特约专栏

The Development of Sustainable Fire Retardant Materials

T Richard Hull

（Centre for Fire and Hazard Science，University of Central Lancashire，Preston，PR1 2HE，UK）

Abstract：Over the last 40 years the demands for less flammable synthetic polymers have changed from ignition suppression to lower smoke and toxicity，to "halogen-free". Over the next decade sustainable fire retarded materials will be required. Meeting all the requirements for sustainability is a complex challenge，requiring a full understanding of the product's life cycle，with particular emphasis on raw materials selection and end-of-life processing. A brief description of the unexpected problems of halogenated flame retardants is presented. This is followed by a discussion on the sustainability requirements of fire safe materials，and the critical areas of the product's life cycle. Finally，some recent examples of sustainable developments of fire safe materials are presented.

Key words：fire retardant；low smoke and toxicity；biobased polymers；sustainable

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可持续性阻燃材料的研究进展

T Richard Hull

（中央兰开夏大学 火灾和灾害科学中心，英国 普雷斯顿）

摘　要：在过去的 40 年，难燃的合成聚合物对"无卤阻燃"的要求已经从抑燃变为降低烟和毒性。在未来十年，对具有可持续性的阻燃材料将有一定需求。满足可持续发展的要求是一项复杂的挑战，涉及到全面了解产品的生命周期，尤其要注重原材料的选择和报废处理。本文将介绍卤系阻燃剂不曾考量到的问题，并对防火材料的可持续发展要求和产品生命周期的关键领域进行讨论，最后，将介绍一些最近的可持续发展防火材料的实例。

关键词：阻燃剂；低烟低毒；生物基高分子；可持续的

1　Introduction

The widespread use of synthetic polymers in Europe and the U. S. led to an increase in fires and fire fatalities. In the 1970s halogenated flame retardants started to be used to make products less flammable. While halogen-based fire retardants are very effective in reducing fire risk，i. e.，the probability of occurrence of a fire，they show a high fire hazard，that is，the probability of producing toxic，corrosive，obscuring smokes or when involved in a developed fire，and the fire is too big to be extinguished. Halogenated flame retardants act by releasing hydrogen bromide (HBr) or hydrogen chloride (HCl) which interferes with the gas phase free radical reactions，typically producing more carbon monoxide，smoke and other products of incomplete combustion. The dense smoke obscures escape routes and contaminates property，while the resultant halogen acids are highly corrosive-significantly increasing the costs of unwanted fires. The threat to people，structures，and goods involved in the fire

may discourage the use of these fire retardants，despite their versatility and ease of incorporation.

In contrast，modern fire retardants reduce fuel release to the gas phase，often by formation of a protective barrier layer，which acts as a radiation shield，and inhibits the flow of fuel and oxygen. Such barriers have been used in intumescent systems，where gas is released within the molten polymer，causing significant swelling，and so increasing the effectiveness of the thermal barrier. While the formulations required for char promotion and intumescence are often specific to a particular polymer，halogenated flame retardants tend to be non-specific in their action，so one flame retardant can be incorporated into many polymers. This has increased their popularity amongst plastic compounders and product manufacturers，who do not have the expertise to develop such formulations. The ease of incorporation of halogenated FRs is matched by their ease of release，particularly at elevated temperatures，such as in televisions and other electronics，or during breakdown of the polymer，during use，or at end-of-life，and leaching (especially in foam or textile products)，allowing significant quantities to escape into the environment. In addition，losses of brominated flame retardants have been reported during manufacture and end-of-life processing.

Many halogenated flame retardants are persistent and bioaccumulative，and are now ubiquitous throughout the built

and natural environment[1-2]. In 2010 a group of over 100 eminent environmental scientists signed the San Antonio statement on halogenated flame retardants[4] condemning their continued use and requesting urgent remedial action. These persistent organic pollutants (POPs) take several years to break down in the environment, are bioaccumulative (they accumulate in plants and animals, becoming more concentrated as they move up the food chain), and are toxic. All of the 22 chemicals currently designated as POPs by the Stockholm Convention on POPs[5] are halogenated organics. Studies have shown higher levels of halogenated flame retardants in house dust in California and the UK, where the most stringent furniture flammability regulations operate[6]; at lower levels they have been detected in flora and fauna, from the developed world to the pristine Himalayan and Arctic regions. Very high levels have been detected in the Pearl River delta in southern China, where many electronic recycling activities are based. The most detailed studies of health effects have concentrated on polybromodiphenylethers (PBDEs), proven endocrine disruptors in both experimental animals and humans. Elevated levels have been found in human blood serum in Californian children at 5 times the US average, and 10 ~ 100 times the European and Mexican average. These elevated levels have been linked to infertility, and hyperactivity and attention disorders in children etc.

Several of the most widely used halogenated flame retardants, including PBDEs and polybromobiphenyls (PBBs), have already been banned in Europe and the US. Tris-dibromopropyl phosphate (TDBPP) was banned by the U. S. Consumer Product Safety Commission in 1977[7]. In some cases they have been replaced by similar organohalogen compounds with unknown eco- and human toxicity. The release of flame retardant from a product, during, or at the end of life, its stability and transport through the environment, uptake and bioaccumulation by humans and other living organisms, and the resultant toxic effects, are very difficult to predict; it took nearly 40 years of exposure to PBDEs to accumulate sufficient evidence for action to be taken, and it may take as long for environmental levels to fall below safe limits.

The market for fire retardants continues to grow, but there are very clear drivers in Europe, Japan, and the U. S. for development of sustainable products. In Europe, proposals to identify the presence of brominated flame retardants using "eco-labels" will provide consumers with additional information, and raise awareness of the potential hazards of certain materials. Inevitably, manufacturers will want to harmonise their global product range (so are less likely to offer a choice of products with and without halogenated flame retardants); to demonstrate their "green" credentials, are therefore more likely to opt for halogen-free solutions. All the major personal computer manufacturers are committed to producing products free of halogenated flame retardants.

