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Review

Sound management of brominated flame retarded (BFR) plastics from electronic wastes: State of the art and options in Nigeria

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ABSTRACT

Management of flame retarded plastics from waste electrical and electronic equipment (WEEE) has been posing a major challenge to waste management experts because of the potential environmental contamination issues especially the formation of polybrominated-dioxins and -furans (PBDD/F) during processing. In Nigeria, large quantities of electronic waste (e-waste) are currently being managed—a significant quantity of which is imported illegally as secondhand electronics. As much as 75% of these illegal imports are never reused but are rather discarded. These waste electronic devices are mostly older equipment that contains brominated flame retardants (BFRs) such as penta-brominated diphenyl ethers (PBDEs), and polybrominated biphenyls (PBBs) which are presently banned in Europe under the EU WEEE and RoHS Directives. Risk assessment studies found both to be persistent, bio-accumulative and toxic. The present management practices for waste plastics from WEEE in Nigeria, such as open burning and disposal at open dumps, creates potential for serious environmental pollution. This paper reviews the options in the environmentally sound management of waste plastics from electronic wastes. Options available include mechanical recycling, reprocessing into chemicals (chemical feedstock recycling) and energy recovery. The Creasolv® and Centrevap® processes, which are the outcome of the extensive research at achieving sound management of waste plastics from WEEE in Europe, are also reviewed. These are solvent-based methods of removing BFRs and they presently offer the best commercial and environmental option in the sound management of waste BFR-containing plastics. Because these developments have not been commercialized, WEEE and WEEE plastics are still being exported to developing countries. The industrial application of these processes and the development of eco-friendlier alternative flame retardants will help assure sound management of WEEE plastics.

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1. Introduction

Fires are a common cause of harm to people and property around the world. Fires are also sources of pollution and generate a host of acute and chronic pollutants including acid gases and persistent organic pollutants. Estimates by the International Association for the Study of Insurance Economics in Geneva shows that the cost of fire is around 1% of the gross domestic product (GDP) of most advanced countries (Dawson et al., 2004). Components of electrical and electronic equipment (EEE) such as the housing units or enclosures and printed wiring board (PWB) contain flame retarded resins, which are effective in delaying the ignition and spread of fire, in turn saving lives and the destruction of property. In our present society, the potential for fires in EEE is significant and more likely due to the increasing use of EEE in the homes (including children's rooms), schools and commercial/industrial settings. However, concerns over the materials used in flame retardancy especially in electrical and electronic manufacturing industries have been increasing.

There is much concern over the disposal of plastic waste from waste electrical and electronic equipment, WEEE, since about 11% of the plastic material is flame retarded and some other applications in the manufacture of EEE (for example, PWB production) make use of brominated organic compounds (Vehlow et al., 2003). Large quantities of WEEE are being managed around the globe. For example, quantities of WEEE generated are estimated at 2.26 million tonnes in 2001 for US, 6 million tonnes in 1998 for the EU, 1.1 million tonnes in 2005 for Germany, 6.77 million tonnes in 2004 for Korea and 1.5 million tonnes for France (Lee et al., 2007; Kang and Schoenung, 2005; Cui and Forssberg, 2003; Schlummer et al., 2007; Nnorom and Osibanjo, 2008).

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) as all flame retardants (FRs), acts to decrease the risk of fire by increasing the fire resistance of the materials in which they are applied. However, due to their potential to form polybrominated dioxins and furans (PBDD/F) during processing, the use of certain BFRs is being restricted especially in Europe. For example, the European Union's Directive on the Restriction of the use of Certain Hazardous Substances (RoHS Directive) limits the use of polybrominated biphenyl (PBB) and polybrominated diphenyl ethers (PBDEs) in EEE. In fact, the recycling of waste plastics is considered a very important route in meeting with the requirements of the European Union's Waste of Electric and Electronic Equipment (WEEE) Directive. Among the different groups of BFRs, the most common are PBDEs, PBB, tetrabromobisphenol-A (TBBPA), and hexabromocyclododecane (HBCD). Plastics are low-cost materials widely used because they can be easily processed into light but durable materials with low thermal and electrical conductivity. However together with the strong increase in plastic consumption more and more plastic waste is accumulated that poses serious problems to the environment due to the unpleasant aspect of BFRs and their long persistence in the environment (Brebu et al., 2004). In fact, the last decade has witnessed an increase in concern over the environmental impact and toxicology of certain FRs.

There is concern that the present low-end management activities of plastics from WEEE in Nigeria, may result in high levels of emissions of BFRs (and PBDEs in particular) into the environment. Studies aimed at investigating the levels of PBDE and related pollutants in animal/plant tissues samples and environmental samples in Nigeria are scarce. This is probably as a result of cost implications, the complicated nature of the analysis and the state-of-the-art equipments (GC–MS) required. In this paper, we review the management practices for WEEE plastics in Nigeria and the options available in achieving sound management practices.

2. Waste electrical and electronic equipment

2.1. E-waste: definition

Electronic waste (e-waste) or waste electrical and electronic equipment (WEEE) is unwanted EEE that are obsolete, at the end of their lives or that have been discarded by their original users. In most cases, WEEE consists of more or less durable products used for data processing, telecommunications or entertainment in households and commercial places. This includes all components, sub-assemblies and consumables, which are part of the product at the time of discarding. Examples include refrigerators, air conditioners, cell phones, personal stereos, and computers, which have been discarded by their users.

Plepys (2002) noted that e-waste is (presently) the most obvious environmental problem and the infrastructure to manage it properly is still poorly developed. The recycling and reuse of post consumer electronics is technologically problematic, is not feasible economically, or simply lacks an appropriate physical infrastructure, which will require huge investments to build.

2.2. Plastics in WEEE

Plastics are the materials of choice because they make it possible to balance modern day needs with environmental concerns (Bhaskar et al., 2002). Plastics make a significant contribution to the properties of EEE offering a balance of properties that no other class of material can match (Dawson et al., 2004). Plastics in EEE

Table 1
Polymer resin types used in selected EEE

EEE type	Resin type
Televisions	HIPS, ABS, PPE, PVC, PC
Computers	ABS, HIPS, PPO, PPE, PVC, PC/ABS
Miscellaneous (fax, telephone, refrigerator)	HIPS, ABS, PVC, PPE, PC/ABS, PC

Adapted from Kang and Schoenung (2005). PPO – polyphenylene oxide.

are used for insulation, noise reduction, sealing, housing, interior structural parts, functional parts, interior electronic components among other uses. They are low-cost materials and are widely used because they can be easily processed into light but durable materials with low thermal and electrical conductivity (Brebu et al., 2004). They are design-friendly, durable, lightweight, and affordable. For example, the use of plastics helped in the lowering of raw material use and overall cost in mobile phone manufacturing that resulted in the drop of the weight of a mobile phone from 500 g to less than 100 g over the last decade (Fisher et al., 2004).

