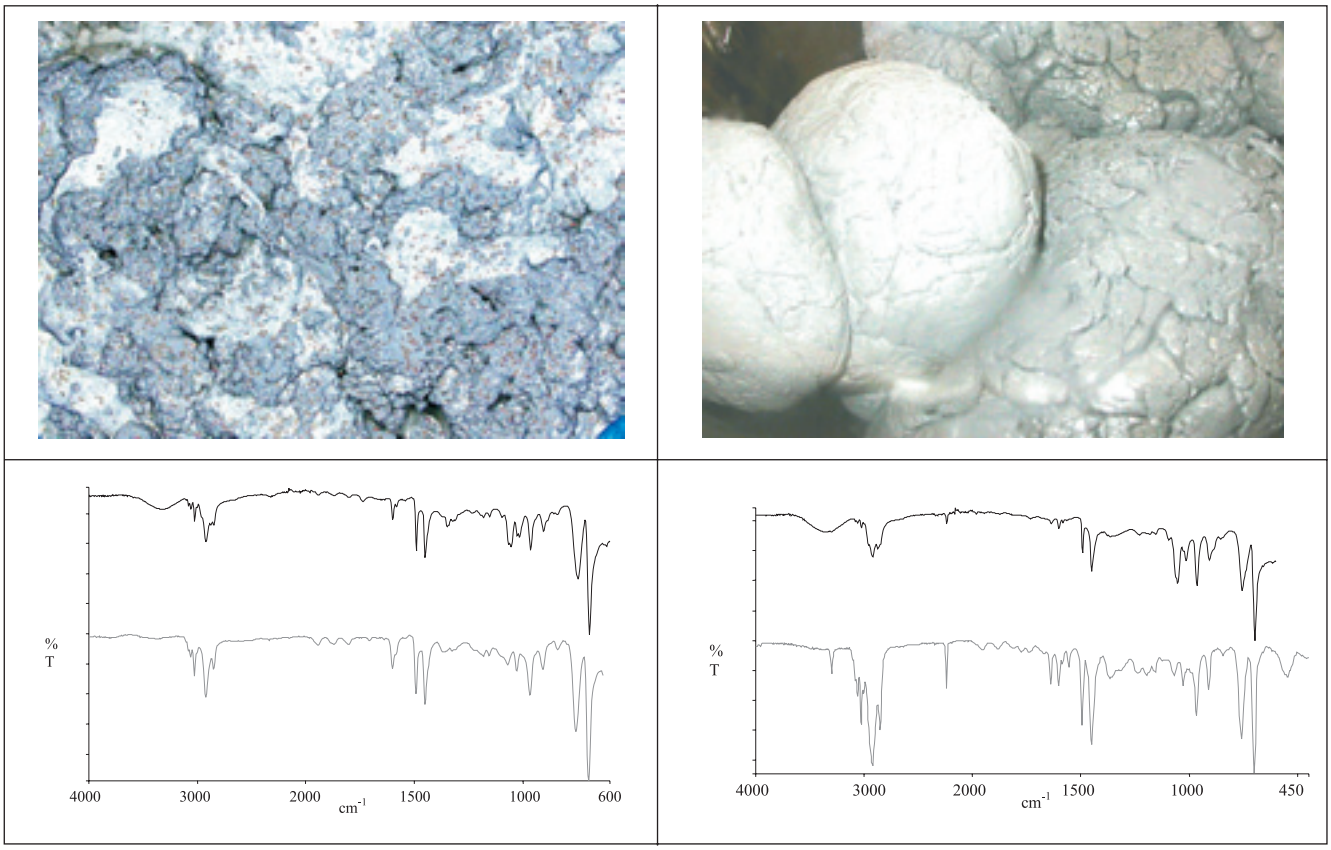

Fig. 5: Material separation observed in the polymer separation step. During the treatment, mixed polymer phases from the precipitation step (upper left) build two separated phases (upper right), which were identified as HIPS and ABS: The FT-IR spectra of the recycled HIPS (lower left) and the recycled ABS (lower right) were compared with reference spectra of HIPS and ABS from the Perkin Elmer ATR library of polymers (grey lines in lower figures).

Elimination of BFR

As discussed above, recycled polymers are intended to comply with European threshold values for PBB and PBDE, and require the elimination of BFR. On the basis of a mass balance and the analysis of input, by-products and products for bromine and four selected flame retardants, a substantial removal of BFR could be demonstrated in our pilot trial.