Fire causes £ 1. 7 billion of direct losses per year in the UK, or overall, 0. 7% of GDP[8], while fire safety measures represent 2. 5% of the cost of a new building. Fires represent a complex sequence of chemical reactions, which are not well understood and, as synthetic polymers replace wood and wool, we are surrounded by more flammable materials. Recently, pressure has mounted to make buildings more energy efficient, and therefore traditional building materials such as brick, stone and timber are being replaced by more flammable alternatives, such as polystyrene or polyurethane foams. The manufacturing process of synthetic polymers often allows the incorporation of fire retardant additives, while the porosity of most naturally occurring polymeric materials allows incorporation of fire retardants.

2　Classification of fire retardants

Fire retardants have been classified in many ways: place of action-gas or condensed phase; mode of action-physical or chemical; chemical nature of agent-halogen, phosphorus, metal hydroxide or carbonate, etc.; means of incorporation of agent-additive or reactive (i. e. bound onto the polymer chain). Unfortunately, these classifications cannot be unambiguously applied to particular fire retardants-for example, the most widely used fire retardant, aluminium hydroxide releases water, so acting in the gas phase, but in doing so absorbs heat and leaves a protective residue in the condensed phase[9]. It is useful to distinguish within the broadest category: fire retardants include any material which reduces the flammability of the polymer; flame retardants inhibit the gas phase free radical reactions responsible for flaming combustion[10], although less careful authors seem to use the terms interchangeably. Figure 1 illustrates how the major fire retardant strategies could be subdivided. Fire retardants have evolved over the last four decades in order to meet the demands of industry and regulators, from halogen based flame inhibitors to cleaner, char promoters, resulting in less smoke and toxic gas emissions. While halogenated flame retardants continue to be used in a wide range of existing products, very little new work has been published on them. Instead, research has been heavily focussed on finding suitable halogen-free replacement fire retardants, indicating that the industry has indeed recognised the need for change, in the face of increasing pressure, predominantly resulting from environmental concerns.

3　Drivers in fire retardant development

The history of fire retardants goes back to Egyptian times when solutions of alum (hydrated potassium aluminium sulphate ($KAl(SO_4)_2 \cdot 12H_2O$)) were used to treat timber. Gay-Lussac protected theatre fabrics from fire by treatment with mixtures of ammonium phosphate, ammonium chloride and borax which formed a glassy layer on heating[11]. However, the main driver for development came with the growth of the plastics industries and the resultant widespread
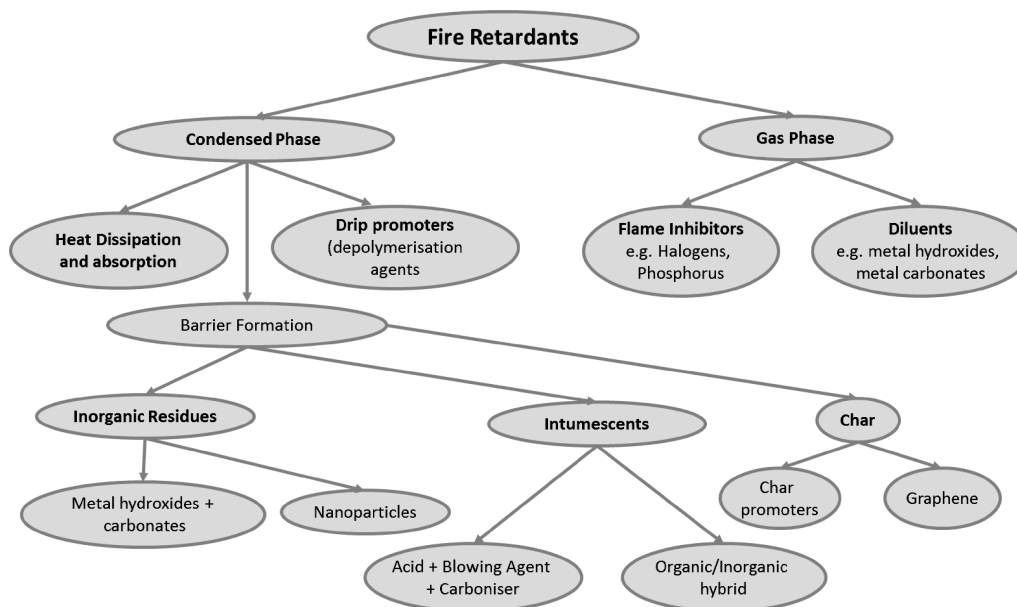
Fig. 1　Classification of fire retardant strategies

distribution of synthetic polymers across the anthrosphere. From the 1960s to 1970s fires became more common and more severe. Anecdotally, fire fighters reported a change from fires with limited visibility, to those with almost no visibility due to the dense smoke, primarily resulting from newly available low-cost polyurethane foam furniture. In the 1960-70s this was accompanied by a shift from skin burns to a predominance of harm caused by toxic gas inhalation. The increasing severity of the fire problem led to the development from empirical tests for flammability to engineering models capable of providing data on burning behaviour. This was accompanied by a shift in emphasis from ignitability to peak heat release rate. The physical fire model chosen to quantify this behaviour, the cone calorimeter, is only capable of replicating penetrative burning into a sample, not surface spread of flame.

