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

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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 several studies have been carried out in the past. Now a specific study is done for plastics coming from flat panel displays. The study is in line with the newly recast EU Directives on RoHS and WEEE (Restriction on Hazardous Substances/ Waste Electrical and Electronic Equipment) - and higher requirements of recycled plastics - as well as the need to use flame retardants compliant with EU Regulation on chemicals REACH.

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” better data exchange for a better and higher value of recycled materials must be achieved.

Due to higher external fire safety requirement in the standard EN60065 A11 for TV housings in Europe, more plastics containing flame retardants need to be recycled in the future. Therefore WEEE plastics need to go through mechanical recycling as opposed to energy recovery. The study describes the composition of plastics containing flame retardants from liquid crystal display units (LCDs), and different techniques for plastic identification and separation. It provides insight in limitations due to the mixing of different plastics, guidance and solutions for mechanical recycling on the basis of best available technology (BAT). As such the study indicates how to achieve better and higher value recycled material.

The study, a joint effort between REWARD and EFRA, is characterizing and defining via different techniques of identification the main properties of plastics and the presence of flame retardants within the 500 LCD back covers as a first step in setting up a scheme for further mechanical recycling. It provides guidance on how to achieve the desired results and describes the limitations due to miscibility or lack of it of the different plastics and separation.

1 Introduction

In today’s world electrical and electronic equipment needs to comply with EU legislation on recycling while - at the same time - meeting international fire safety standards. This study for plastics containing flame retardants from LCDs provides guidance on how to achieve better and higher value recycled materials.

EFRA (the European Flame Retardants Association) 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, Voluntary Emissions Control Action Programme (VECAP) – 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 advocating 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.

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

In order to avoid the uncontrolled or diffuse release of dangerous substances[ii] into the environment during recycling, the European Union adopted the directive on the restriction of certain hazardous substances in electrical and electronic equipment (RoHS directive) in 2006. The RoHS directive restricts the use of lead, mercury, cadmium, hexavalent chromium, PBBs, and PBDEs in E&E equipment.

A revised RoHS directive was adopted on June 8, 2011, repealing the original RoHS Directive and introduces a methodology for future substance restrictions and opens the scope covering all E&E equipment except for equipment that is excluded explicitly. No changes were made to the list of restricted substances, thus substances used in electrical and electronic equipment today, such as brominated flame retardants, can be used further on.

The European Commission is currently working with Member States to develop implementation guidelines and a methodology for restricting substances.
Link to the RoHS:
http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:174:0088:0110:EN:PDF

2.2 WEEE

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 45% of the average weight of electrical and electronic equipment annually 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 member 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 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

3 Recycling Standards

The global International Electrotechnical Commission (IEC) has approved recycling standard TC111 in the form of *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.* The purpose of this standard is an improved data exchange for better and higher value recycled materials.

4 Recycling Study on Plastics

In 2011, cooperation between EFRA and REWARD has resulted in a joint project. The study describes the composition of plastics containing flame retardants from LCDs, and different techniques of identification and separation that can be used. The focus of this study is to come up with solutions for mechanical recycling with best available technology (BAT) for size reduction and separation.

Higher fire safety requirements for TV set housings sold in the EU make materials with a UL 94 fire safety standard rating better than V1 mandatory. As indicated in the previous chapter, the WEEE directive is imposing higher recycling rates. Therefore WEEE plastics need to be separated with mechanical recycling techniques as opposed to energy recovery. Chemical recycling is a second best option as it is most of the time more expensive The EFRA study for plastics containing flame retardants from LCDs indicates how to achieve better and higher value recycled material.

4.1 Main Issues and Challenges for Plastics Recycling

Today's main issues and challenges for plastics recycling in Europe are:

- Relatively limited recycling rate compared to plastics manufacturing. Whereas recycling facilities have an output between 5.000 and 20.000 tons per year, polymer manufacturers produce between 200.000 and 500.000 tons per year.
- The complexity of the different types of plastics used in EEE products and like the black coloured materials
- The lack of techniques for separating all plastic types into individual streams for a high end application
- A limited understanding of the effect of the mixing of different plastics on the physical properties of the recycled material.

