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Polymer Degradation and Stability 88 (2005) 35–40
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Waste electrical and electronic equipment plastics with brominated flame retardants – from legislation to separate treatment – thermal processes

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Received 5 December 2003; accepted 30 March 2004

Abstract

Bromine is used as the building block for some of the most effective flame retarding agents available to the plastics industry today. Brominated flame retardants (BFRs) are used to protect against the risk of accidental fires in a wide range of electrical and electronic equipment (EEE). It is the industry's responsibility to come up with solutions to handle the waste plastics in an environmental manner in order to comply with the WEEE directive. In this context, EBFRIP, the European Brominated Flame Retardant Industry Group, is committed to sharing its knowledge regarding opportunities in handling plastic waste containing BFRs.

Keywords: Brominated flame retardants; Electrical and electronic equipment; Waste of electrical and electronic equipment; European Brominated Flame Retardant Industry Group

1. Emerging legislative picture for Europe

The recycling of WEEE foreseen in the new EU Directive on the waste of electrical and electronic equipment (WEEE Directive) is based on the experience of a few European Countries, where organisations managing voluntary take back systems on behalf of the EEE producers have been responsible for the collection and recycling of the WEEE. In order to comply with this directive, the existing national associations managing the WEEE take-back systems have set up a WEEE Executing Forum. This Forum, founded in April 2002, today includes associations from 6 countries: Austria, Belgium, The Netherlands, Norway, Sweden and Switzerland. The Dutch association has taken the lead in the European forum. This directive, which is currently been transposed into national legislation, contain a number of prescriptive requirements such as collection per capita, treatment standards and recovery targets. During the last couple of years these countries have already established individual targets rating from 4 to 8 kg WEEE per inhabitant per year. The targets set by the Directive can easily be met by recycling metal, glass and other materials, and therefore the plastic parts of the WEEE will not be an immediate issue in the coming years. However plastic treatment will be encouraged as a consequence of the implementation of both the landfill directive (ban on dumping high calorific valued waste-plastics) and the incineration directive, which encourages handling (incineration) high calorific waste for energy recovery.

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0141-3910/$ - see front matter
doi:10.1016/j.polymdegradstab.2004.03.025

2. Current practices

The existing collecting systems in the different countries deal with the E&E Equipment once it has become waste. This is done via local municipal depots with the support of the original electro manufacturers (OEMs), who in many countries are already responsible for the collection of the WEEE. The equipment is manually dismantled: glass and large parts are separated. Those components which can be of potential hazard are separated as well. Plastics are very often shredded with metal to recover the metal itself. A plastics waste stream which includes metals like copper (up to 8%) represents the feed stream for the different thermal processes. These processes can be a preferable recovery route when mechanical recycling turns out to be impractical.

As long as legislation is not in place, the industry will look for the cheapest solution. Landfill still represents the cheapest solution in many EU member states. More than 90% of the waste stream is landfilled as landfilling is the cheapest option currently available (prices vary from 50 to130 Euro). Replacing fuel in cement kiln processes with waste can be an additional available option. However a large part of the E&E waste from household waste ends up in household waste incinerators.

During the dismantling process printed wiring boards are manually separated and shredded, as they contain valuable precious metals A metal smelter like Boliden, in Sweden, has restrictions regarding the treatment of material containing substances like PCB, Hg, Be. Furthermore penalties have to be paid for excess contents of substances like chlorine and mercury (need for extra handling), alumina (extra slag losses), antimony (too much of it causes process problems) etc. Boliden [1] has carried out some full scale trials with E&E plastic waste. Because of PXDD/F and other emissions many smelters have installed and adapted gas-cleaning devices to keep emissions of dioxins well below European emission limits (<0.1 ng TCDD/m3N). As metal values in the products from these gas-cleaning units are sufficiently important, it becomes attractive to recycle them internally, and therefore landfilling is minimal. These trials show that it is possible to treat this plastics waste from the local communities as replacement of fuel. Finally the trials clearly demonstrate that Brominated flame retardants do not increase the dioxin/furan emissions, if industrial processes are carried out with the appropriate technical and hygiene standards The Rönnskär Smelter recycles more than 35,000 tonnes of electrical scrap per year, containing base and precious metals and other substances needed in electronics. Boliden has checked the stack emissions, slags, heavy metal and polybrominateddiphenylethers (PBDEs) in worker's blood, as well as emission deposition around the plant and technicians came to the conclusion that electronic scrap can be handled on a large scale without leading to any environmental and health and safety problems.

