Recycling of plastics containing flame retardants in electronic waste, a technical and environmental challenge for a sustainable solution

Lein Tange, ICL-IP Europe representing EFRA, *Frankrijkweg 6, 4538 BJ, Terneuzen, Netherlands*

Jan van Houwelingen, Recycling Consult BV, *Eindhovenseweg 29A, 5633 BD Eindhoven, Netherlands*

Willem Hofland, ICL-IP Europe, *Fosfaatweg 48, 1013 BM Amsterdam, Netherlands*
Florian Kohl, Albemarle, *Rue du Bosquet 9, 1348 Louvain La Neuve, Belgium*
Mike Kearns, Chemtura, *Neerpoortenstraat 111, 3040 Ottenburg -Belgium*
Philippe Salemis, Cefic EFRA, *Avenue E. Van Nieuwenhuyse 4, 1160 Bruxelles, Belgium*

Nourredine Menad, BRGM, *Avenue Claude Guillemin 3, 45060 Orleans, France.*

ABSTRACT:
The European Flame Retardant Association (EFRA) is the sector group of Cefic that brings together the leading companies offering the largest spectrum of flame retardants (FR) in Europe. For recycling of plastics containing flame retardants by EFRA many studies were carried out where now a specific study is done for plastics coming from flat panel displays. The study fits into the new RoHS/WEEE (Restriction on Hazardous Substances/ Waste Electrical and Electronic Equipments) recast related to a higher requirement of recycled plastics amount combined with the use of REACH compliant flame retardants.
Recycling standards development within the global committee IEC TC111 via a new technical report IEC/TR 62635 Ed. 1.0: "Guidelines for End of Life information provision from manufacturers and recyclers, and for recyclability rate calculation of Electrical and Electronic Equipment" aiming to also facilitating data exchange for better and higher value of recycled materials.
Due to higher external fire safety requirement in the standard EN60065 A11 for TV housings in Europe, in the future, more plastics containing flame retardants need to be recycled following the recast of the WEEE directive. Therefore WEEE plastics need to go through mechanical recycling as opposed to energy recovery. The joint EFRA recycle study with REWARD describes the plastics composition, different techniques of identification and separation that can be used and provides guidance on how to achieve the desired results and where the limitations will be due to miscibility of the different plastics

1 INTRODUCTION

1.1 *EFRA*

The European Flame Retardants Association (EFRA) brings together the leading companies that manufacture and market flame retardants (FR) in Europe. EFRA activities are committed to improve the level of fire safety. EFRA is a Sector Group of Cefic, the European Chemical Industry Council. EFRA aims to align itself with the industry it serves, and covers all types of flame retardants: substances based on bromine, chlorine, phosphorus, nitrogen and inorganic compounds. EFRA organisation is centered around four application Forums: Upholstered Furniture & Textiles (UF&T), Electrical and Electronic Devices (E&E), Building, Construction and Transportation. These Application Forums are complemented with ad-hoc working groups, addressing regulatory, or substance-specific issues as they arise, as well as a Product Stewardship (PST) group. Recent examples of activities include: advocacy on the revision of the EU RoHS directive (Restriction on Hazardous Substances) revision, VECAP – Voluntary Emissions Control Action Programme – and studies about the End-of-Life phase of products containing flame retardants such as the recycling of Flat panel displays. By bringing together the different players in the relevant value chains, the EFRA working groups allow to look for improved and sustainable fire safety solutions, to protect the public and the environment. EFRA is seeking for science based decisions from its members and from other stakeholders like regulatory bodies or NGO's, to allow maintain or improve the level of fire safety which is needed with current modern materials used in our day to day life. For more information please visit www.flameretardants.eu or contact the authors of this paper.

1.2 *Recycling Consult*

Recycling Consult is a company (2005) specialized in recycling and energy. Its director Jan van

Houwelingen has a background in mining, mineral processing, recycling and metallurgy. He has experience as consultant for Philips Mirec, the European Aluminum Association. (EAA) including a range of recycling companies. Currently, various projects[1,2] are running together in Europe and in the USA. REWARD is a project in the Eco-Innovation program with partners such as Dolphin Metals, Van Gansewinkel and Bureau de Recherche Geologiques et Minières (BRGM) in Orléans investigating smart size reduction and separation methods for WEEE. The LCD recycling project of plastics is running jointly in cooperation with EFRA and its experts on flame retardants and REWARD. While PRIME is a similar project on LCD recycling running in Belgium with focus on the business model disassembly including the economics.