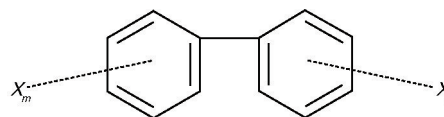Table 1　Drivers in fire retardant development during different periods

Decade	Event	Demand
1960s	Widespread availability of cheap polymer products-more serious fires	Reduced ignitability
1970s	Smoke much worse (PU foam furniture and halogenated flame retardants)	Reduced smoke
1980~1990s	Development of Cone Calorimeter (and emphasis on peak heat release rate, rather than ignitability). increase in deaths from smoke inhalation	Reduced peak heat release / Reduced fire toxicity
2000s	Halogen FRs found across the ecosystem	Halogen-free FRs
2010s	Climate change and other environmental concerns become mainstream	Sustainable FRs

4　Halogenated flame retardants

4.1 History

In order to understand the sustainability requirements of future fire retardant systems, it is necessary to understand the development, and problems caused by halogenated flame retardants. One of the main reasons for using organohalogens as fire retardants is their low reactivity and high thermal and oxidative stability. Unfortunately, this is also the reason for their persistence in the environment 40 years after their production ceased. The first halogenated fire retardants were the polychlorinated biphenyls (PCBs) (Figure 2), which were widely used as fire retardants before their very high toxicity was discovered in the 1960s[11]. Unfortunately, as fire retardants, PCBs were replaced by chemically analogous polybrominated biphenyls (PBBs) (also Figure 2) without any prior toxicity evaluation. PBBs have a structure similar to PCBs,

their use as flame-retardant additives for plastics begins in the 1970s as mixture of many different congeners. In 1973, 200 ~400 hundred kilograms of PBB-based fire retardant were accidentally mixed with livestock feed that was distributed to farms in West Central Michigan, United States[12-13]. Millions of domestic animals consumed this feed, and 85% of Michigan's population received some exposure to PBBs, inadvertently alerting the authorities to their toxicity. The immune systems of exposed farmers showed significant abnormalities, and the production of PBBs was rapidly discontinued.

Fig. 2　Generic Polyhalobiphenyl (X = Cl for PCB or Br for PBB)

4.2 Current use

The withdrawal of PCBs and PBBs led to a proliferation of different halogenated fire retardants. There are more than 40 brominated flame retardants in current use[14] (reference 14 contains a useful summary of which halogenated flame retardants are in current use and provides clear guidance for their nomenclature) and an additional number of chlorinated FRs[15]. These are used by simple melt blending with the polymer (additive fire retardants) or by incorporation into the polymer chain during polymerisation (reactive fire retardants). Some additive fire retardants are small molecules while others are oligomers or polymers. From a health and environmental perspective, small molecules will be easiest to release from the polymer matrix (by evaporation, leaching, end-of-life processing etc.). Oligomeric or polymeric additives may be released during end-of-life processes, while reactive FRs, which have been successfully incorporated into the polymer are most likely to be problematic during burning or incineration processes.

Of the small molecule BFRs, the PBDEs have been widely used in acrylonitrile-butadiene-styrene (ABS), high impact polystyrene (HIPS), polyvinyl chloride (PVC), polybutylene terephthalate (PBT), polyethylene (PE), polypropylene (PP) and flexible polyurethane (PU) foam, and cited in a large number of environmental and toxicological studies. Typically products are PentaBDE, OctaBDE and DecaBDE, although in practice each contains mixtures of the 209 possible congeners of polybrominateddiphenyl ethers (Figure 3).
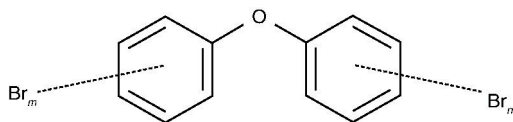
Fig. 3 Generic polybrominateddiphenyl ethers (where for example, $m + n = 8$ for the major OctaBDE congeners).

Toxicity and environmental concerns led to submission of a proposal to European Union to ban the use of PBDEs in 1989 (111-4301-89-EN Draft). The proposal was rejected on the basis of recommendations issued by a thorough debate between scientists, regulators, producers, and users of fire retardants, stating that banning would involve an unacceptable fire risk since alternatives were not available to replace halogenated flame retardants with comparable effectiveness. Ever since, fire retardant research has focused on the development of non-halogenated replacements for halogenated flame retardants. PentaBDE and OctaBDE have now been withdrawn from use in the US and European Union, while DecaBDE is under increasing pressure and has been voluntarily withdrawn from many applications. Alternatives are being introduced, often showing structural similarity to PBDEs. For example, one group of alternatives being recommended for facile substitution are the polybromodiphenylethanes(PBDPEs) (Figure 4).
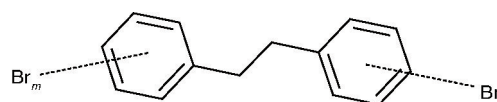
Fig. 4 Generic Polybromodiphenylethane

Hexabromocyclododecane (HBCDD) (Figure 5) has been widely used, particularly in very large quantities in polystyrene foam for building insulation etc. , PP and textile applications. Bromination of cyclododeca-1, 5, 9-trienes theoretically results in 16 stereoisomers, 6 enantiomeric pairs and 4 meso forms, since each bromine can occupy axial or equatorial positions, which will then affect the puckering of the ring . The first three pairs of enantiomers, the α -, β -, and γ -HBCDD stereoisomers, dominate in technical products[16]. The isomers have different environmental and toxicological properties, and biological and thermal isomerisation have been reported[17-18], thus the ratio of molecular forms identified in the ecosystem may not correspond to those produced industrially. HBCDD has been listed as a persistent organic pollutant by the Stockholm Convention and is now in the process of being eliminated from use.
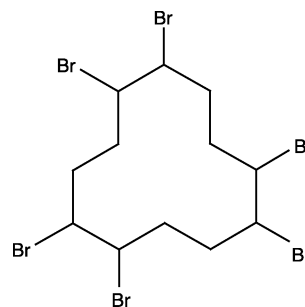
Fig. 5 Hexabromocyclododecane (HBCDD)