About 60% of the bromine input was eliminated from the target fraction by density separation (compare Figure 4) due to the presence of reactive tetrabromobisphenol A (TBBP A), mainly in printed circuit boards.

Further bromine was separated by the CreaSolv® process. As listed in Table 1, 66–78% of the residual total bromine was eliminated. Product levels of four selected BFR, viz. TBBP A, 1,2-bis(tribromophenoxy)ethane (TBPE), octabromodiphenyl ether (OctaBDE) and decabromodiphenyl ether (DecaBDE), account for 4–33% of the levels obtained in the medium density fraction. PBB could not be identified in input and products.

Table 1: Flame retardant levels investigated in input and products of the CreaSolv® process. The input sample refers to the medium fraction of the preceding density separation.

	TBBP A (ppm)	OctaBDE (ppm)	TBPE (ppm)	DecaBDE (ppm)	Bromine (4 FR)[a] (ppm)	Total bromine[b] (ppm)	PBDD/F (ppb sum 4)	PBDD/F (ppb sum 5)
Input	5428	861	1478	1198	5920	7959	n.a.	n.a.
HIPS product	244	98	156	392	657	1778	0.16	< 0.30
ABS product	295	111	155	323	639	2691	n.a.	n.a.
Mix product	236	94	126	288	542	2522	0.45 [c]	< 1.04 [c]
Threshold limit	–	1000	–	–	–	–	1	5

[a]Calculated bromine content which refers to bromine in TBBP A, OctaBDE, DcaBDE and TBPE, only.
[b]Total bromine measured by X-ray fluorescence analysis.
[c]Results refer to an extruded sample.
n.a., not analysed.

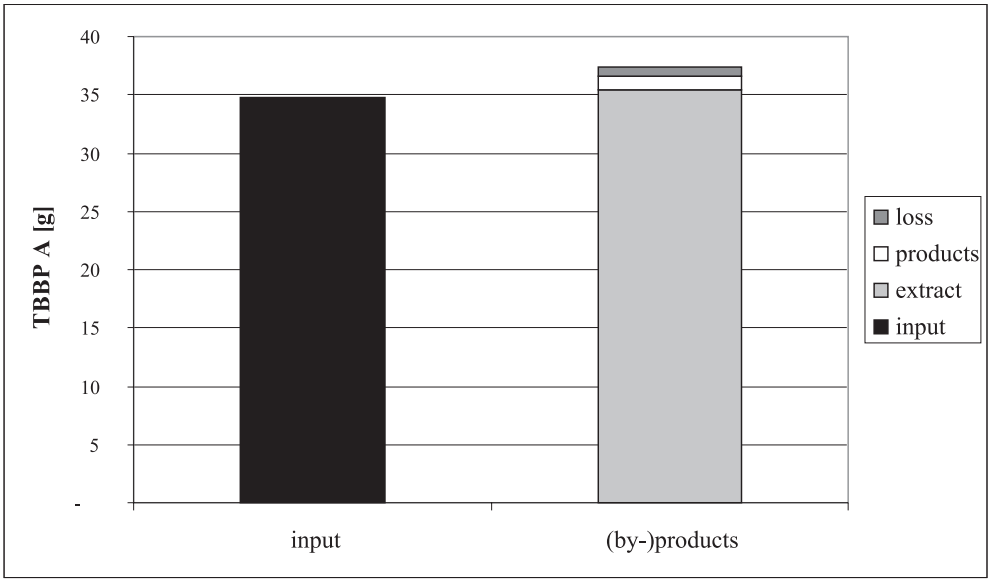

Fig. 6: Material flow analysis of TBBPA in the CreaSolv® process. Masses of TBBP A were obtained by multiplication of sample weights and their corresponding concentrations. Input refers to the medium fraction of the preceding density separation.

However, in both, input and products, the bromine content measured by XRF was higher than the calculated bromine content, when considering the four detected BFR. Furthermore, the discrepancy between measured and calculated bromine content was almost constant, indicating that the differing bromine amount had not been eliminated from the polymer matrix. The authors attribute this bromine to oligomeric BFR, whose high molecular mass prevents them from effective extraction and which have been shown not to form PBDD/F under thermal stress (Lange & Drohmann 2004). This is supported by Morf *et al.* (2005), who balanced the flow of bromine and BFR in a WEEE recycling plant. With respect to shredded polymers from small electric and electronic equipment, they allocated OctaBDE, DecaBDE and TBBP A to 41% of the total bromine.