2 ROHS AND WEEE RECAST

The European Union has adopted legislation that establishes the framework for the management of electronic and electrical waste. The legislation has been subject to a recast or revision with a view to update and clarifies the legal provisions

2.1 *RoHs recast*

In order to avoid the uncontrolled or diffused release into the environment of dangerous substances during recycling, the European Union adopted the directive on the restriction of certain hazardous substances in electrical and electronic equipment (RoHS directive). The RoHS directive restricts the use of lead, mercury, cadmium, hexavalent chromium, PBBs, and PBDEs in electronic and electrical equipment. The revised RoHS directive was adopted on June 8, 2011 and it repeals the original RoHS Directive which has regulated hazardous substances in electrical and electronic equipment (EEE) since June 2006. No changes were made to the list of restricted substances, so that substances used in electrical and electronic equipment today, such as brominated flame retardants, can continue to be used.

The revised RoHS introduces a methodology for substance restrictions and opens the scope now covering all electrical and electronic equipment except for equipment that is specifically excluded.

The European Commission is currently working with Member States to develop implementation guidelines and a methodology for restricting substances. The Commission has indicated that HexaBromoCycloDodecane (HBCD) (minor used in Polystyrene for making electrical switch boxes) will be one of the substances that will be evaluated first under this methodology.

Link to the RoHS:
http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:174:0088:0110:EN:PDF

2.2 *WEEE recast*

The directive on the waste of electrical and electronic equipment (WEEE directive) aims to prevent the production and disposal of WEEE through reuse and recycling targets. Moreover, it is set up to improve the environmental performance of all operators involved in the life cycle of electrical and electronic equipment.

The WEEE requires Member States to ensure that producer-financed systems are set up to separately collect, treat, recover and dispose of WEEE.

In June 2012 the revised WEEE directive was adopted. Under the new directive, member states must collect annually 45% of the average weight of electrical and electronic equipment placed on their national markets four years after its entry into force. Three years later, member states are to achieve a 65% collection rate. Some EU states where consumers use fewer electronic devices may achieve the targets with some flexibility. Moreover, the directive establishes the producer responsibility, as a means of encouraging design and production of EEE which take into full account and facilitate its repair, upgrading, re-use, disassembly and recycling.

Link to the Commission website on the WEEE:
http://ec.europa.eu/environment/waste/weee/index en.htm

2.3 *Recycling standards*

A recycling standard is approved within the global International Electrotechnical Commission (IEC) TC111 in the form of a technical report (TR) IEC/TR 62635 Ed. 1.0: Guidelines for End of Life information provision from manufacturers and recyclers, and for recyclability rate calculation of Electrical and Electronic Equipment.

[1] REWARD. *Recovery of Electronic Waste through Advanced Recycling and Demonstration.* A 3 year project in the Eco-Innovation Program of EACI, Brussels. www.reward-weee.eu.

[2] SATURN. *Sensor Sorting Automated Technology for Advanced Recovery of Non-Ferrous Metals.* A 3 year project in the Eco-Innovation Program of EACI, Brussels. www.saturn.rwth-aachen.de.

3 RECYCLE STUDY FOR PLASTICS COMING FROM LCD'S

Cooperation between EFRA and REWARD has resulted into a joint project which started in 2011 to investigate and define the plastic composition in flat panel displays and come up with solutions for mechanical recycling with best available technology (BAT).
Due to higher fire safety requirements for TV set housings sold in the EU, they need to be made out of materials such as FR containing plastics in addition to the WEEE directive recast imposing higher recycling rates. Therefore WEEE plastics need to be separated with mechanical recycling techniques as opposed to energy recovery. The EFRA recycle study for plastics containing flame retardants from LCDs will give guidance on achieve the desired results and what can be the limitations.