TetrabromobisphenolA (TBBPA) (Figure 6) is widely used in epoxy resins and polycarbonate where it is copolymerised into the polymer structure. Once bound into the polymer, it is much less likely to be released until the polymer itself is broken down. It is also used as an additive flame retardant in ABS and HIPS[19], where losses to the environment may occur more readily. It is less stable than PBDEs or HBCDD and appears less persistent in the natural environment. It is also ubiquitous throughout the anthropogenic and natural environments[1], and has been identified in particularly high concentrations in Asia, near sites of manufacture and recycling of polymeric products[20].
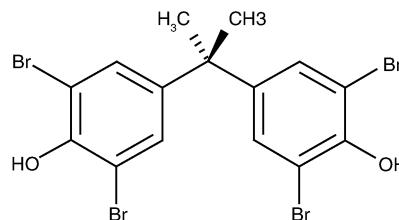
Fig. 6 Tetrabromobisphenol A

4. 3　Novel, polymeric brominated flame retardants

A small number of polymeric brominated flame retardants[21] have recently been developed. They are considered better since they are too large to penetrate cell membranes. They have also very low solubility in water, so that, once incorporated into the polymer matrix, leaching is unlikely. Examples include polybrominated acrylate, brominated epoxy polymers, and brominated polystyrene. They are used as flame retardants in a range of polymers including polystyrene and copolymers, polycarbonates, polyesters, polybutylene terephthalate and polyamides.

According to a survey carried out by SRI Consulting[22], the total market for flame retardants in the United States, Europe and Asia amounted to about 1. 8 million metric tons (Figure 7). It is split roughly equally between Europe, America and Asia, with halogenated flame retardants and antimony oxide comprising around 37. 5%.
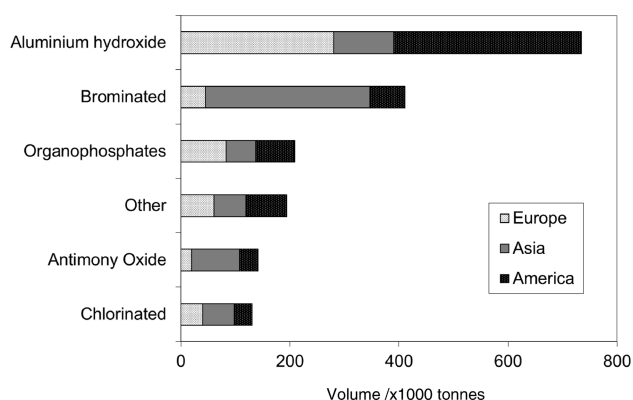

Fig. 7　Volume consumption of flame retardants in the USA, Europe and Asia[22]

In terms of tonnage, brominated FRs are second only to the inorganic compounds such as aluminium hydroxide (ATH), although this is primarily due to the large use of these compounds in Asia. In terms of value, the global market is worth between $ 4. 2-4. 25 billion, of which brominated flame retardants have the greatest value (Figure 8). 44% by value of flame retardants are consumed in Asia, with 67% globally being halogenated or antimony oxide.
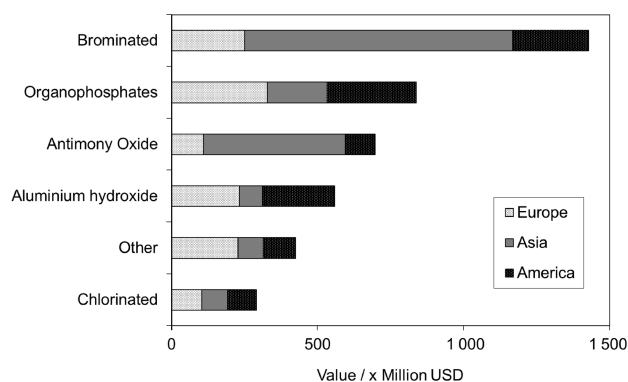

Fig. 8　Value of flame retardants worldwide[22]

5　Fire safety considerations for sustainable fire retardant development

5. 1　Fire toxicity

Gas phase flame retardants interfere with the free radical reactions responsible for flaming combustion. This results in incomplete oxidation of vapour phase fuel molecules, leading to higher yields of all products of incomplete combustion. These are all more toxic than the cleaner products of complete combustion (carbon dioxide and water), and include carbon monoxide, hydrogen cyanide, hydrocarbons, oxygenated organics (including organoirritants, such as acrolein and formaldehyde) and larger cyclic molecules such as polycyclic aromatic hydrocarbons and soot particulates. Fire toxicity increases as combustion becomes more incomplete, which can arise from chemical quenching (for example by gas phase flame retardants), insufficient heat (for example during smouldering), or when the fire becomes ventilation controlled, and there is insufficient oxygen for complete combustion[23-24].

Thus in a fire, gas phase flame retardants will act to increase the gas phase products of incomplete combustion, and hence the yields of toxic gases and smoke, when compared to either the non-flame retarded polymer, or the same polymer incorporating a condensed phase fire retardant, which increases the char yield. As most fire deaths, and most fire injuries result from toxic gas inhalation, the use of gas phase flame retardants is a compromise, between supressing ignition and increasing the fire toxicity (or decreasing the fire risk at the expense of increasing the fire hazard). Recently it has been shown that the phosphorus flame retardants which act in the gas phase have a smaller influence on CO and HCN yields than the corresponding brominated flame retardants in industry standard formulations of PA 6. 6 meeting UL 94 V-0 at 0. 8 mm[25].

5. 2　Fire retardancy and performance in large scale fires

The effect of fire retardants on large scale fire behaviour is less clear. Fire retardants can delay ignition, or reduce heat release rate in small-scale tests, and are most effective in the "first object ignited". However, they are only effective on a larger scale if they decrease the radiant component of heat transfer. Radiant heat allows the flames to spread horizontally or even downwards. Soot particles absorb heat from the flame, and emit infrared radiation in all directions, which can heat adjacent objects causing flame spread, and is ultimately responsible for the devastating impact of unwanted fires. Gas phase free radical inhibitors, such as halogenated flame retardants, which act by interfering with the combustion process increase the soot yields and hence the severity of a large scale fire, as soot particles convert more heat in flames into radiation, spreading the fire to other objects, alongside and below the flames[26].