WEEE items contain a complex mix of materials including a range of different, often incompatible, polymer types. This complicates the task of recycling WEEE (Freegard et al., 2006). In general, about 8–12 different basic types of plastic are found in EoL consumer electronics. The major resins in the electronic industry are high-impact polystyrene, HIPS (56 wt.%), acrylonitrile butadiene styrene, ABS (20 wt.%) and polyphenylene ether PPE (11 wt.%). The remaining 13 wt.% is made of other resins such as polyvinyl chloride (PVC), poly carbonate (PC), polyphenylene oxide (PPO) (Kang and Schoenung, 2005). The resins commonly used in selected EEE are given in Table 1.

However, there is concern over waste plastics from WEEE because of composition and quantities. WEEE plastics constitute up to 30% of WEEE (11–30%) (Vehlow et al., 2003; Fisher et al., 2004; Schlummer et al., 2006; Delgado et al., 2007). The amount of plastics in electronics varies substantially by product and ranges from very small amounts to more than half the material composition of some mobile phones (Fisher et al., 2004). For instance, ICT and consumer equipment contain less than 30% plastic whereas electronic toys may contain more than 70% plastic (Delgado et al., 2007). As a result, large quantities of waste plastics are presently being managed around the world. In Nigeria, for example, the 60,000 tonnes of secondhand EEE imported annually (Nnorom and Osibanjo, 2008), may contain as much as 18,000 tonnes of plastic. Estimates have it that up to 75% of these imported devices are unusable, and are discarded before any form of reuse takes place. These wastes are managed using inappropriate methods, and this creates the potential for environmental contamination.

2.3. Flame retarded plastics

2.3.1. Mode of action of flame retardants

Flame retardants acts to decrease the risk of fire, thereby increasing the fire resistance of the materials in which they are applied. They are a large group of substances based on organic and inorganic halogen, phosphorus, nitrogen and mineral containing compounds with strongly differing individual sets of properties. Brominated FRs are prevalent among other types of FRs because lower quantities of these compounds ensure the highest fire safety (Drohmann et al., 2004). BFRs contain up to 50–95 wt.% of bromine, and can be separated into aromatic, aliphatic and cyclo-aliphatics (Tohka and Zevenhoven, 2002). FRs provide up to 15 times more available escape time from fires. Damage to materials is considerably reduced as typically 50% less material is consumed by fire when FRs are used (Cahill, 2005). Presently, there are more than 175 chemicals classified as FRs (Alaee et al., 2003). BFR formulations are applied annually to over 2.5 million tonnes of polymers (Law et al., 2003).

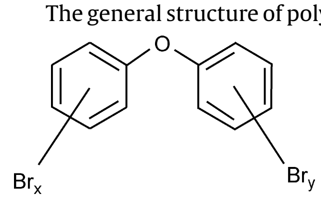
2.3.2. Brominated flame retardants

2.3.2.1. A review of PBDEs. The choice of which FR to use depends on the application, resin, fire safety standards that must be met, cost implications, and recyclability (Dawson et al., 2004). A BFR may be defined as "*a non-organo phosphorus organic compound where one or more hydrogen atoms are been replaced by bromine*". (Tohka and Zevenhoven, 2002). BFRs act primarily by a chemical interference with the radical chain mechanism taking place in the gas phase during combustion. High-energy OH^- and H^+ radicals formed during combustion are removed by bromine released from the FRs (Tohka and Zevenhoven, 2002).

BFRs are used preferentially because;

(i) of their number (about 75 diverse and different chemicals with various properties are available, though only about 30–40 are widely used in EEE);
(ii) of their efficiency in flame retardation;
(iii) of their universal applicability;
(iv) for some polymers, they are the only viable method of achieving the required flammability standards with some plastic resins;
(v) there is a lot of information on these compounds; and
(vi) they can easily be recycled (De Boer, 2004; Dawson et al., 2004).

The general structure of poly brominated diphenyl ether (PBDE).



PBDEs are produced by bromination of diphenyl ether in the presence of a Friedel-Craft catalyst (i.e. $AlCl_3$) in a solvent such as dibromomethane. Diphenyl ether molecules contain 10 hydrogen atoms, any of which can be exchanged with Br, resulting in 209 possible congeners. PBDEs are produced at three different degrees of bromination to give Penta-BDE, Octa-BDE and Deca-BDE corresponding to the average bromine content of the various compounds (Bocio et al., 2003). PBDEs are used as additives in polymeric materials ranging from polyurethane foam cushioning to PWBs and casing (housing) for electronics. The use of PBDEs has risen sharply over the last 20 years. It is estimated that about 40% of the world total consumption of PBDEs occurs in North America (Manchester-Neesvig et al., 2001).

The relatively weak carbon–bromine bond is thermally labile, this then led to the thermal energy release of bromine radicals. These radicals intercept carbon radicals to decrease flame while simultaneously reducing heat and carbon monoxide production. PBDEs are very hydrophobic (log K_{ow} range 4–10). They are also very resistant to degradation. The water solubility and vapor pressure of PBDEs decrease with increasing degree of bromination (WHO/IPCS, 1994).

2.3.2.2. Plastic types containing BFRs. Flame retardants are present in housing and parts of EEE items that are exposed to high internal heat (e.g. TVs, laser printers), connection cables and PWBs. BFRs are likely to be added (ca. 10 wt.%) to styrenic plastics including HIPS, ABS, polystyrene (PS) and ABS/polycarbonate components. In this group of resins, Deca-BDE is mostly used especially in the housing of EEE. For PC/ABS, phosphorus-based FRs are used (Freegard et al., 2006; Delgado et al., 2007). BFRs are less likely to be present

Table 2
Flame retardant content of polymer resins in selected EEE

EEE item (casing)	Most common polymer type	Other polymers	Flame retardant wt.% (bromine)
TV casing	PS	HIPS	1.10
VDU casing	ABS	PVC, PS, PPE	3.90
Telephone casing	ABS	PS, POM, PC/ABS	0.00
Mixed IT	PC/ABS	PS, PC	1.40
Photocopier[a]	PC/ABS	PC/ABS, PS	0.80
Washing machine[a]	PP	ABS, POM, PA66	0.02
Vacuum cleaner	ABS	PC, PS	0.00

[a] Parts: data adapted from Delgado et al. (2007): POM – polyacetal (polyoxymethylene); PVC – polyvinyl chloride; PA – polyamide.

in polypropylene components. However, there is a growing market for BFRs for use in polypropylene in EEE (Freegard et al., 2006). BFRs are more likely to be present in small brown goods, IT equipment and small domestic appliances than in large white goods. Many of these smaller items are made in Asia where the use of brominated flame retardants is growing.