3.1 *Main issues and challenges for plastics recycling*

The main issues today in plastics recycling are:

- The scale of economy of recycling facilities is in the range of 5000 to a maximum of 20.000 tons/yr of recycled plastics as output. Where plastic manufacturers produce in the range of 200.000-500.000 tons/yr of plastics. This is a ratio of 10-100 times more.
- The complexity of the many different types of plastics used in WEEE. The main barrier is in the black color combined with the lack of sorting techniques to be able to separate every plastic type into the individual plastic stream for a high end application. If techniques do exist at all, then high investments are needed compared to the relatively small yield of recyclate produced.
- Lack of understanding on the type of plastics and flame retardants used and in various applications which quantities do they appear at the recycle facility
- Understanding of effects of miscibility of the different plastics and the consequences on the physical properties after recycling.

3.2 *Current situation in Europe*

Flat Panel Displays (FPDs) are collected separately from other WEEE categories. Liquid Crystal Displays (LCD's) that are contained in this batch have mercury lamps, a RoHS substance to be kept and processed separately.

A photo is showing the collected stacks of LCD's on pallets ready for transport. The required collection procedure provides the advantage for separation options to sort the plastic mix after shredding. A similar situation is found for Polystyrene from selectively collected refrigerators.

Figure 1 Selectively collected FPDs from NW-France

Selective collection systems are beneficial and facilitating the rather clean collection of these batches of LCDs. The LCDs are prepared for treatment, the plasma displays and

CRTs are treated separately and electrical cords are disconnected. Current practice consists of two principal ways of treatment: disassembly or shredding. In this particular case of study the LCDs are shredded. After magnetic and eddy current separation a plastic mix remains. This mix currently is the subject for this study. The produced particle size distribution with a d50 of 40 mm is the starting point.

4 SAMPLING INCLUDING PLASTICS FROM FLAT PANEL DISPLAYS

Part of the study is the analysis of a sample of 623 Flat Panel Displays taken in the area North West of France and Flanders in Belgium. This batch contains 500 LCDs, 94 laptops and 29 plasma displays. From each LCD a photo is taken of the front with the brand name and of the back with the tag numbers. A material sample is taken from the back cover (BC) for further study. A list of data is composed of brand, diagonal width, weight (of LCD), density (of BC), plastic type of BC and additive (brominated, Br or phosphor, P flame retardants). Relations between brands and other features are documented. Information from plastic producers and original equipment manufacturers (OEMs) is collected; the data is used for cross checking the information.

5 MEASUREMENTS AND ANALYSES

Some LCDs are examined for their full composition in plastics, metals, printed circuits and other components and materials. A typical composition is given by Salhofer[3].

The sample of 500 LCD BCs is analyzed with a focus on its separation after granulation. The physical properties like density, plastic type, and additives are determined. The density is determined with an air pyknometer. Plastic types are determined with a NIR device. Black plastic types are determined with an FTIR device[4]. Different plastic library scans are used. It appears that analytical equipment such as NIR and FTIR have to be stored with the known plastics examined in order to give the device a closer range of recognition; however, this is not always possible as the complete library is not always available. The additive Br-FR is determined with a calibrated XRF device but sometimes also found via FTIR or NIR. Other additives such as phosphor sometimes are determined with NIR and FTIR depending on their libraries contained. Different analytical laboratories and companies are involved in the analyses making cross control possible. From these collected data a strategy for separation is determined. A description of how to analyse WEEE with a focus on shredding and separation is given in Menad[5].

It appears that manufacturers have produced LCDs with certain preferred plastics and additives for the BCs. These data are helpful in the full interpretation of the 500 LCD samples. For the LCD BCs the brands Grandin, Samsung, Toshiba and LG predominantly use high impact polystyrene (HIPS) (sometimes with Br-FR), and Philips and Sony use HIPS/PPE or PC-ABS (with P-FR). Producers of these plastics are Bayer, SABIC and Styron and have contributed to important product data generation within this project.

5.1 *Results and interpretation*

Brand	[%]
Samsung	17.8
Philips	17.6
LG	7.6
Toshiba	5.8
Sony	4.6
Grandin	4.4
Thomson	4.2
Sharp	4.0
Funai	2.4
Sum	68.4
Other	31.6
Total	100.0

Table 1 Brands in descending frequency in 500 LCD's

The brands found are listed in Table 1.