5. 3　Regulatory considerations

5. 3. 1　Flammability standards and regulations

Fire retardants are generally more expensive than the

base polymer, and their addition is usually detrimental to its physical properties. Regulatory requirements generally drive the deployment of fire retardants and other strategies for fire safety. Standards typically define methods for quantifying performance, such as ignitability, heat release rate, flame spread and smoke production. They may apply to materials or finished products, and from a flammability perspective, should reflect likely fire scenarios in normal usage. There are a large number of industry standard tests for specific product types designed to achieve this. Regulations require these standards in order to define minimum levels of performance, which can then be stipulated for particular applications or conditions (railway vehicles, high rise buildings or electrical products etc.).

In Europe, Directive 2001/95/EC on general product safety (GPSD) imposes a requirement on any consumer product to ensure that it is safe with regard to normal or reasonably foreseeable use. The definition of "safe" is provided in guidance documents. For example, upholstered furniture is expected to meet the cigarette and match ignition requirements of BS 5852. There are also specific sectorial directives covering the safety aspects and non-flammability requirements of certain products are:
- The Toys Safety Directive 2009/48/EC;
- Directive 2006/95/EC on Electrical Equipment designed for use within certain voltage limits;
- Directive 1999/5/EC on Radio Equipment and Telecommunications Terminal Equipment;
- Directive 2006/42/EC on Machinery;
- The Construction Products Regulation (EU) No 305/2011.
- Directive 2008/57/EC on Rail System: interoperability

At present, the fire safety of furniture and textiles is not regulated by specific European legislation.

5.3.2 Current regulation of ecotoxic fire retardant materials

In Europe the Restriction of Hazardous Substances Directive (RoHS) restricts the use of certain hazardous substances in electrical and electronic equipment (Directive 2002/95/EC), including the use of six hazardous materials, including brominated flame retardants, in the manufacture of various types of electronic and electrical equipment. It is closely linked with the Waste Electrical and Electronic Equipment Directive (WEEE) 2002/96/EC, which sets collection, recycling, and recovery targets for electrical goods and is part of a legislative initiative to solve the problem of huge amounts of toxic electronic waste[27]. The maximum concentrations of PBBs and PBDEs allowed are 0.1 wt% of homogeneous material, without separate collection and treatment.

The RoHS procedure has now combined with European Union Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), to become a new regulation EC/2006/1907. REACH addresses the production and use of chemical substances and their potential impacts on both human health and the environment, regulating manufacture and use of all man-made non-polymeric chemical substances.

The 10 year phased implementation of REACH started in 2007. Brominated flame retardants were one of the first categories investigated by REACH and was almost complete within 2 years. The use of Penta-BDE and Octa-BDE has ceased, while Deca-BDE uses have been severely restricted. Hexabromocyclododecane (HBCDD), widely used in expanded polystyrene foam, has not been approved by REACH, and is to be phased out in 2015.

5.3.3 Voluntary regulation -Ecolabels

To help consumers and institutions assess the sustainability of products, manufacturers can demonstrate compliance with environmental standards through the use of Ecolabels. Although the framework for the operation of ecolabel schemes is governed by regulation, their actual use is voluntary. Individual schemes develop and publish environmental performance criteria for particular product groups (for example televisions, furniture etc.), which have to be met to qualify for an ecolabel.

The European Ecolabel is the most widespread scheme, established in 1992 to encourage businesses to market products and services that are more environmental-friendly, and aims to substitute hazardous substances with safer ones. For example, the latest European Ecolabel proposals would prohibit the use of flame retardants which are banned in electronic appliances, including Deca-BDE, in Ecolabelled textiles and bed mattresses[28].

The current proposals use "risk phrases" which ignore environmental and other non-occupational effects, such as fire toxicity. They use separate classification for additive and reactive "flame retardants" putting mineral fillers, such as aluminium or magnesium hydroxide, or even naturally occurring mixtures of the minerals hydromagnesite and huntite (HMH), which show fire retardancy comparable to ATH[29] in same category as small moleculebrominated flame retardants, while permitting the use of polymeric brominated flame retardants, such as brominated polystyrene, which may not leach into the environment, but will still increase fire toxicity, act as precursors for dioxins, and may increase the radiation and hence flame spread. Although Ecolabels are voluntary, they could be adopted into purchasing policy by local authorities and large institutions, with potentially greater impact on markets.

6 Requirements of sustainable fire retardants

Sustainability generally refers to processes or products capable of being continued with minimal long-term effect on the environment. The International Union for Nature Conservancy (IUNC) define sustainability as something that improves the quality of human life while living within the carrying capacity of supporting eco-systems. In terms of fire retardant polymers, meeting these requirements is highly dependent on the existing practices and processes used during manufacture, and particularly during end-of-life process-

ing. Given the dependence of polymer manufacture on petro-chemicals; the problems of halogenated flame retardants; the environmentally damaging manufacturing process of many fire retardants; and the incompatibility of fire retardant polymers with polymer recyclate, improvement in any of these areas could be claimed to increase the sustainability.

The sustainability requirements of a fire retardant polymer can be identified.

1. The polymer would be derived from sustainably farmed biobased sources.

2. Ideally this biobased polymer would be of inherently low flammability-since this is not expected in the foreseeable future it should incorporate a fire retardant whose manufacturer is clean and environmentally sustainable. This could be a naturally occurring material such as hydromagnesite-huntite (HMH)[30], deoxyribose nucleic acid (DNA), starch or lignin, which would not pose problems of biodegradability, or incompatibility in landfill.

3. The fire retardancy should be maintained through the end-of-life processing, such that the material can be readily reused. This may entail more sophisticated identification at end-of-life treatment centres.