About 90% of TBBPA is used as a reactive intermediate in the production of epoxy and polycarbonate resins. The main application of epoxy resins is in the manufacturing of printed circuit boards that contain approximately 20% bromine (Alaee et al., 2003). TBBPA is also used as reactive FR in ABS plastics used in TVs, computers, mobile phones, fax machine, etc. Hexabromocyclododecane (HBCD) is used in HIPS and PS foam for construction application and rarely in EEE (Freegard et al., 2006). Deca-BDE is used in styrenes (ABS, HIPS, etc.), polyolefins (PP, PE), polyester and polyamide (nylon).

2.3.2.3. BFRs used in EEE. The major polymer resins of selected EEE and their BFR content as weight percent of bromine are given in Table 2. The main polymers collected from WEEE plastics in Europe are PS and ABS from inner shelving and liner of cold appliances; ABS, PC/ABS and HIPS from consumer equipment and ICT equipment such as TV sets and computers (especially monitors) and mobile phones; and polyurethane (PU) from large household appliances insulation (Delgado et al., 2007).

The major BFRs currently being used are TBBPA (121,000 tonnes) and PBDEs (67,000 tonnes) (BSEF, 2000; Brown et al., 2004). TBBPA is the primary FR used in electronic circuit boards and is covalently bound to the resin. In this application, it is used as a reactive intermediate in the production of flame retarded epoxy resins used in PWB. A secondary use of TBBPA is as an additive FR in ABS plastic housing (Monchamp, 2000). Deca bromodiphenyl ether (Deca-BDE) and TBBPA account for approximately 50% of the worlds usage of BFRs. TBBPA is the most widely used BFR and in 1999, 13,800 tonnes of TBBPA and 8900 tonnes of HBCD were consumed in the European Union (Table 3) (Tohka and Zevenhoven, 2002; BSEF, 2000, http://www.bsef.com). The demand for BFR in 1999 was 204,000 tonnes (BSEF, 2000; Brown et al., 2004). Recent studies indicated Br of up to 1.7–5.2% and Cl of up to 0.1–4.4% in WEEE plastics (plastic housing shredder residue), reflecting the use of high levels of halogen-based FRs in EEE (Schlummer et al., 2007).

2.3.2.4. Market data. In 1992, about 150,000 tonnes of BFRs were produced (WHO/IPCS, 1994; Brown et al., 2004) and an estimated 56% of BFR productions in 1999 were used in EEE (BSEF, 2000). The total worldwide market demand for PBDEs was about 67,440 tonnes in 2001, including 56,150 tonnes of Deca-BDE (DBDE), 7500 tonnes of Penta-BDE (PeBDE) and about 3790 tonnes of Octa-BDE (OBDE) (Table 3). The eight worldwide (largest) manufacturers of PBDEs are located in the Netherlands, France, Great Britain, Israel, Japan, and the United States (Siddiqi et al., 2003). Market share of the major

Table 3
Global consumption of selected BFRs for 1999 and 2001

Name	America	Europe	Asia	Others[a]	Total
1999[b]					
TBBPA	21600	13800	85900	–	121300
HBCD	3100	8900	3900	–	15900
DBDE	24300	7500	23000	–	54800
OBDE	1375	450	2000	–	3825
PeBDE	8290	210	–	–	8500
2001[c]					
DBDE	24500	7600	23000	1050	56150
OBDE	1500	610	1500	180	3790
PeBDE	7100	150	150	100	7500

[a] Others implies other parts of the world.
[b] Data adapted from LCSP (2005); De Wit (2002); Environment Canada (2004).
[c] Data adapted from Tohka and Zevenhoven (2002).

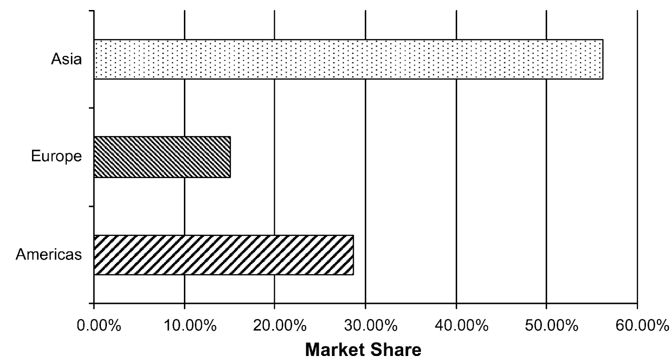


Fig. 1. Market share of the major consumers of BFRs (by region). Data adapted from Tohka and Zevenhoven (2002).

consumers of BFRs (by region) is shown in Fig. 1. The global market demand for BFRs continues to grow substantially. For example the global market demand for BFRs in 1990 was 145,000 tonnes, this grew to over 310,000 tonnes in 2000, which represents a growth of over 100% over the past decade (Alaee et al., 2003). The quantities of BFRs as consumed by Asia, Europe and United States (the major consumers) for 1989, 1994 and 1999 are given in Fig. 2.

2.3.3. Toxic ingredients of WEEE plastics

Elements such as cadmium, lead, nickel, chromium, antimony and barium are found in EEE as part of pigments and stabilizers. BFRs are generally compounded in polymers with antimony trioxide. Antimony is used in the form of Sb_2O_3 as a synergist for BFRs at quantities ranging from 3 to 5% (Delgado et al., 2007). Antimony trioxide does not have flame retarding properties of its own, but is an effective synergist for halogenated FRs. It acts as a catalyst, facilitating the breakdown of halogenated

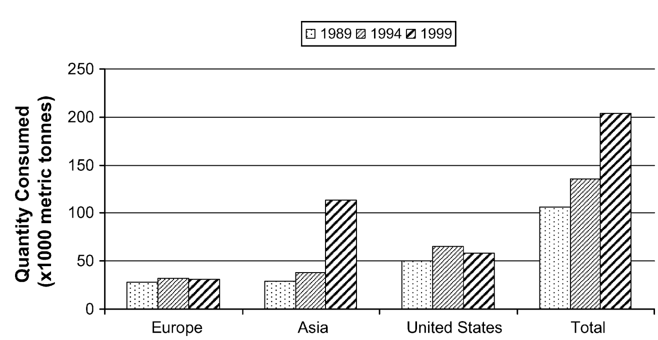


Fig. 2. Global consumption of BFRs for selected countries. Data adapted from Alaee et al., 2003.