The total weight of 1 LCD varies from 1.5 to 46 kg. The density range for the BC is from 1.03 to 1.25 g/cc. Sorting the excel list of 500 BC samples to density results in a split or separation in HIPS-PPE and PC-ABS. Both fractions of HIPS and ABS can contain brominated plastics.

Further sorting into brominated and non-brominated results in an almost perfect split in HIPS (no Br-FR), HIPS (with Br-FR) and PC-ABS (with P-FR). Due to analytical reasons with the FTIR sofar no guaranteed HIPS/PPE differentiating from HIPS could be defined. This offers the possibility to set a scheme of sorting starting either with density or with XRF sensor sorting. The latter with the advantage of creating a batch of HIPS with Br-FR. Density sorting after that gives the split in HIPS (no Br-FR) and PC-ABS. The HIPS-PPE with P ends in the lower density range.

The basic mixture of plastics consists of 2 types: HIPS (w/o Br-FR), PC-ABS (w/o Br-FR). Other plastics found are PMMA (seems not evident), ABS, SAN, HIPS/PPE and variations of HIPS and PC-ABS. NIR sorting can be used to scalp colored plastic contaminants in one step prior to further sorting. However, colors are mostly black (444→>93%), other colors (32→ <7%) found are white, blue and grey. NIR sensor sorting has the disadvantage of detecting only colored plastics; this is depending on the soot level.

The approach of separation therefore is twofold based on the properties density and additives. The sequence XRF (for the HIPS with Br-FR – blue in Figure 2) followed by density as second separation gives the fractions PC-ABS and HIPS (w/o Br-FR). Separations are never perfect. Imperfections are the cross contamination of other plastics in either fraction. Nevertheless density separation tests show a good separation between HIPS and PC-ABS for the BC's.

---

3 Salhofer, S., Spitzbart, M., Maurer, K. *Recycling of LCD Screens in Europe – State of the Art and Challenges*. In: Glocalized Solutions for Sustainability in Manufacturing. Proc. of 18th CIRP Int. Conf. on Life Cycle Engineering. Technische Universität Braunschweig. Eds. J. Hesselbach, C. Herrmann. Braunschweig, 2011.

4 Zachmann, G. *Rapid Characterization of Black Plastics by MID Infrared Reflectance Spectroscopy*. R'97 Recovery Recycling Re-integration. Vol III. Mechanical Processes Separation Technologies, Logistic Networks. Eds. Anis Barrage, Xaver Edelmann. 1997.

5 Menad, N., Guignot, S., Van Houwelingen, J.A. *New Characterization method of electrical and electronic equipment wastes (WEEE).* Waste Management, 2012. To be published.

5.2 *Sorting and Separation*

The plastic material mix from shredded LCDs contains more than the two predominant types of main plastics and needs to be classified. This can be achieved with a higher level density separation, metals like stainless steel need to be removed (by metal detection) and foils by air classification[6]. The Indium-Tin-Oxide (ITO) bearing laminate and printed circuits are then removed from the other plastics. In a second step the plastics PS and PC-ABS can be separated (Figure 2[7]).

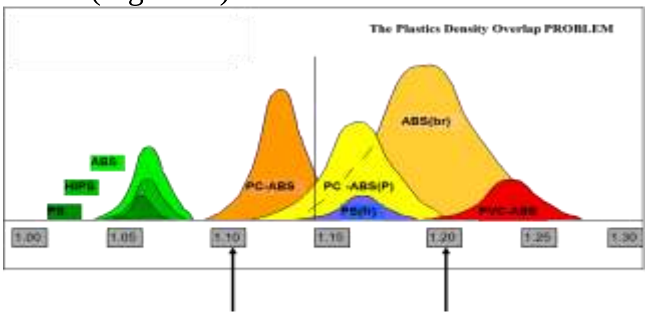

Figure 2 Density distribution most common plastics (Ref. 7)

Recent developments in electronic sorting opens a range of possibilities for sorting plastics. Properties like color, type and additive are the criteria for sorting. Even wood, fiber, tetrapack and some brominated plastics are recognized. Combined with traditional sorting techniques as sink-float, electrostatic and others, acceptable grades can be produced. Separation tests have been performed with a selected batch of black particles from BCs with known properties with an XRF sensor separator. Results are shown in Table 2 and Figure 3. NIR sorting on colored plastics provides information of the full composition of the input mix (Table 3). A choice of approach can be made whether to sort 1 polymer in 1 run, or 2 different polymers in 1 run. A NIR sensor sorter is a versatile machine which can be equipped with one single lane or 2 lanes to sort 2 different (colored) fractions.