Figure 9 illustrates a "cradle-to-grave" schema showing possible problem areas where sustainability criteria may not be achieved. This type of process has been formalised into life cycle analysis (LCA). Although somewhat discredited by clumsy attempts from marketing specialists to show their products in the best possible light, clear guidance has now been agreed by ISO. ISO 14040[31-33], LCA is defined as "A technique for assessing the environmental aspects and potential impacts associated with a product by compiling an inventory of relevant inputs and outputs of a product system; evaluating the potential environmental impacts associated with those inputs and outputs; interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study". LCA of FR chemicals provides information on its environmental performance at all stages in its life cycle. Its main objective is to identify which materials pose greater impacts, where these impacts occur in the chemical life cycle, and their impact on humans and the environment.
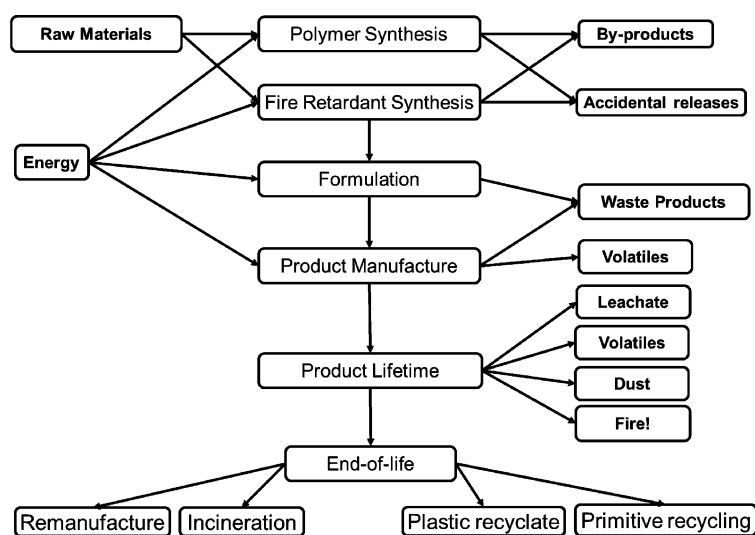

Fig. 9　Outline of processes requiring consideration in assessment of sustainability

6. 1　Fire retardant synthesis

Consideration there must be given to both the raw materials and the energy requirements for polymer and fire retardant synthesis. In addition, the by-products and accidental releases of the manufacturing process can be equally harmful. For example, the world's most widely used fire retardant, aluminium hydroxide (ATH), uses very large amounts of energy in the extraction of aluminium from bauxite, and the process generates equal volumes of ATH and toxic red sludge, for which there is currently no viable remediation strategy. Thousands of tons of this highly alkaline toxic red sludge escaped in Hungary in 2010 causing 10 deaths. From 2016, European manufacturers are prohibited from dumping this sludge in the sea, and must identify uses for it.

6. 2　Formulation

During the formulation of a polymeric material for use as a plastic product, a number of additives are usually required. These include pigments, antioxidants, u. v. stabilisers, fillers and fire retardants. Each must be rendered compatible with the host polymer. This usually involves surface treatment of the additive to decrease its polarity and control of the particle size. Once compounded into the host polymer, insoluble additives are relatively immobile. Conversely, soluble additives, such as brominated flame retardants have been shown to migrate to the surface where they evaporate or are otherwise released, causing problems of human and environmental tox-

icity. In other applications, such as textile processing, where fire retardants are applied as aqueous suspensions or solutions, for example, for direct treatment of fabric, or incorporation into a back-coating, the processes lead to greater losses. The factory effluents have consisted of a dilute stream of flame retardants. Some of the highest concentrations of brominated flame retardants in marine ecosystems in the UK were found close to a textile flame retardant treatment works[34].

6.3　Product manufacture

Polymer compounding and processing provides the most extreme environment for a polymeric material during normal use, except when involved in a fire. Indeed, the ability of a polymer to be recycled is often quantified in terms of the number of polymer processing cycles it can withstand before decomposition is so severe its mechanical properties fall outside acceptable limits. The fire retardant must, therefore, be able to withstand these conditions without degradation. However, in order to be effective, most fire retardants need to be activated at slightly higher temperatures corresponding to polymer decomposition, when its breakdown products are released as a fuel. The activation of a fire retardant varies with mode of action from volatilisation (for gas phase flame retardants) to decomposition resulting in formation of a char promoter (often phosphoric acid) or gas release causing swelling for an intumescent fire retardant. The temperature range above melting but below polymer or fire retardant decomposition is often known as the "processing window", while the highest temperature at which the polymerization is thermodynamically more favourable than polymer depolymerisation is known as the "ceiling temperature". Thus, careful selection of the fire retardant-polymer combination and processing temperature are necessary if decomposition, or release of fire retardant, is to be avoided during processing. Wastage of up to 10% is common in many manufacturing processes. Provided this waste stream can be fed back into the process line this is not a problem, and is much easier than recycling post-consumer plastic waste. Where the polymer is cross-linked or otherwise unsuitable for feeding back into the process stream, suitable alternative uses for the waste must be employed.

6.4　Product lifetime

Releases of toxic or ecotoxic species during product lifetimes has made a significant contribution to the overall release of the halogenated flame retardants. Since the release of volatile or semi-volatile components is a function of the temperature, products operating at elevated temperature, such as computers, video and audio equipment, are more susceptible to such releases. Distribution is enhanced when cooling fans are used to reduce the temperature. Very high levels of brominated flame retardants have been identified in household dust in jurisdictions requiring fire retardants to be added to upholstered furniture, such as California and across the UK[35-36]. Although the exact release pathway has yet to be positively identified, it seems likely that the progressive dete-

rioration of combustion modified polyurethane foam and the flame retarded latex backcoating are the main contributors to brominated flame retardants in household dust. Other releases during a product lifetime which have been reported, and are likely to lead to unnecessary human exposure, include the presence of the toxic brominated flame retardant PBDE in children's toys in China[37] and its presence in the lids of flasks used for holding hot drinks[38], both of which have enhanced routes to ingestion by humans.