As an example, Figure 6 depicts the mass balance of one specific BFR, TBBP A. Firstly, the balance is almost complete, recovering 107% of TBBP A analysed in the input. This indicates that material balance and chemical analysis were on an appropriate level. Secondly, TBBP A was transferred into the extract fraction almost completely and can be discarded after substantial enrichment during solvent recovery.

Compliance with legal thresholds

Two European directives define BFR levels in marketable products (EC 2003b, c). Consequently, OctaBDE levels must not exceed 1000 ppm but it was close to this threshold. As shown in Table 1, the OctaBDE level in the input was below 1000 ppm but was very close to this threshold. Therefore, a compliance with both cited European directives is uncertain, considering the inhomogeneity of the input matrix WEEE shredder.

However, the OctaBDE levels of the products of the CreaSolv® process were between 94 and 111 ppm and thus are a factor of 10 below the European thresholds. The concentrations of the other BFRs were below 400 ppm and do not influence their market value negatively.

For the German market, recycled polymers have to comply with the German ChemVerbotsV, especially with the threshold values of brominated dioxins and furans (PBDD/F). PBDD/F levels were obtained in two products, the pure dried HIPS product, which was subjected to maximal drying temperatures of 50°C but not to extrusion conditions, as well as an extruded ABS/HIPS mixture, which was produced for initial material evaluation. The latter sample was subjected to the usual extrusion temperatures of 220–240°C.

The results are given in Table 1 and indicate that both products were in compliance with the German ChemVerbotsV. Due to the applied chromatographic separation on a non-polar phase, a co-elution of non-2,3,7,8-substituted PBDD/F cannot be excluded. Thus both, sum 4 and sum 5, refer to maximum concentrations. 'Real' levels of both sums may be even smaller.

These findings show that the residue of BFR in the products are uncritical with respect to a formation of PBDD/F and support our assumption that most of the residual bromine can be attributed to oligomeric BFR.

Material properties

The initial processing of 11.5 kg of PS and copolymer sample produced only small amounts of recycled polymers, which were not sufficient for detailed material testing. However, an extrusion trial of the ABS/HIPS mixture was quite promising

Table 2: Material properties of recycling products compared to virgin material.

Test	Unit	R-ABS	R-HIPS	R-MIX	ABS, virgin [a]	HIPS, virgin [b]
Density (sample)	g cm^{-3}	1.809	1.751	1.812	1.04 (1.03–1.07*)	1.028 (1.03–1.05*)
Melt flow index (MFR)	g/10 min	5.14[++]	0.56[+]	0.21[+] 4.64[++]	–(0.1–95**)	–(0.4–18.5*)*
Melt volume index (MVR)	cm^3/10 min	5.12[++]	0.57[+]	0.20[+] 4.61[++]	22[++]	9.5
Ashing content	%	3.807	2.253	3.559	–	
Vicat softening temperature	°C	107.1	106.6	92.70	95 (86–132**)	98 (80–108**)
Tensile/EN ISO 527-1						
Elongation at break	%	1.68	1.52	1.69	2.1 (1–80**)	–(1–125**)
Modulus	MPa	2591	2706	2702	2300 (2200–3000*)	2000 (1400–2100*)
Flexural/EN ISO 178						
Flexural elongation at break	%	3.38	3.00	2.83	–	–
Flexural modulus	MPa	2739.50	2815.30	2691.60	2100 (1400–20 000**)	2100 (400–3400**)
Impact strength CHARPY/EN ISO 179						
Unnotched 23°C [+++]	kJ m^{-2}	24.9 (CB)	46.2 (CB)	19.3 (CB)	180 (NB***)	NB (> 65– NB***)
Notched 23°C [+++]	kJ m^{-2}	2.0 (CB)	4.9 (CB)	2.8 (CB)	22 (8-12***)	17 (5.5–7***)

[a]Numbers indicate properties of Novodur® P2M-AT (Bayer Polymers), a typical housing material, ranges in parentheses are obtained from different material databases.
[b] Numbers indicate properties of Polystyrene 495 F (BASF), a typical housing material, ranges in parentheses are obtained from different material databases.
[+]200°C, 5 kg.
[++]220°C, 10 kg.
[+++]CB indicates complete break, NB non-break.
*Ranges obtained from Oberbach *et al.* (2001).
**Ranges obtained from online materials database of Plastics Technology available at www.ptonline.com
***Ranges obtained from Carlowitz (1995).

and led to a flexible band of about 1 mm thickness with quite good optical surface properties.