Table 4
Concentrations of BFRs reported in WEEE plastics

WEEE-plastic category	BFR type	Concentration	Reference
Waste shredder residue	PBB	50 ppm	Vehlow et al. (2000)
WSR	PBDE	100–20 000 ppm	″
WSR	TBBP-A	100–6000 ppm	″
Waste plastic residue	TBBPA	5428 ppm	Schlummer et al. (2006)
WPR	Octa-BDE	861 ppm	″
WPR	Deca-BDE	1198 ppm	″
WPR	Total Br	7959 ppm	″
WSR	PBDE	800–7400 ppm	Schlummer et al. (2007)
Housing shredder residue	TBBP-A	0.1–1%	″
HSR	Octa-BDE	0.08–0.44%	″
HSR	Br	1.7–5.2%	″
HSR	Cl	0.1–4.4%	″

FRs to active molecules (Freegard et al., 2006). WEEE plastics have been shown to contain in some cases high levels of heavy metals. For example, our earlier study indicated metal concentrations of up to 340 mg Pb/kg (mean 58.3 mgPb/kg); 1005 mg Cd/kg (69.9 mg Cd/kg), and 11,000 mg Ni/kg (432 mg Ni/kg) (Nnorom and Osibanjo, in press). Schlummer et al. (2007) reported Sn and Ni with levels of up to 1500 ppm; and Cd, Cr, and Cu in the range 200–900 ppm. The summary of BFRs and halogens obtained in WEEE plastics is presented in Table 4. Lower concentrations of PBDE was reported by Schlummer et al. (2007) in 2007 (800–7400 ppm) as compared to the very high concentrations reported by Vehlow et al. (2000) in 2000 (100–20,000 ppm). Similarly, Schlummer et al. (2007) were unable to detect PBB in waste shredder residues as compared to the results of Vehlow et al. (2000) (Table 4), indicating that these BFRs have either been phased out or that lower quantities are still in use. Unfortunately, WEEE plastics presently being managed in Nigeria are products much older than the EU WEEE and RoHS Directives. Similarly, a significant quantity of 'used' electronics presently at their end-of-life are imported from the US – 45% of imports are from US – where BFRs are still used in large quantities in the EEE manufacturing sector (BAN, 2005; Nnorom and Osibanjo, 2008). Concerns over the management of BFR-containing wastes, especially during thermal treatment include the following:

- The potential for the emission of ozone depleting substances (ODS) such as methyl bromide;
- The possible formation of brominated analogues of dioxin and furans; and
- The formation of bromine containing flue gases such as HBr, which are very corrosive (Tohka and Zevenhoven, 2002).

Bromine, chlorine and nitrogen from polymers or the FRs in WEEE give rise to the formation of acid or toxic gases such as HCl, HBr, HCN, and NH_3 during thermal decomposition.

The fate of PBDEs in the environment is not fully understood. Because PBDE are seeded into, but not covalently bound into the polymer matrix. Over time, they diffuse out of the polymer matrix and become air borne and widely dispersed (Siddiqi et al., 2003).

2.4. Concern over WEEE plastics

2.4.1. BFRs in humans and the environment

It is not yet fully understood how humans are exposed to the BFRs (especially PBDEs), but ingestion (food and dust) and inhalation seem to be important routes of exposure. BFRs have been reported in air, water, sewage sludge, sediments and biota. The solubility of BFR in water is very low. For example, the extremely low solubility of for example Deca-BDE in water (<0.1 mg/L) explains why there is very limited uptake of Deca-BDE in fish (De Boer, 2004). BFRs especially PBDEs have the potential to form brominated dioxins and furans (PBDD/F) during the processing of waste plastics containing FRs (Schlummer et al., 2006). The less brominated congeners of PBDE are highly bio-accumulative and bio-magnify in human, fish and other animal adipose tissues. PBDEs have been found in human blood, serum, adipose tissue, breast milk, placental tissue and in the brain (Sellström et al., 1993; Patterson et al., 2000; Siddiqi et al., 2003; Meironyté et al., 1999; Norén and Meironyté, 2000). It has also been observed in humans occupationally exposed to PBDE (Thuresson et al., 2005) and in humans exposed to background concentrations (Schecter et al., 2006; Thuresson et al., 2005). Law et al. (2003) reviewed the available data for PBDEs and other flame retardants in wildlife.

Among all BFR products, PBDEs and PBB are of particular concern with respect to their impact on human health (Brown et al., 2004). PBDEs are known to be environmentally persistent with a propensity for bioaccumulation in eco-system, and are suspected carcinogens, neurotoxins and endocrine disruptors (De Wit, 2002; Brown et al., 2004). They are believed to cause liver tumors, neurodevelopmental and thyroid dysfunctions (Siddiqi et al., 2003). De Boer (2004) observed that 'more information on the toxicology and behavior of BFRs is needed to enable better estimation of the risks associated with the environmental occurrences of BFRs'.

Studies in Sweden that examined human milk samples collected over the period of about thirty years showed that the concentration of some BFRs i.e. PBDEs have increased exponential, with the concentration doubling approximately every 5 years during that period (Meironyté et al., 1999; Norén and Meironyté, 2000). Brown et al. (2004) observed that this trend coincided with the increased production and use of BFRs. In fact, in 1999, approximately 98% of the global demand for PBDE was used in North America (Renner, 2000; Siddiqi et al., 2003). Due to high consumption of PBDEs in North America, it is not surprising that PBDEs have been found in the fish of all the great lakes (Zhu and Hites, 2004; Song et al., 2005; Luross et al., 2002). For instance, Asplund et al. (1999) reported that Lake Michigan fish contain six times more PBDE than Baltic salmon.

2.4.2. Sources to humans and environmental

Studies have indicated the presence of sometimes high levels of additives and contaminants in plastics including heavy metals. Over the last few decades, there have been indications of increased concentrations of FRs in the environment and humans, although their levels are still lower than those of PCBs and DDT (Verslycke et al., 2005). For example, the widespread use of PBDEs since the 1970s has resulted in PBDEs being found in measurable amounts throughout the environment (Song et al., 2005). BFRs and PBDEs in particular could be released into the environment from WEEE plastics at the following stages:

1. during manufacturing and polymer processing operations;
2. during the service life of the electronic products (especially for additive FRs, such as PBDEs); and,
3. during the end-of-life management activities (mechanical processing, disposal, open burning/incineration, etc.).