6.5　End-of-life processing

Meeting the goal of sustainability is a particular problem for plastic materials, compared to the wood and metals they have replaced. Wood makes a net zero contribution to atmospheric carbon dioxide levels, and is biodegradable, and the few metals in common use show negligible deterioration on recycling and remanufacture. In contrast, the vast range of polymeric materials, each containing different levels of various additives, must be separated by polymer structure, and only then can they be remanufactured or reprocessed.

When plastics first grew in popularity, they were disposed of by landfill. Their resistance to biodegradation resulted in landfill sites being permanently contaminated by plastic waste. The EU Landfill Directive (1999) introduced a Europe-wide landfill tax to discourage this practice. One solution was incineration (sometimes described as "energy recovery"). Incineration was restricted for wastes containing potentially hazardous substances by the EU WEEE Directive (2003) and RoHS Directive (2003).

The WEEE/RoHS Directives require the separation of plastics in electrical and electronic (E & E) waste containing brominated flame retardants prior to recycling, followed by treatment at a specialist facility (Figure 10), rather than energy recovery or disposal. Unfortunately, the facilities to meet the demand do not yet exist. Instead, WEEE containing brominated flame retardants has been shown to leave the approved authorised treatment facility (AATF) after separation of metals, and was then granulated and reclassified as halogen-free plastic recyclate[39].
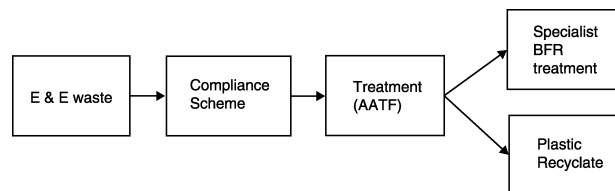
Fig. 10　Schematic diagram of WEEE process for dealing with electrical and electronic waste

In addition, it was reported by the German environmental agency (UBA) that 155 000 tonnes of German WEEE were exported outside EU, including 50 000 tonnes TV and PC monitors which are highly likely to contain brominated flame retardants, possibly exploiting the loophole of waste being classified as being in working order, to permit their export[40]. This is one of the most worrying aspects of the current attempts to improve sustainability: the dumping of elec-

trical and electronic and other waste in third world countries with no proper facilities for its remediation, separation and disposal. Instead, it is burnt in open air to recover small quantities of precious heavy metals, exposing humans to toxic effluents and releasing ecotoxic species into the environment[41-42]. It has been reported that in India, toxic metals such as Hg, Pb, Cd, Cr, Cr(IV), Co, Cu, Ni, and Zn, together with PBDEs and PCBs have been released into the environment from primitive recycling[43-44].

The remaining range of possibilities for end-of-life processing is necessary to deal with the complexity of the challenge. In an ideal world, each component of each product would be returned to the manufacturer for remanufacturer into their current product. For large objects which are frequently replaced, such as television casings and certain motor vehicle components, this is already being undertaken. In this way the appropriate level of fire retardant is already present, and while the shape and design may change, the material formulation can remain the same.

6.6 End-of-Life-Plastic Recycling

One of the main goals of any sustainable fire retardants strategy is that end-of-life processing is environmentally benign. For most polymeric materials this effectively means it must be suitable for recycling. The additives present will dictate the quality of the recyclate, which will limit its loading in combination with virgin polymer. To illustrate the current quality of the recycled plastics, it is informative to consider a detailed study investigating the bromine content of plastics present in consumer products[45].

The study tested almost 2000 products, of which 25% contained bromine above $0.5 \text{ g} \cdot \text{kg}^{-1}$, and around 12% were analysed for 6 target flame retardants PBB, Penta-BDE, Octa-BDE, Deca-BDE, TBBPA and HBCDD. The results (Figure 11) were surprising. 72% of the ~200 plastics analysed did not contain any of the target compounds above. Brominated flame retardants are unlikely to be effective at loadings below 10%, and certainly not below 5%. The results show that most samples contained less than 5% bromine. This indicates that the origin of the bromine was from the plastic recyclate, rather than new flame retardant added to the product. It also suggests that the brominated flame retardants had decomposed during recycling, and that there are significant quantities of other brominated flame retardants in common use. If the survey is representative of the world's stock of recycled plastic, it underlines the importance of eliminating contamination from the recyclate, and asks the question "how long will bromine remain in the world's stock of plastic recyclate?" This study shows the persistence of additives and fire retardants in the polymer recyclate, where they will typically have adverse effects on physical properties and recyclability. The sustainable solution requires much more sophisticated techniques for identifying and separation of fire retardant plastics at end-of-life, or use of more expensive, but inherently lower flammability plastics not requiring additional fire retardants.
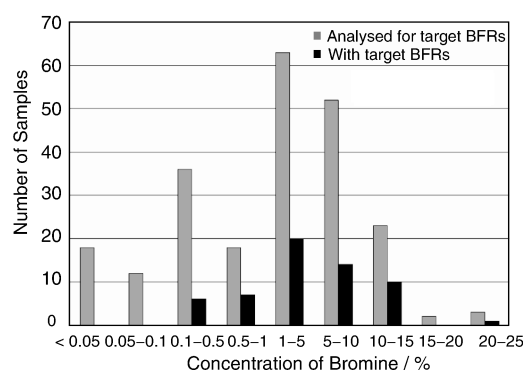

Fig. 11 Distribution of bromine and known brominated flame retardants (BFRs) in consumer products[43]

7 Sustainable fire retardant development

At loadings of 5 to 20% halogen, sufficient flame inhibition is observed to alter the performance in standard tests from a fail to a pass. Thus, finding a halogenated flame retardant that can be incorporated into the flammable polymer at a suitable loading without detriment to the physical properties provides a quick and easy solution. Unfortunately, this ease of incorporation is matched by an ease of release of the flame retardant into the surroundings, increasing human exposure through direct contact, inhalation and especially through household dust (ingestion and inhalation).

In contrast, the halogen-free fire retardants are often polymer specific-melamine is an excellent fire retardant for polyurethane foam, but ineffective in polypropylene-in general, specialist knowledge is required to develop and optimise halogen-free fire retardant formulations.