4.2 Current Situation in Europe

Flat Panel Displays (FPDs) are collected separately from other WEEE categories. Liquid Crystal Displays (LCDs) that are contained in this batch have mercury lamps. Mercury is a restricted hazardous substance under the RoHS directive and therefore needs to be kept and processed separately. Selective collection systems are beneficial and facilitate 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 cables 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 polymer mix is the subject of this study. Starting point is the fraction with a median particle size distribution of 40 mm.

4.3 Recycling of Selectively Collected LCDs

A recent study is undertaken to set out a strategy for processing plastics from selectively collected Liquid Crystal Displays (LCDs). One of the activities of the study is to determine the material composition of the LCD and the properties of the materials, more specific the plastics. The back cover is the major part of plastic of a TV set. This part is subject for a more detailed study into the properties with the purpose to develop a size reduction and separation scheme for a full LCD. An LCD contains more plastics than the back cover, e.g. the screens which consist of PET and PMMA. Part of the study is to determine decision criteria for separation.

4.4 Sampling

Sampling primarily is an activity to learn more about the content of a waste stream with a focus on processing and recovery. A sample of 500 LCDs, 94 laptops and 29 plasma displays were collected in the North West of France and Flanders in Belgium. From each LCD a photo was taken of the front with the brand name and of the back with the tag numbers (

Figure 1). A plastic material sample was taken from the back cover for further study. A list of data is composed of brand, diagonal width, weight (of LCD), density (of back cover plastic), and polymer additives like brominated-, phosphorus- or no flame retardant. The first objective is to establish a correlation between brands and technical features. Another target is to cross check the information collected with plastic producers and Original Equipment Manufacturers (OEMs). The main objective, however, is to utilize the physical properties found for the design of a flow sheet for optimal processing.

Figure 1 Documentation of sample of 500 LCDs. Left: back side with serial number, brand. Right: front side with brand.

4.5 Measurements and Analyses

A selection of LCDs is then examined for their full material composition. An LCD can contain various types of polymers in the back cover (HIPS/PPE, PC/ABS, HIPS-ABS w/o FRs) and in the screens (PMMA and PET). Other plastic types can be found as well. Ferrous and non-ferrous metals are present such as stainless steel, galvanized steel, aluminium and copper (mainly in cables and in printed circuit boards). Sometimes a glass screen is used (mainly in plasma's). A detailed composition is given by Salhofer[iii]. LCDs are processed separately from other e-waste because they contain mercury back lights which have to be removed before shredding or as in this project are shredded in a closed environment to trap the mercury.

4.6 Final Specs and Requirements

The predominant purpose of the analysis is to design a size reduction and separation scheme to recover most of the materials in a quality that is suitable for further use and sale. Each processor in the recycling chain has its own requirements and specifications varying from size (does it fit in the shredder or furnace) to composition (disassemble before shredding), properties (which separator fits best?) and final quality (can it be sold after compounding or melting?).

4.7 Grade and Recovery

Each material contained in an LCD has its own set of properties which provides a route for mechanical separation (after shredding). For instance magnetic properties for metals provide a means of separation from non-magnetic particles. Before separation, the LCD has to be shredded into small particles. Depending on the type of shredding a certain particle size distribution is produced. A uniform set of particles is a better start for sorting than a broad particle spectrum. A slow rotating shredder with a preset grid or an impact crusher without grid will give different broad particle spectrum. A second requirement is the liberation of materials. Suppose we have a mixture of peas, beans and nuts, then sizing is easily accomplished with a screen. And this might be fairly accurate, but what about a broken nut, some of the nut shreds will appear in the pea fraction. After that a separation might be the sorting of white and brown beans with equal size. The property colour here seems the only criterium for sorting, in this case colour sorting. This is how a scheme of size reduction and separation is set up for shredded LCDs.

4.8 Miscibility and Purity

Mechanical separations in plastics recycling never are 100% perfect, cross contamination or false positives are incurred with each separation and in each separated fraction. Perfect grades are never accomplished unless an infinite sequence of subsequent separations is set through which is inefficient eventually. Recyclers compromise between grade and recovery. In other words, a recycler is required to recover most of the wanted material with an acceptable grade (based on physical properties) (Figure 2).