A typical example is the study at WEEE processing plants in Sweden by Sjödin et al. (1999). The study found that workers at WEEE dismantling plants, where dust containing flame retardants is spread in the air, had 70 times the level of one form of flame retardant compared with a control group of hospital cleaners (Sjödin et al., 1999). However, when conventional occupation hygiene techniques were introduced at the dismantling plants exposure levels dropped substantially.

Hypothetically, some sources of BFR into the environment include:

1. *Combustion sources*: Combustion of WEEE plastic leads to the formation of toxic brominated by-product can be formed in most combustion systems. These include waste incineration such as municipal solid waste and inappropriate management practices such as open burning.
2. *Chemical sources/degradation products*: Commercial PBDEs are manufactured by bromination of diphenyl ethers resulting in a mixture of diphenyl ethers containing tetra-, penta-, hepta-, octa-, and deca-, congeners in various percentages. Deca and octa brominated congeners have lower bio-accumulative and biological activities. Nevertheless, they remain a source of public health concern in that they can degrade to less brominated, more toxic congeners in the environment after release.
3. *Reservoir sources*: Material which contain BFRs/PBDEs (or previously formed dioxins) like PWB and plastics act as reservoir for these chemical in the environment. Such materials have the potential for redistributing and circulating these compounds into the environment. For example, the dismantling and grinding of waste plastics for recovery may result in the release of BFRs. The various activities during the informal crude recycling activities for e-scrap may also contribute to BFR emissions.

High PBDE concentrations in house dust are attributed to the numerous emission sources within the indoor environment. Similarly, buildings with poor ventilation can also achieve high concentration as degassed PBDEs accumulate in the indoor environment. Humans are exposed to such house dust through direct inhalation of re-suspended dust and dermal exposure on the body (Jones-Otazo et al., 2005) and also through ingestion of contaminated food (Bocio et al., 2003). Concerns over the toxicity of BFRs especially with the increasing human and animal exposure to this toxin have been increasing.

3. Management of e-waste in Nigeria

3.1. E-waste importation statistics in Nigeria

The developing countries are facing a fast increasing load of WEEE originating from local consumption and from illegal importations (BAN/SVTC, 2002; BAN, 2005). The challenges posed by e-waste management in the developing countries have been discussed (Osibanjo and Nnorom, 2007). Series of well-coordinated studies/documentaries have indicated there is an increase in the trans-boundary movement of e-waste from developed into developing countries. For example, a documentary of trans-boundary movement of e-waste into Nigeria coordinated by Basel Action Network (BAN) – *Exporting Reuse and Abuse to Africa* – brought to the fore the level of e-waste dumping in Nigeria. The study observed that an average of 500 containers enter Nigeria through the Lagos ports monthly with each containing about 800 monitors or CPUs. This indicates an average of 400,000 second hand or scrap personal computer CPUs or monitors enters the country monthly through the Lagos ports. This amounts to an annual importation of an estimated 5 million scrap units or 60,000 metric tonnes containing up to 18,000 tonnes of plastic materials (Nnorom and Osibanjo, 2008).

The study also observed that 25–75% of the e-waste exports are unusable junk that are non-functional or un-repairable which amounts to an importation of 15,000–45,000 tonnes of hazardous wastes containing about 1000–3,600 tonnes of lead (Nnorom and Osibanjo, 2008). These unusable devices end up being discarded before any reuse takes place, or are stockpiled in warehouses indefinitely. In Nigeria, there is virtually no capacity for material recovery operations, for example, for Cu, Pb, steel, precious metals, plastics, etc., or collection mechanism for electronic waste for appropriate disposal. Thus, these imported junk EEEs simply become discarded in local dumps. In addition, the local dumps are not sanitary landfills, lined, or monitored and are regularly set afire (BAN, 2005). Currently, exact statistics on the level of e-waste being managed in Nigeria is unavailable. However, the quantities of waste been managed in the country is reduced by the observation that Nigeria has a remarkable capability to accomplish very high skilled repair and refurbishment operations—which are usually carried out by the large number of unemployed graduate engineers.

3.2. Management practices in Nigeria

The phenomenal rate at which the ICT sector is developing poses threats to sustainable development—large amounts of natural resources are involved in the life cycle of ICT products and hazardous wastes are generated (Plepys, 2002). In most developing countries, electronic waste is managed through various low-end means that poses threat to the principles of sustainable development—“development which meets the needs of the present without compromising the ability of future generations to meet their own needs”. The principles of sustainable development came as a result of a report commissioned by the United Nations Commission on Economic Development (UNCED). The report is various known both as the “Brundtland Report” and as ‘Our Common Future’. Sustainability has now been accepted and adopted at an international level as a framework for guiding future development within which, social, economic and environmental goals must be adopted which are consist with each other and mutually attainable. To achieve sustainable development (or sustainable consumption, rather), it has become necessary to adopt a global strategy for sound management of WEEE plastics. This strategy must take into account an integration of economic, environmental, social and technical consideration, especially as it relates to the developing countries. The prevailing management practices for WEEE plastics around the globe has not been sustainable. These valuable ‘wastes’ are often landfilled or incinerated, which results not only in the loss of large quantities of resource, but also in adverse environmental consequences. Unfortunately, neither of these options (landfilling and incineration) is presently in use in Nigeria as there are no functioning landfills of incinerator in the country.

Presently, the management approach to waste plastics from EEE and e-waste in general in Nigeria and most other developing countries, is to burn or bury it. These poor waste management approaches are no longer acceptable internationally. Increasing awareness of environmental issues by the population in most developing countries has resulted in most communities demanding for the adoption of sound waste management practices. Unfortunately, majority of the population and authorities in the developing countries are unaware of the danger associated with the open burning of WEEE plastics and WEEE in general with its cocktail of toxins.

The management of e-waste in Nigeria includes

- *Reuse*: this is a case where the malfunctioning part of the electronic equipment is replaced with new parts of the equipment.
- *Open dumps*: in Nigeria, WEEE plastics and other electronic components are simply disposed into dumpsites, which may or may not be government approved sites for dumping wastes.
- *Unlined landfills*: this is another e-waste management method that is commonly used in Nigeria. In this scenario, the waste materials are buried with municipal solid wastes at unlined landfills usually located few kilometers from the city centers.