Another metal smelter using large quantities of precious material is Umicore. Umicore [2] treats 250,000 ton/year in their metal smelter plants. Typical materials are TV's, video's, desktops, laptops, servers and mobile phones. The printed circuit boards contained in mobile phones represent from 2% up to 30% of a mobile phone weight. Umicore thinks that out of a 75% recycling target, 10% can be achieved through energy recovery from replacing fuel with plastic, and 65% thanks to a metal recovery process. Since the volumes of printed circuit boards (PCBs) are growing worldwide from 90,000 mtons in 2003 up to 156,000 mtons/y in 2009 the importance of this process will increase in time. This process offers many advantages: the recovery rate for metals is as high as 98%, which is the highest possible recovery rate in any thermal process; in this process antimony, used as synergist to BFR's in most of the electrical and electronic (E&E) plastic in concentrations of 4%, is recovered (this is not possible in other thermal processes).

An eco efficiency study carried out by APME in Belgium shows that metal smelter provides the highest recovery rate for handling mobile phones, without high dismantling costs.

3. Potential solutions

New technologies for handling plastics from E&E waste already exist. These basic technologies are used in commercial installations for plastics coming from the packaging waste. This waste does not contain high amounts of heavy metals or halogens. Therefore these processes need to be upgraded for the E&E waste.

3.1. Feedstock recycling

According to an economic evaluation carried out by Jung [3] from the Belgian University ULB Brussels Belgium, the potential energy value of polymers is nearly 40 MJ/kg which corresponds to €80/mton (at €2/GJ). This study compares all thermal processes and shows that the transformation of plastics into fuel or gas through feedstock recycling results in a very high yield in terms of energy and end material. It is also a particularly clean process, with emissions close to zero.

For plastic waste from E&E, energy recovery in cement kilns or in the steel industry can be a possible option. An alternative one consists in pelletizing the mix in order for it to be gasified, but the preparation costs are relatively high. A clean alternative consists in producing solid, liquid and gaseous fuels by pyrolysis.

The solid fuel could be upgraded by mechanical separation of metals and minerals in order to produce a cheap feedstock for a classical gasifier. A lot of waste streams contain wood, mixed plastics with halogens and metals. Incineration of this contaminated waste could be difficult. However, in this case, pyrolysis is an attractive alternative. During pyrolysis, all the metals will be recovered (and separated) in the char. However during the pyrolysis there are interactions between the halogens, lignin and the metals. Selected additions during pyrolysis can entrap components such as chlorine and bromine and heavy metals. If metals or calcium carbonate are present in the waste, bromine and chlorine are selectively captured by these products. The main advantage of pyrolysis over direct combustion in a waste-to energy unit is that the volume of gases produced is greatly reduced. This leads to a significant reduction in the complexity of the exhaust gas purification system. Moreover, pyrolysis of waste containing plastics could be performed with less charge preparation, so that minerals and metals are easily separated during the solid fuel conditioning and less ash is produced.

What is exactly a pyrolysis process? Pyrolysis is a pretreatment of waste at moderate temperature (450–750 °C) in the absence of oxygen. The decomposition of the contained organic matter leads to the formation of gaseous and solid phases. These phases have a homogeneous composition which enables their thermal energy recovery to be performed easily and in better environmental conditions than in the case of direct incineration. The pyrolysis technique adds value to the heat content of waste by producing a stable storable solid fuel and an excess of gas to be burned. Pyrolysis furnaces can be sized for variable tonnage. Current trend seems to fit a scale from 2 to 6 mton/h per unit corresponding to a capacity between 15,000 and 50,000 mton/year. On the other hand, small pyrolysis furnaces from 1 to 2t/h (8000 to 15,000 mton/y) can be decentralised to reach local waste elimination. After pyrolysis, both solid and gaseous phases have to be valorised. There are different Furnace technologies, such as moving bed and fluidised bed. The furnaces can be classified as follows:

- with indirect heating by fuel, electricity or fumes (pyrolysis)
- with direct heating by the gases produced by total or partial combustion of the pyrolytic gases and/or solid (gasification).