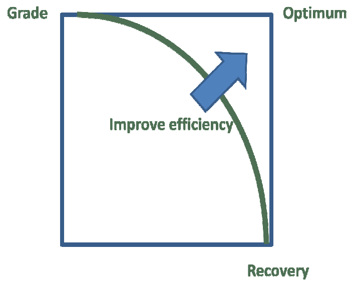

Figure 2 Relationship grade and recovery for separation processes.

For this purpose miscibility charts are developed for metals and for plastics. An example is to be seen in (Figure 3). In the given example in 4.7 the nut fraction is pure (100% grade), however, the recovery is less than ultimate, part is in the pea's fraction.

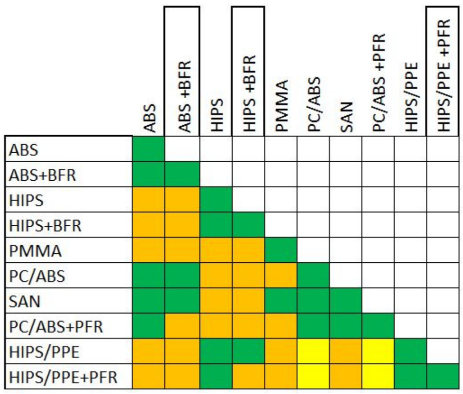

Figure 3 Miscibility chart of polymers with an overlay of flame retardant additives. Green, good mixing, yellow, mixing small quantities, ochre, compatible in small quantities.

The processing starts in the lower right corner with 100% recovery and a low grade and to move vertical to the optimum grade with a minimum of losses of the targeted material. Since losses cannot be avoided the search is to improve the efficiency of the process. Here for the grade of the pea's fraction is less than pure, whereas the recovery is 100%. For the beans recovery and grade are max.

4.9 Results and Interpretation

Looking at the results of our investigation from the back covers a number of things are found. From

Table 1 it appears that Philips and Samsung were the most frequently found brands in the sample. Other brands represent 64.6% in more than 20 different brands.

From the total weight of an LCD several other parameters can be determined such as the average weight which indicates volumes to be expected for processing. The density range found for the back cover opens the possibility to separate plastics in water or salts (with different density). The back cover samples are sorted based on density resulting in a fairly accurate separation in 2 types of plastics (Figure 5). All samples are checked for bromine with a hand held x-ray device. With a separation device the brominated plastics can be separated.

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
Other	31.6
Total	100.0

Table 1 Brands in descending frequency in 500 LCDs

Sorting on these properties result in an almost perfect split in HIPS - with and without bromine - and PC/ABS with phosphorus. This offers the possibility for setting up a scheme of sorting by density and x-ray sensor techniques.

The reason for doing this is to produce relatively fairly pure fractions which can be mixed with virgin polymer of a single type. The miscibility chart helps finding the acceptable concentrations that can be tolerated in the separation process. Ultimate purity is not always a necessity.

4.10 Sorting and Separation

LCDs are shredded in a closed environment to trap most of the mercury that is released during crushing. The shredded mix is subjected to magnetic separation and eddy current separation. After this process

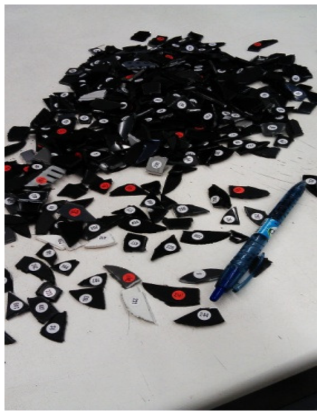

Figure 4 Labelled plastic particles for sorting test

the remaining polymer mix appears to be more complicated than from back covers only. This mix contains more than the two predominant types of main plastics and needs to be classified and more steps to separate. Foils and dust can be removed by air classification[iv]. Many possibilities are at hand, choosing the appropriate one is a matter of economy and availability. With density separation, heavy plastics, glass, the indium-tin layer and metals like stainless steel and aluminium are removed in one step. Recent developments in electronic sensor based techniques open a range of possibilities for sorting plastics. Properties like color, transparency, shape, type and additive loading are criteria for sorting. Even wood, fiber, tetrapack and some brominated FRs can be detected by Near Infra Red (NIR) radiation. Combined with traditional sorting techniques as sink-float, electrostatic and others,