By processing 50 kg material, we produced sufficient amounts of recycled ABS, HIPS and ABS/HIPS blend which allowed detailed testing of the material properties. The results are listed in Table 2. Most processing and mechanical properties of the three investigated recycled materials were in the range of virgin ABS or virgin HIPS without significant differences.

Only the Charpy impact strength was reduced with recycled HIPS, exceeding the values of recycled ABS and the recycled blend by a factor of two we consider three reasons: firstly, the low impact strength may be attributed to the input material, since the styrenics fraction contains high-impact ABS and HIPS, but also pure PS and SAN with reduced impact strength. Therefore, all products, the recycled blend, recycled ABS or recycled HIPS may contain low impact materials, whereas we expect SAN in the ABS fraction and PS in the HIPS fraction. Secondly, the CreaSolv® process might extract impact modifiers from the polymer matrix and thus lead to a lack of high-impact additives in the products. Thirdly, the input material might exhibit a deficiency of stabilizing additives that might in turn lead to thermal degradation of the polybutadiene phase in HIPS or ABS, which is responsible for their high impact properties.

Thus, impact properties might be improved by an improved material separation and/or the addition of stabilizers and impact modifiers. The relatively higher impact strength of the recycled HIPS indicates that the material separation approach has a positive effect on the mechanical properties of the products. Experiments on optimising the extraction process and upgrading the products by compounding with appropriate additives were addressed successfully during further developments.

Conclusions

This case study reveals that shredder residues from WEEE processing may serve as a valuable raw material for polymer recycling. A low-cost density separation pre-concentrates styrenics to an extent that the resulting intermediate fraction serves as an appropriate input for a sophisticated extraction, namely the CreaSolv® process. The results of the case study were convincing with regard to the yield of the combined processes, as well as analytical and mechanical product properties.

However, further work will be done to prove the economy on a larger scale using a series of different input materials.

Acknowledgements

We thank the Bavarian Ministry of Economic Affairs, Infrastructure, Transport and Technology for their financial support.

Appendix

List of abbreviations

ABS	acrylonitrile butadiene styrene	PC	polycarbonate
Al	alumina	PE	polyethylene
ASA	acrylester styrene acrylonitrile	PeBDD	pentabrominated dibenzodioxin
BFR	brominated flame retardant	PeBDF	pentabrominated dibenzofuran
Br	bromine	PET	polyethyleneterephthalate
Ca	calcium	POM	polyoxymethylene
Cd	cadmium	PP	polypropylene
ChemVerbotsV	Chemikalienverbotsverordnung	PP-GF	glass fibre-reinforced polypropylene
Cl	chlorine	PP-T	talcum-filled polypropylene
Cr	chromium	PS	polystyrene
Cu	copper	PU	polyurethane
DecaBDE	decabromodiphenyl ether	PVC	polyvinylchloride
EP	epoxy resins	RoHS	restriction of hazardous substances (EC directive)
FT-IR	Fourier transform infrared	SAN	styrene acrylonitrile
HIPS	high impact polystyrene	Sb	antimony
HxBDD	hexabrominated dibenzodioxin	Si	silicon
MFR	melt flow index	Sn	tin
MVR	melt volume index	TBBP A	tetrabromobisphenol A
NIR	near infrared	TBPE	1,2-bis(tribromophenoxy)ethane
OctaBDE	octabromodiphenyl ether	TeBDD	tetrabrominated dibenzodioxin
PA	polyamide	TeBDF	tetrabrominated dibenzofuran
Pb	lead	Ti	titan
PBB	polybrominated biphenyl	UP	unsaturated polyester
PBDD/F	polybrominated dibenzodioxins/dibenzofurans	WEEE	waste electric and electronic equipment (EC directive)
PBDE	polybrominated diphenyl ether	XRF	X-ray fluorescence
PBT	polybutyleneterephthalate	Zn	zinc

References

Altwaiq, A., Wolf, M., and van Eldik, R. (2003) Extraction of brominated flame retardants from polymeric waste material using different solvents and supercritical carbon dioxide. *Analytica Chimica Acta*, **491**, 111.

APME (2001) Plastic: A material of innovation for the electrical and electronic industry. Insight into consumption and recovery in Western Europe 2000. Association of Plastic Manufacturers in Europe. Brussels, Belgium. Available from http:// www.apme.org.