The residence time lies generally between 30 and 60 min (rotating kiln) or up to a few hours for a fixed bed. These technologies are economically well suited for a decentralised treatment of the waste (small units where waste is dismantled locally) which it is generated at rather small scale.

3.2. Haloclean project

In view of the recycling requirements of the WEEE directive, which will be implemented by Summer 2004, a technology for the bromine contained in electronic devices is required. To this end a European project with 10 European partners from industries, universities and research centres has developed a process called "Haloclean" pyrolysis procedure. The purpose of the Haloclean pyrolysis process [4] is to separate brominated additives from inert and valuable materials in electronic scrap. This process is based on a dual staged pyrolysis which takes place in a plant situated in Forschungszentrum Karlsruhe Germany. A dual-stage thermal chemical treatment pilot plant of two gas tight rotary kilns has been developed to transform halogen containing materials like WEEE into "clean" fuels and residues for noble metal recovery. The temperature has been varied between 250 °C and 450 °C. The residence time varied between one and four hours. The bromine content of all products was determined in relation to the different temperatures. The bromine components in the pyrolysis oil were investigated. The objective of the project includes bromine recovery and production of oil, which is "bromine free". Next year this process will be carried out for six months as a marketing trial in Germany next to a dismantling company for further practical evaluation of its results.

A pilot installation using printed circuit boards from PC's as input with a gold content of 300 g/t and a 5% bromine content from brominated flame retardants has given the following results. The pyrolysis products, oil and residue, were analysed and components of the pyrolysis oil were found to be mainly phenol. The content of phenol and substituted phenols was up to 80%. But also brominated compounds were found in the oil, mostly being characterised as bromophenol and dibromophenol. Since the bromine content after the second step was still too high to use the pyrolysis oil in further chemical processes like methanol synthesis of phenol recovery, a post-treatment with e.g. polypropylene is necessary. From the pyrolysis residue, it could be shown that after the two pyrolysis steps approximately 45% of the material remained in the residue, regardless of the process temperature or process time. The concentration of bromine in the residue was nearly the same then as it was in the feed, whereas the gold concentration was twice as high as in the feed. It could be shown that electronic scrap can be converted into gaseous hydrogen bromide, an almost debrominated oil and a residue that contains the noble metals in a more concentrated form. All three fractions are suitable for further use.

In a pilot trial carried out for the bromine industry (EBFRIP) at Energy Research Centre (ECN) [5,6] in Holland it was shown that it is possible to recover this bromine via thermal processes. The process staged-gasification, comprising pyrolysis (550 °C) and high temperature gasification (>1230 °C) is used as a potential option. In test pilot test runs in the ECN installation "Pyromaat", the HBr was recovered by "wet" alkaline scrubbing of the syngas from the plastic fraction of WEEE and tested successfully by the bromine industry.

3.3. Co-combustion as a potential solution

Today only a small part of plastics from WEEE are treated through incinerators. In Europe, there is sufficient household waste incinerating capacity which could absorb current and future levels of plastic waste. This solution is particularly attractive for areas where distances between production and processing facility are long and a local solution (waste incineration) is needed.

Incineration tests and combustion studies have demonstrated that waste from E&E equipment can be safely added to today's municipal solid waste (MSW) to generate energy in an environmentally sound manner. Pilot trials co-combustion FZK-APME-EBFRIP [7–9].

In order to determine whether co-combustion with MSW is a viable option for end-of-life treatment of BFRs containing EEE waste, tests have been carried out, such as the co-combustion of E&E equipment with MSW at a pilot plant (TAMARA) at the Forschungszentrum Karlsruhe (FZK) in Germany. Amounts of up to 20%.wt. of EEE plastic waste have been added to MSW to explore under extreme conditions. The incineration parameters were investigated with respect to combustion efficiency, halogen content, and emissions of organo-halogen compounds. The experiments have demonstrated that amounts up to 3 wt.% of plastic waste from EEE can be safely added to today's MSW. The formation of PBDD/F or so called dioxins and furans, is not altered by the presence of the bromine-containing waste and remains well within emission standards in these processes. The report again confirmed that controlled MSW combustion serves as a "dioxin sink" with a destruction efficiency of >95% (Fig. 1).