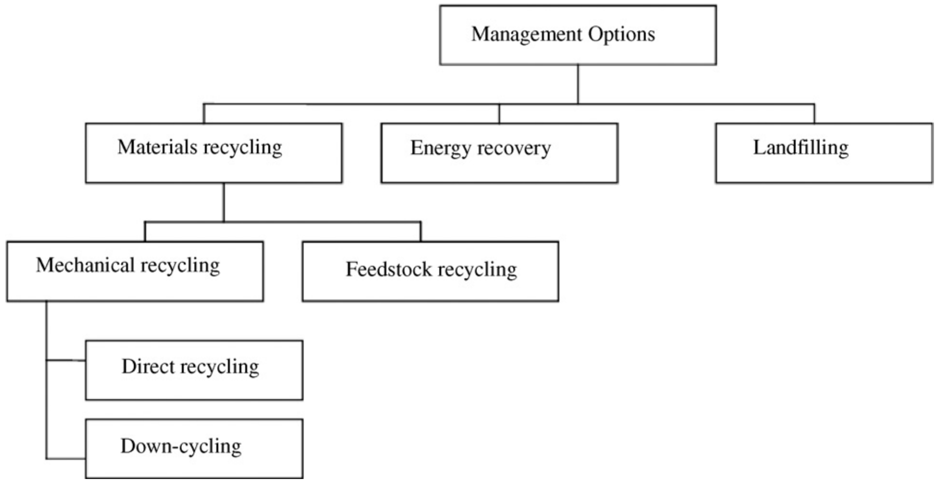


Fig. 3. Management options for WEEE plastics.

- *Open burning*: in this method, e-wastes are burnt as they are dumped in the dumpsites. Electronic markets such as the famous Computer Village and Alaba International Market in Lagos Nigeria, have sites for the open burning of unusable electronic devices, replacement parts/modules and other wastes from repair and refurbishing activities. This method of management is extremely hazardous and has both health and environmental consequences. Wires and cables, as well as other components of EEE, including PWBs and plastic housing/enclosure are routinely burned in the open. This creates the potential for the release of heavy metals and other persistent toxic substances (PTS) such as poly aromatic hydrocarbons (PAHs), poly-chlorinated biphenyls (PCBs), heavy metals, dioxins and furans.

Presently, there is a high level of repair and reuse of EEE in Nigeria. However, the broken/outdated/replaced or unusable components resulting from such reuse activities are rather disposed with municipal solid waste into open dumps. The inappropriate management of WEEE results in the emissions of highly toxic dioxins, furans and polycyclic aromatic hydrocarbons (PAHs), caused by burning PVC plastic and wire insulation; soil and water contamination from chemicals such as: BFRs (used in circuit boards and plastic computer cases, connectors and cables); PCBs (in transformers and capacitors); and lead, mercury, cadmium, zinc, chromium and other heavy metals (in monitors and other devices). Damage to the environment due to poor waste management practices can be avoided by implementing environmentally sensitive waste management techniques, through the principle of the best practicable environmental options; whereby minimization, reuse, recycling, and recovery techniques are employed.

4. Sound management options for BFR-containing plastics

Presently, the options available in the management of WEEE are incineration, landfilling and recycling. Unfortunately, these basic waste management options are presently not applied in WEEE management in most developing countries, including Nigeria. Incineration and landfilling results in the loss of large amounts of scarce resources (especially precious metals) as well as in adverse environmental impacts as a result of emissions and leachates. Considering the large quantities of WEEE being managed at the global level, it has become obvious that sound EoL management of these devices be applied even in the developing countries. The globally recommended option is recycling. Recycling results in both economical and ecological gains, and is in line with the principles of sustainable development. Extensive literature exists on the mechanical and chemical processing of WEEE (Cui and Forssberg, 2003; Zhang and Forssberg, 1997, 1998; Schlummer and Mäurer, 2006). The European Waste Electrical and Electronic Equipment (WEEE) Directive has been effective in encouraging appropriate management of e-waste. The Directive sets recovery targets of between 60 and 80% and reuse/recycling targets of between 50 and 75% depending on the type of EEE involved. Similarly, the EU RoHS Directive restricts the use of PBB and PBDE in EEE as well as the use of heavy metals such as chromium(VI), lead, and mercury (Riess et al., 2000; Schlummer et al., 2006). Developmental works on thermal treatment of BFR-containing waste streams are getting more important as a result of the EU RoHS Directive. Therefore, in practice, it is anticipated that many countries will adopt policies that will separate all FR plastics prior to recycling or energy recovery in order to maximize the potential value of these materials (Dawson et al., 2004). Waste plastics from EEE that contain BFRs can be managed using the “reduce, reuse, recycle, recovery” concept. Mechanical recycling, feedstock recovery, and energy recovery are options in the environmentally sound management of waste plastics (Fig. 3). Open burning and landfilling are not recommendable options in the consideration of eco-efficient management of waste plastics.

4.1. Reuse options

Various reuse options are available for WEEE plastics containing BFRs. Typical examples are the re-filling and reuse of ink/toner cartridges of printers and copiers. End-of-life EEE can also be reused through the reuse options: repair, refurbish/recondition, and remanufacture (Nnorom et al., 2007). In these applications, the plastic housing units can be reused ‘as is’ after cleaning.

4.2. Material recycling

Several recycling studies have shown that plastics containing specific BFRs can be mechanically recycled (Tange, 2002). WEEE recycling activity was expected to grow by about 18% annually between 1998 and 2007, with over 40 million units of electrical electronic equipments estimated to be recycled in USA by the end of 2007 (Dawson et al., 2004). Plastics can be separated based upon the differences in physical properties such as mass, density, or particle size. Techniques such as sink–float separation, air classification, electrostatic separation and ultrasonic methods take advantage of physical properties in separating plastics into pure streams (Sodhi and Reimer, 2001; Schlummer et al., 2006). Brennan et al. (2002) noted that for high quality recycled polymers to be obtained, efficient separation of waste polymers that are not compatible must be accomplished. Alternatively, incompatible polymers can be separated via the application of special additives such as compatibilizers and impact modifiers (Schlummer et al., 2006).

Special precaution is required in the recycling and energy recovery operations from WEEE plastics. This is because some BFRs form highly toxic brominated dioxins and furans when exposed to thermal stress (Ebert and Bahadir, 2003; Schlummer et al., 2007). Dioxins are also produced within hot shredder/granulation equipment when processing BFR plastics. The smaller the particle size of the plastics, the more dioxins and furans are produced. However, state of the art incinerators with state of the art flue gas cleaning and energy recovery may be one of the safest treatment options beside the Creasolv process.