Bockhorn, H., Hornung, A., Hornung, U., and Jakobström, P. (1998) New mechanistic aspects of the dehydrochlorination of PVC – Application of dehydrochlorination to plastic mixtures and electronic scrap. *Combustion Science and Technology*, **134**, 7–30.

Brennan, L.B., Isaac, D.H., and Arnold, J.C. (2002) Recycling of acrylonitrile-butadiene-styrene and high-impact polystyrene from waste computer equipment. *Journal of Applied Polymer Science*, **86**, 572–578.

Carlowitz, B. (1995) *Kunststoff-Tabellen* (4th edn). Hanser, Munich, Vienna.

Chemikalienverbotsverordnung (1996) *Verordnung über Verbote und Beschränkungen des Inverkehrbringens gefährlicher Stoffe, Zubereitungen und Erzeugnisse nach dem Chemikaliengesetz (Chem Verbots V)*. Bundesgesetzblatt I, 19 July 1996, p. 1151.

Ebert, J., Lorenz, W., and Bahadir, M. (1999) Optimization of the analytical performance of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/F). *Chemosphere*, **39**, 977–986.

European Commission (2003a) Directive 2002/96/EC on waste electrical and electronic equipment (WEEE). *Official Journal of the European Union*, **L 37**, 24–38.

European Commission (2003b) Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS). *Official Journal of the European Union*, **L 37**, 19–23.

European Commission (2003c) Directive 2003/11/EC amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether). *Official Journal of the European Union*, **L 42**, 45.

Hornberger, M. (2002) Stoffliche Verwertung von Kunststoffen aus E-Schrott möglich: Pilotversuch bestätigt. (Material Recycling of polymers from E-scrap. A pilot study.). *Recycling Magazin*, **57/9**, 48–49.

Lange, T. and Drohmann, D. (2004) Environmental issues related to end-of-life options of plastics containing brominated flame retardants. *Fire and Materials*, **28**, 403–410.

Marioth, E., Bunte, G., and Härdle, T. (1998) Supercritical fluid extraction of ABS-composites in order to separate organic flame retardants. *Polymer Recycling*, **2**, 303–308.

Mäurer, A. and Schlummer, M. (2004) Good as new. Recycling plastics from WEEE and packaging waste. *Waste Management World*, **3/2004**, 33–43.

Mäurer, A., Schlummer, M., and Beck, O. (2005) German Patent application DE 10 2005 026 451.4.

Meyer, H., Neupert, M., Pump, W., and Willenberg, W. (1993) Flammschutzmittel entscheiden über Wiederverwertbarkeit. (Flame retardants are decisive for material recycling). *Kunststoffe*, **83**, 253–257.

Morf, L., Tremp, J., Gloor, R., Huber, Y., Stengele, M., and Zennegg, M. (2005) Brominated flame retardants in waste electrical and electronic

equipment: substance flows in a recycling plant. *Environmental Science & Technology*, **39**, 8691–8699.

Oberbach, K., Saechtling, H., and Pabst, F. (2001) *Kunststoff-Taschenbuch 2001*. Carl Hanser, Munich.

Riess, M., Ernst, T., Popp, R., Müller, B., Thoma, H., Vierle, O., Wolf, M., and van Eldik, R. (2000) Analysis of flame retarded polymers and recycling materials. *Chemosphere*, **40**, 937–941.

Schlummer, M., Brandl, F., Mäurer, A., and van Eldik, R. (2005) Analysis of flame retardant additives in polymer fractions of waste of electric and electronic equipment (WEEE) by means of HPLC-UV/MS and GPC-HPLC-UV. *Journal of Chromatography A*, **1064**, 39–51.

Schlummer, M., Gruber, L., Mäurer, A., Wolz, G., and van Eldik, R. (2006) Characterisation of polymer fractions from waste electric and electronic equipment (WEEE) and implications for waste management. *Chemosphere* (in press).

Schwarz, G. and Schultheiss, K. (2000) Mattscheibe im Recycling. (Recycling of focussing screen.) *Umwelttechnik*, **3/2000**, 24–27.

Uddin, M.A., Bhaskar, T., Kaneko, J., Muto, A., Sakata, Y., and Matsui, T. (2002) Dehydrohalogenation during pyrolysis of brominate flame retardant containing high impact polystyrene (HIPS-Br) mixed with polyvinylchloride (PVC). *Fuel*, **81**, 1819–1825.