The effect of increasing levels of bromine on the combustion process was investigated as well. In addition to analyzing dioxin/furan emissions, the positive effect of bromine on metal volatilization and the reuse of slag for road construction and the potential for recovering and recycling the bromine were evaluated. In line with earlier studies it was shown that the volatilization of heavy metals, such as Cu, Zn, Sb, Sn, is increased substantially by the presence of chlorine and bromine. The metals are transferred out of the fuel bed to the fly ashes, where they can be recovered. The slag is being cleaned up from metals and can be re-used in road construction. The heavy metals are being concentrated in the fly ashes and can be disposed of properly. Using suitable wet scrubbing systems, it is technically feasible to recycle the bromine contained in WEEE from the combustion gases. If we can recover bromine, bromine can then be used to produce different types of commercial bromine-based products such as bromine itself, hydrogen bromide, or sodium bromide.

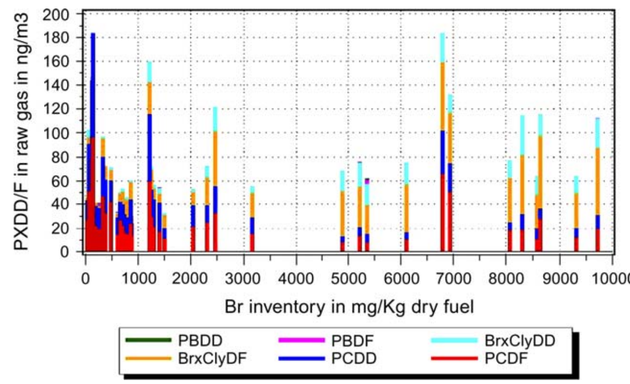

Fig. 1. Bromine inventory in mg/kg dry fuel.

Emission measurements confirming earlier tests, showed that the addition of BFR-containing WEEE did not increase the total level of halogenated dioxins/furans produced. An increase of bromine in the fuel led to an increased formation of mixed halogenated PXDF/Ds. Purely brominated congeners were rarely found, the majority of mixed halogenated congeners contained 1 or 2 bromine atoms only. Overall, the total PXDF/D level was not affected.

3.4. Co-combustion and corrosion, a study related to HBr and free bromine: [10]

There is a general perception that plastics from WEEE are added to modern household waste incinerators can contribute to additional corrosion. A corrosion study was initiated by EBFRIP at TNO and AKZO Nobel Engineering in Holland to evaluate the effects of HBr in the incinerator. Levels of bromine in the plastic waste stream going to energy recovery can easily increase by a factor of 10 to 20 without any additional adverse effects occurring in the equipment. Plastics with BFR's currently form an average 0.35% of the waste stream going to household waste incinerators. If BFR plastics do not exceed 3% of the total weight (which is 10 to 15 times more than the present situation), there is no increased corrosion of the energy recovery equipment (this percentage taking into account a substantial safety margin). The main reason is that all bromine in the feed is transformed into HBr (Hydrobromic acid) and not into bromine. The presence of sulphur in the feed prevents the presence of free bromine at these levels.

Given the presence of other potential corrosive materials like hydrochloric acid and the comparatively low levels of bromine (up to 100 times lower than chlorine) in this waste stream, it was important to find out up to what level plastics containing BFRs could be added to a feedstock recycling or an energy recovery facility without causing additional equipment corrosion. The study came to the conclusion that the presence of bromine in plastics (as a flame retardant) does not adversely affect energy recovery equipment of household waste incinerators.

From an energy recovery point of view, sufficient capacity exists to handle all plastics from WEEE FR plastics. In Germany, more than 60 modern incinerators exist, with a capacity of more than 13 million ton/y while only 37,000 tons of flame retarded plastic waste are produced every year. In general the existing installed capacity is within a ratio of 100 to 1400 times more household waste produced compared to FR plastics waste produced. This means in general there is more than enough capacity today for adding up to 3% plastics containing 2–3% bromine and being within the safety margin of corrosion (Fig. 2).