Studies have shown that plastics containing specific BFRs can be mechanically recycled to meet limits if recycling is done properly. In fact, Drohmann et al. (2004) observed that new plastics containing BFRs have been successfully recycled up to five times whilst meeting required safety and performance standards. There are indications that the presence of BFRs may hinder the reuse of certain recycled plastics. For example, the use of recycled ABS (acrylonitrilebutadiene-styrene) as a blend with PC (polycarbonate) is not possible because the BFR causes the PC to depolymerise, resulting in poor quality of the recyclate (Zhang et al., 2000; Tohka and Zevenhoven, 2002). Studies by Schlummer and Mäurer (2006) using different mixtures of TV sets and PC monitor plastic housings revealed that only 5–20% of the original bromine contents of the waste plastics remained in the recovered fractions, resulting in bromine levels between 0.18 and 1.39%. The study also reported that recycled polymers from fractions rich in high-impact polystyrene (HIPS)-based TV-set casings did not exceed given threshold limits for PBDD/F and Octa-BDE. The recovered plastics exhibited mostly virgin-like mechanical properties, with a yield of 52–63%.

4.3. Feedstock recycling

Feedstock recycling that converts plastics to their original chemical constituents is seen as one of the most valuable options in the treatment of mixed plastic waste from WEEE (Zhang et al., 2000). Pyrolysis is one of the best methods to recover the material and energy from polymer waste, as only 10% of the energy content of the waste plastic is used to convert the scrap into valuable hydrocarbon products (Brebu et al., 2004). From industrial waste incineration, it is known that at high bromine concentrations in the fuel, elementary Br_2 is insufficiently absorbed in wet scrubbing systems if no reducing agent is added to the neutral scrubber (Vehlow et al., 2003).

Steps in feedstock recycling of WEEE plastics as outline by Zhang et al. (2000), and Drohmann and Tange (2000) include the following processes:

1. *Pyrolysis* – the plastic will be converted into hydrocarbon, hydrogen bromide and antimony bromide. This is achieved by breaking down the plastic polymer at high temperature into petrochemical feedstock component from which they originate.
2. *Gasification/incineration* – the hydrocarbons will then be mixed with air and converted into syngas or CO_2, water and heat.
3. The slag from the pyrolysis goes into a molten metal bath where the metals are recovered. The remaining carbon fraction from the plastics is then used to heat the molten metal bath.
4. The hydrogen bromide and flue gas is then neutralized and converted into salt. There is a possibility of producing hydrobromic acid as an end-product.
5. The bromine salts or residues are converted by the bromine industry into bromine products. This closes the bromine loop.

Studies have been carried out to investigate the potential of a sustainable production of bromine. The objective has been to recover bromine from BFR-containing WEEE plastics. In this scenario, the WEEE is sorted and dismantled and the brominated waste plastics co-fed with municipal solid waste either to a pyrolysis unit or to an incinerator unit for syngas generation or energy recovery (Dawson et al., 2004). The resulting flue gas is scrubbed and bromide salts recovered. The bromide salts are then converted to bromine. This is a potentially important step to close the bromine loop as to enable a sustainable production of bromine and to avoid potential releases of bromine containing substances through improper and uncontrolled disposal. The recovered bromine can then be used to produce different types of commercial bromine-based products such as bromine itself, hydrogen bromide or sodium bromide (Drohmann et al., 2004).

Feedstock recycling has more advantages than mechanical recycling or energy recovery, as the energy consumption of the process is very low (only about 10% of the energy content of the waste plastics are used to convert the scrap into petrochemical products) (Bhaskar et al., 2002).

4.4. Energy recovery

Drohmann et al. (2004) reported that incineration tests, pyrolysis and combustion studies have demonstrated that WEEE can be safely added to today's municipal solid waste to generate in an environmentally sound manner, useful energy when incinerating BFR-containing materials. Many electronic products contain small amounts of many different plastics in highly integrated parts, which are difficult to recycle. Instead of investing heavily in mechanical recovering these plastics, it may be better to use them for their energy value by direct combustion, for example, in modern waste-to-energy plants (Fisher et al., 2004). Dodbiba and Fujita (2004) observed that energy recovery is a consumptive recycling process as it turns 'recycled material' into energy rather than into usable material. Usually the waste plastics from WEEE are separated and sorted. This is followed by energy recovery though incineration. The energy content of waste plastics is recovered at temperatures above 1450 °C (Dodbiba and Fujita, 2004). The waste plastics can also be used as fuel sources in smelters and cement kilns.

However, co-incineration of WEEE plastics requires high standards of exhaust cleaning to check environmental pollution. This will require the application of scrubbers and air pollution abatement technologies. The resulting ash will require stabilization/treatment before disposal at a landfill. Incineration with heat recovery in addition to having an excellent capacity of handling waste stream and minimizing landfill space depletion is an attractive process of recovery energy in some countries. For instance, Japan owned 181 large-scale incineration plants that can generate 769 megawatts of electric power in 1998. Moreover, in 1994 USA used 106 large-scale incineration plant to generate >2964 MW of electric power (Chen et al., 2005).

4.5. Landfilling

Landfilling is the least preferred option in achieving eco-efficient management of waste plastics. This is however preferred to the current management practices in Nigeria which include open burning and burial. There is however the possibility for the leaching of contaminants from the landfills to contaminate the soil and ground water. The application of state-of-the-art landfill technology with leachate monitoring (recovery/treatment) system will be required to check pollution.

5. Future perspectives

5.1. Non-halogenated substitutes for PBDE

The concern over fire safety is justified and there is need for the use of FRs to check fire outbreaks. However, there is also the urgent need to introduce a regional/global initiative for the appropriate management of devices containing toxic FRs in order to protect man and the environment. This is particularly important in the developing countries where basic waste management infrastructures are virtually non-existent. Alternatively, less toxic substitutes can be used where possible specifically for goods meant for the developing countries. Regulation in the form of legislation and voluntary Eco labels have been effectively used in electronic waste management. Eco labels applied in the control of use of BFRs include the Nordic Swan, Blue Angel and the European White flower. These prohibit the use of BFRs in various consumer products. Therefore, a combination of regulation, market drivers and consumer pressure has prompted an industry-wide move from halogenated FRs to more environmentally and socially acceptable alternatives, principally non-halogenated.

Halogen-free materials and products are presently commercially available. However, the products are more expensive compared to the BFR-containing products, thereby making the EEEs costlier. These products are now more available in Europe than in the United States as a result of the implementation of the EU WEEE and RoHS Directives. The most cost-effective ways of substituting PBDEs is changing the polymer resin system and using phosphorus-based FRs. Considering the risk of formation of PBDD/F from PBDEs and PBB-type FRs, more and more of the applications of these BFRs are being replaced by TBBPA and other non-halogen FRs (Tohka and Zevenhoven, 2002). The most widely marketed and available non-halogenated alternatives are based on phosphorous compounds such as phosphonates, phosphinates and phosphorous esters. Typical examples of FRs presently in use – that have substituted Deca-BDE – are: resorcinol bis diphenyl phosphate (RDP), bis-phenol-A diphosphate (BPADP), phosphate esters and metal hydroxide (LCSP, 2005).