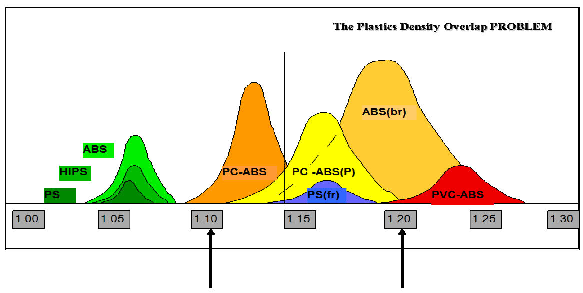

Figure 5 Density distribution most common plastics[v]

grades of acceptable purity can be produced. Separation tests have been performed with a selected batch of black particles from back covers with known properties with an x-ray sensor separator. In this particular case a complication is caused by the black colour of the plastics, which cannot be identified by Near Infra Red. A Near Infra Red sensor sorter, however, is a versatile tool for coloured plastics which can be equipped with one single lane or 2 lanes to sort 2 different coloured fractions. The preset library can recognize the full content of the input mix qualitatively. 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).

An additional test run was made with an x-ray sensor based sorter. Black plastic particles are labelled brominated and non-brominated (Figure 4). The results of the separation represent the number of particles in the accepted and rejected fraction. The threshold in this case is 1% bromine in plastic.

Collection and interpretation of the data offer a strategy for separation. It appears from analyses that plastics can contain BFRs or not or may contain PFRs offering a perfect set for separation. The sequence is determined partly by economic requirements.

5 Where to Go?

The studies undertaken have the objective to recycle more plastic materials with a better quality than present operations. Critical parameters are the final quality of the recyclate and the miscibility with virgin polymers. Numerous tests are necessary for finding out the influence of recycled materials on the final properties. A complication can be the interaction between bromine, antimony and phosphorus present which once mixed can cause lower physical properties of the plastics. What is often seen is the application of recycled plastics in less critical parts. The mixing of virgin with recycled plastics is now at a ratio of 95 to 5 or more. The first objective is to increase the share of recyclate. The second purpose is to produce plastic parts for more demanding applications.

Since separation is never perfect, the produced fractions of plastics do not have the optimal quality that virgin plastics have. Therefore they are mixed with virgin plastics in low ratios to dilute the contaminant in the recycled plastic as well. The authors have developed a miscibility preference scheme for mixing.

Figure 3 shows the influence of small quantities (yellow or ochre) of plastics of semi-pure separated batches into virgin stock. For recycled plastic material after shredding and separation the procedure is to mix recycled (e.g. impure PS) with virgin PS at a ratio of e.g. 10% to 90%, causing the simultaneous dilution of contaminants in recycled PS (e.g. PC-ABS) from assumed 1% to 0.1%[1]. It is evident that improved grades of recycled PS allow a larger share in the virgin stock. The miscibility chart shows that most of the plastics with their contaminants in LCDs are in the yellow or ochre range and not harmful to final quality. Additional testing is planned to define the real quality in the range of mixing 1-3 up to 10% recycled PS (including the contamination) with virgin for each individual plastic (Figure 3).

6 Conclusions

The recycling rate of plastics from WEEE (Waste from Electrical and Electronic Equipment) is still very low. Recyclers are faced with issues such as scale of economy, the lack of identification and sorting techniques and the lack of information of the used plastics and flame retardants. Mixing virgin plastics with recycled fractions has a risk; contaminants with bad compatibility may be introduced, the table shows 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 it would have been the case with mixed WEEE as input (a similar case is found with 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 back covers (BC) is a first step in is setting up a 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.

Although it introduces additional costs, the study shows that the main plastics found in the back covers - HIPS, ABS (w/o Br-FR), PC/ABS and HIPS/PPE (with P-FR) can be closed loop recycled if disassembled and processed separately[vi]. The study presented here has searched for a full mechanical solution.

Depending on the quality of the identification and separation techniques it should be possible to obtain acceptable grades. Additional work to define the reachable quality after recycling and to identify the

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[1] 0.1% is often taken as the threshold value for "being free of" a certain contaminant

limitations due to lower physical properties is required and planned.

7 Acknowledgement

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