3.5. Halogen removal step for blast furnace as an option

Although the metal industry is running some pilot trials, the E&E plastics industry hasn't initiated any trials. If trials were conducted, they would first be treated with a pyrolysis process or other HCl/HBr removing process and as such a coke or other fuel is produced.

3.6. New advanced technology

Processes like solvolysis or supercritical water oxidation are potential alternatives for the future if these processes can be scaled up to larger units before they become economically viable. Depending upon the definitions of what is considered as contributing to the recycling targets, and on cost, new technologies could become preferred processes.

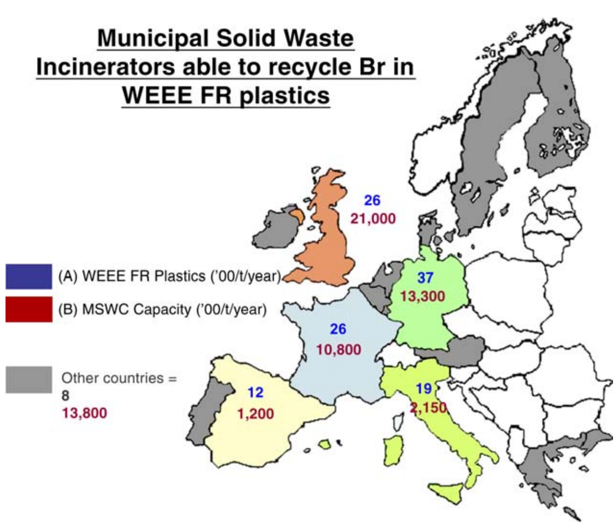

Fig. 2. Municipal solid waste incinerators able to recycle Br in WEEE FR plastics.

4. Future trends

A new trend will only make fast progress if the WEEE directive is in place plus new higher targets for recycling rates will be defined.

While a wide variety of options could potentially develop, from dumping in landfill to high tech Haloclean process) sound economics and political acceptance of a process are key determinant factors for which solutions will be favoured in the future.

Today's political pressure to opt for only environmentally sound options may shift to a need for greater eco-efficiency.

The advantages for energy potential from plastics waste providing a 15% reduction in coal Imports and a 20% reduction of Greenhouse gases, should be recognised by the European Commission. Energy efficiency and the security of energy supply are firmly on the political agenda. If we follow last year's Commission white paper on energy efficiency, the European Parliament in March 2003 adopted a resolution outlining the need to develop legislation addressing the objective of overall energy saving. In its Green Paper on security of supply the Commission emphasised the European Union's long term strategy to ensure "the uninterrupted physical availability of energy products on the market, at a price which is affordable for all consumers (private and industrial), while respecting environmental concerns and looking towards sustainable development." In order to achieve this, all potential energy sources should be examined to enable a balanced and sustainable energy policy. A waste material with the high energy value of plastic must be considered within the framework of this policy. The starting point for consideration should be that plastics are almost all derived from oil, a combustible raw material, which is already used to generate power in the EU.

Plastic recycling is a growing industry and the figures discussed here refer only to that portion of plastic waste that cannot be sensibly recycled. The diversion of waste with a high calorific value to landfill represents resource inefficiency at a time when efficient resource use is a high priority in the EU. It is estimated that, if all of Europe's plastic waste which it is not feasible to recycle were turned to energy, it would be equivalent to at least 17 million tons of coal. This represents 15% of the total EU coal imports and approximately 5% of EU energy needs for power generation. Replacing fuel by plastics reduces the global warming and reducing overall greenhouse gas CO_2 emissions as per the Kyoto objectives. An equivalent of around 10 Million tons of CO_2 or the equivalent of over 2 million cars is circulating per year.

Plastics can also be co-incinerated with other combustible products from the waste stream, which will give even greater contributions to the reduction of greenhouse gases through prevention of the emission of methane gas from landfill.

As soon as the WEEE Directive is implemented in Europe, most of the countries will reach the 4 kg target. Looking at 2008–2010, if higher values are set for recycling targets only then will solutions such as feedstock recycling and other processes become important for plastics.

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