Although on the face of things the non-halogenated FRs appear to be environmentally more attractive than the halogenated predecessors in that they are not persistent in the environment, they do not appear to accumulate in mammalian tissues or appear to be toxic to human or wildlife, they do have their drawbacks. These include:

1. Limited environmental data is available for many of these new formulations and so their true potential health effects are relatively unknown.
2. They are also less effective than their brominated counterparts and so require far higher loading (40–60% compared with 5–20% for brominated FRs), which can increase their cost (Cahill, 2005).

The above issues have made many producers to be reluctant in abandoning their proven halogenated FR products for such alternatives due to inherent economic risk and uncertainty over performance. However, extensive research is on-going into finding better alternatives. Some of the researches aimed at finding alternatives to BFRs include:

- *Nano-composites* – One such emerging technology is that of nano-composites. These are materials based on layers of silica clay, which are being investigated for their flame retardancy in various widely used polymers and plastics (polyurethane resins for example).
- *Polymer siloxanes* – Another interesting area is research into polymer siloxanes that may have inherent FR properties. This of course would be ideal as it could potentially eliminate the need for FR addition, avoiding the problem altogether. It is hoped that these technologies as they become industrially feasible, will gradually replace the BFRs (Cahill, 2005).

5.2. The creasolv®[2] and centrevap® processes

The Creasolv and Centrevap are the recent outcomes of extensive research at achieving sound management of waste BFR-containing plastics from WEEE in Europe. They are solvent-based methods of removing BFRs and presently, they offer the best commercial and environmental option in the sound management of waste BFR-containing plastics. Creasolv was initially created by the Fraunhofer Group (Fraunhofer IVV in Germany) but was extensively evaluated by the United Kingdom's Waste & Resources Action Programme (WRAP) (http://www.wrap.org.uk;[3] Freegard et al., 2006). The Creasolv process was reported to be able to remove most BFR types from styrenic WEEE polymers including the PDDD/F (dioxins and furans). Centrevap was solely developed by WRAP and tested at a technical scale. Trial studies by WRAP revealed that while Creasolv is more successful at removing BFR from WEEE polymers, both processes provide financially viable alternatives to landfill and incineration as options in the management of WEEE plastics (Coakley et al., 2007;BP and R, 2007; Freegard et al., 2006; http://www.wrap.org.uk).

The studies indicates that the Centrevap does not remove the same level of BFR content as Creasolv, but was successful at removing other submicron insoluble impurities from a wide range of polymer types including non-polymeric materials and contaminants such as dust and fillers from the polymer solution. Hence, the combination of both processes may present the possibilities of combining the best features of both processes in order to produce a process that can remove not only the majority of BFRs but also the majority of other fine particulate contaminants. In this case, Creasolv would be applied in BFR removal, while the Centrevap will be applied in the removal of other insoluble impurities.

The advantages of these processes includes the following:

- They can turn mixed plastics waste into polymers such as ABS and HIPS,
- Flame retardants, dioxins and furans can be reduced by 70–99%, whereas 98–99% are the usual removal rates.
- The polymer product has properties similar to virgin polymers, and,
- Both processes consume less than 20% of the primary energy used in the virgin polymer production process (Cahill, 2005; Coakley et al., 2007; http://www.wrap.org.uk).

However, both processes are currently on a laboratory scale, and there is the urgent need to commercialize these processes. Experts indicate that these BFR polymer treatment processes could be deployed commercially in as little as two to four years. Creasolv process for extraction of BFRs from WEEE polymers has potential to

[2] ® Creasolv and Centrevap are Registered Trade Names.
[3] WRAP Project PLA-037.

be commercially viable in the UK context at a throughput of 10,000 tonne/year (Coakley et al., 2007; Freegard et al., 2006).

Environmental impact comparisons of these processes and other options in the management of WEEE plastics indicated that both processes have a net environmental gain across all environmental impact categories and are environmentally beneficial compared to landfill, incineration with energy recovery, export of waste plastics and feedstock recycling options. Unfortunately, because these developments have not been commercialized, WEEE and WEEE plastics are still being exported to developing countries.

6. Conclusion

Mechanized recycling and feedstock recycling are closer to the ideal management option for WEEE plastics in that they produce materials that can be reused. These are the option available in achieving sound management of WEEE plastics in Nigeria. However, technologies for the application of these are presently unavailable in Nigeria and there is the issue of removing the BFRs from the recycled plastics. In the short-term WEEE plastics can be applied in incineration and energy recovery in facilities such as the cement kiln with the installation of appropriate pollution abatement techniques. At the global level, the commercialization of the Creasolv and Centrevap processes will be required in the eco-efficient recovery of BFR-free plastics.

There is need for a shift by both regulatory agencies and private industries toward limiting the manufacturing and use of certain BFRs, especially the PBDEs. The Nigerian government should be commended for introducing a framework aimed at regulating the importation of 'used' EEE and in organizing stakeholder's workshop to create awareness on the e-waste crisis in the country in December 2007. A ban on the importation of used EEE older than 3 years and the implementation of an initiative by the government to confirm the functionality of EEE before importation would reduce the amount of unusable 'used' EEE being imported. However, much is still desired especially in introducing legislation to assure sound management of the various components of WEEE. Nigeria and other developing countries currently grasping with the problem of e-waste management should adopt frameworks that are in line with the systems adopted in other countries such as Taiwan, in order to ensure the appropriate management of e-waste (through reuse and recycling) and assure sustainable consumption. The innovations introduced in WEEE management in Europe should be replicated around the world. Several smelters in Europe have developed recycling processes for WEEE components, to recover the metals, plastics and energy. Usually, the plastic wastes provide energy to the smelter process and also acts as reducing agents (Drohmann et al., 2004).

It has been observed that efficient collection is perhaps the most significant hurdle to the economic recycling of plastics from EoL electronics—not technology (which has been developed), not contamination (which can be managed by today's technology), and not the intrinsic value of recovered plastics (Fisher et al., 2004; Dillon, 2001). There is therefore a need for an urgent intervention through waste reduction and reuse strategies in the developing countries in order to mitigate the negative environmental impacts of the present management practices for end-of-life EEE and WEEE plastics in particular.

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