Figure 3 Labeled black plastic particles (5-25 mm size)

6 Morrish, L., Morton, R., Myles, N. *Flat Panel Display Recycling Technologies. TITECH FPD Sorting Trial*. WRAP MDD014 – Trial Report. July 2009. Axion Consulting. www.wrap.org.uk

7 Ronald Kobler and Hal Foss. *Successful Recovery of End of Life Electronics Plastics using RPI's Skin Flotation technology*. GPEC 2004 Paper Abstract #32

The preset library recognizes qualitatively the full content of the input mix. Applications are also possible to separate a group of 2 or more foreign polymers from the targeted HIPS and PC-ABS in one step (scalping).

A test run was made with a XRF sorter. Black plastic particles are labeled brominated and non-brominated. The results of the separation are in Table 2 and represent the number of particles in the accepted and rejected fraction. The threshold in this case is 1% Br in plastic.

XRF Sensor	Accept	Reject	Input
Brominated	2.2	86.7	16.5
Non-Br	97.8	13.3	83.5
Recovery Br	11.0	89.0	100.0
Rec Non-Br	97.3	2.7	100.0
Balance	83.0	17.0	100.0

Table 2 Performance X-Ray sensor sorter

The collection of data offers a strategy for separation. It appears from analyses that HIPS can be either brominated or not and PC-ABS contains phosphor offering a perfect set for separation. The additives Br and P are separated preferably; cross contamination is a disadvantage for granulation and re-moulding. The sequence is determined partly by economic requirements.

Type	Counts	%
ABS	52246	65,15
PA	129	0,16
PBT	39	0,05
PC	276	0,34
PE	142	0,18
PET	308	0,38
PMMA	66	0,08
POM	277	0,35
PP	66	0,08
HIPS	10080	12,57
PC+ABS	15159	18,90
PVC	161	0,20
PUR	1	0,00
PPE+SB	1144	1,43
PVC+ABS	51	0,06
TETRA	34	0,04
PAPER	20	0,02
Total	80199	100,0

Table 3 Input arbitrary plastic mix NIR sorter (Courtesy RTT-Zittau)

5.3 *Final grades and miscibility*

Fractions of produced plastics from separation tests and from disassembly can be tested for their grade, physical properties and applicability in new products.

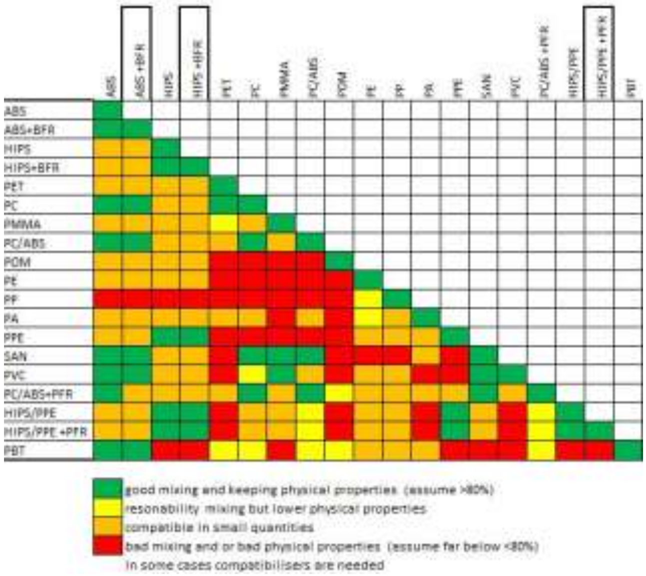

Figure 4 Miscibility chart for common plastics

The tests show good results for the final quality of pre-sorted, re-granulated and re-moulded disassembled BCs.

Since separations are never perfect the produced fractions of plastics do not have the optimal grade that virgin plastics have. Therefore they are mixed with virgin in low ratio's to dilute the recycled plastic and to dilute the contaminant in the recycled plastic. The authors have developed a miscibility preference scheme for mixing.

This chart (Figure 4) shows the influence of small quantities of plastics of semi-pure separated batches into virgin stock. For recycled plastic material after shredding and separation the procedure is to mix it with virgin plastics at a ratio of e.g. 90 to 10%, causing the simultaneous dilution of contaminants from assumed 1% to 0.1%. The miscibility chart shows that most of the plastics with their contaminants in LCDs are in the yellow or orange range and not harmful to final quality. Additional testing is planned to define the real quality in the range of 1-3 and 10% contamination of the different plastics (Figure 5).

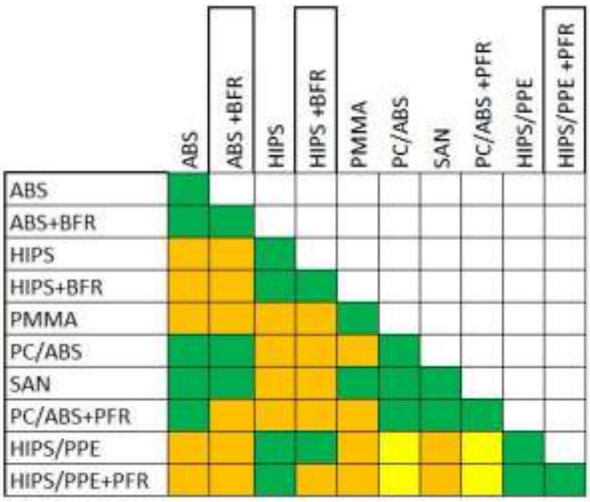

Figure 5 Miscibility chart of polymers of this study

6 CONCLUSIONS

The volume of plastic recycling from WEEE is still low. Recyclers are faced with issues such as scale of economy, lack of identification and sorting techniques plus lack of information of used plastics and flame retardants. Mixing virgin plastics with recycled fractions has a risk; contaminants with bad mixing properties are introduced. A mixing chart is introduced that gives the level of risk. Selective collection of FPDs is required because of the mercury content of the LCDs. This inherent disadvantage, however, is beneficial to the separation after shredding. The produced mix is less complex than would have been the case with mixed WEEE as input (a similar case is found with HIPS in fridges).

Due to the WEEE recast currently higher recycle rates are required with the consequence that plastics need to be recycled at a higher rate with better grades as is done today.

The study of characterizing and defining the main properties of plastics and the presence of flame retardants within the 500 LCD BCs is a first step in the setting up of an *on paper* scheme for further mechanical recycling. The list of 500 BCs shows that separation between HIPS and PC-ABS is possible with a combination of type/additive and density sorting, however, the shredding of a complete LCD set results in a mixture of plastics with more different types that needs more processing steps.

The main plastics: HIPS, ABS (w/o Br-FR), PC/ABS and HIPS/PPE (with P-FR) found in the BCs can be recycled if disassembled and processed separately[8]. However, this is a costly process. The study presented here has searched for a full mechanical solution.

Depending on the quality of the identification and separation techniques it is believed to be possible to obtain acceptable grades that prove the recyclability of the different individual plastic types. Additional work to define the real quality after recycling and the limitations due to lower physical properties is required and planned.

7 ACKNOWLEDGEMENT

Part of the work was sponsored and supported by REWARD a project in the Eco-Innovation program from EACI. The following parties contributed to the study: RTT, Steinert, BEST, REDWAVE, Coolrec France, Apparec, MOS, PHB, BRGM, SGS, Dolphin, Kunststof Centrale, Eco-Systèmes, Philips, SABIC, Styron, Bayer, TOTAL PETROCHEMICALS and Axion Recycling. With the PRIME project we had some interesting discussions.

8 Vanegas, P., et.al. *Closed loop recycling of Philips TV Housing Plastics.* To be published. 2012.