In addition to fire retardant action often being specific to particular classes of polymers, it can also be specific to particular aspects of flammability, such as ignitability, flame spread, or heat release rate. For example, the new generation of nanoparticulate fire retardants often reduce the time to ignition, but in doing so, they also reduce the heat release rate, slowing down burning. Regulatory tests often emphasise just one of these aspects.

As described earlier, the requirements for sustainability extend from cradle-to-grave, and the achievement of sustainability will require an integrated approach to product development. The last 20 years have seen almost all fire retardant development focused on halogen-free solutions. The reasons for this are less clear. Either investigators are driven by individual environmental concerns, or they share a perception of an unstoppable trend away from halogenated flame retardants. The number of publications has grown dramatically (Figure 12) with a total of 813 papers listed by Scopus © on halogen-free flame/fire retardants. These could all be described as developments in sustainable fire retardancy. A total of 157 papers refer to sustainability and flame/fire retardancy in their title or abstract, and these are growing at a similar rate. However 15 of these papers were written by the

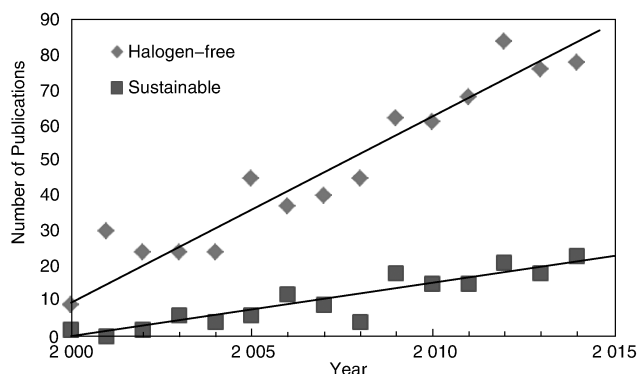leading brominated flame retardant manufacturers Albemarle and ICP-IL!

Fig. 12　Number of publications on "fire/flame retardancy" and "halogen-free" or "sustainability" as listed by Scopus®

A much higher proportion of researchers have made contributions to the development of sustainable fire retardant materials. A small selection is outlined below.

7. 1　Fire retarding biobased polymers

A great deal of effort has gone into devising fire retardant strategies for polylactide (PLA) (a biobased polymer derived from lactic acid)[46]. Polyamide (PA) 11 (which can be made from castor oil) has been fire retarded using a combination of conventional intumescent fire retardant and carbon nanotubes[47]. Soybean oil based copolymers were reactively modified with trimethylsilylstyrene and tris-(4-vinylphenyl-boroxine) adding silicon and boron as reactive fire retardants, and have been compared with the same biobased polymer containing the analogous additive fire retardants. The boron-containing copolymer gave promising results and the reactive-or-additive approach was a significant factor in the fire retardancy[48]. Biobased semi-aromatic polyamide fire retarded with functionalised clay nanocomposites modified with a phosphine oxide moiety and triamine groups showed flame retardancy and high thermal stability[49]. The challenge to address climate change by the use of insulation materials, based on renewable raw materials, has been met by foams made from ammonium alginate and sodium montmorillonite (clay) with properties similar to those of rigid PU foams and inherently low flammability, as measured by cone calorimetry[50]. A number of publications have described fire retardancy of wood (the ultimate sustainable polymeric material?), and the methods have recently been reviewed[51]. Cellulosic and modified cellulose have also been extensively studied for fire suitable fire retardants. The flammability of wood flour/polypropylene composites have been significantly reduced using a combination of ethanolamine and ammonium polyphosphate[52].

7. 2　Using biobased products as fire retardants

Phosphorus based fire retardant plasticisers based on phosphorus esters derived from a diol generated by the esterification of isosorbide (from starch) with 10-undecenoic acid

(from castor oil) have recently been reported[53]. Cellulose nanofiber (CNF)/clay nanocomposites, with "brick-and-mortar" structure have better fire protection properties than other clay nanocomposites and fibrecomposites[54]. Lignin (a biobased waste product from cellulose manufacture) was used as flame retardant for polybutylene succinate (PBS) biopolyester, after grafting phosphorus compounds onto the lignin, to promote a stable char[55]. An aromatic biobased phenolic compound, phloroglucinol, was functionalised with different phosphate groups in order to promote a charring effect[56]. Perhaps most intriguingly, deoxyribose nucleic acids (DNA) and caseins were exposed to different heat fluxes under a cone calorimeter, and exhibited a typical intumescent behaviour, generating a coherent expanded cellular carbonaceous residue (char), extremely resistant to heat exposure[57], which has subsequently been demonstrated to be an effective additive fire retardant[58]. The fire retardant effects of naturally occurring mixtures of huntite and hydromagnesite have been shown to decrease the average rate of heat release and increase the strength of the residue[29].

Thus it appears that the technological advances to make step-change improvements in sustainability already exist. It seems likely that researchers will continue to make further breakthroughs, so that further improvements in sustainability will be ready to meet future requirements.

7. 3　Effectiveness of fire retardancy on recycling

There are relatively few published studies on the suitability and flammability of materials containing fire retardants for recycling. This is a vast area, since each polymer has a number of different fire retardant formulations, compounded using different, and possibility incompatible processing aids. Some studies have shown that the fire retardancy deteriorates. For example, the fire retardant properties of recycled polypropylene composite were compared to the non-recycled formulation containing an intumescent system and zinc borate. A synergistic interaction was observed for the non-recycled materials but not for the recycled ones[59]. A feasibility study to address the annual 2. 7 million tonnes of fire retarded plastics in waste electrical and electronic equipment (WEEE) focussed on LCD TVs. By weight, 18% of the housings contained brominated FRs and 31% phosphorus FRs. It was demonstrated that poly-carbonate (PC)/acrylonitrile-butadiene-styrene(ABS) fire retarded with phosphorus could be recycled into new TVs but a minimum factor of 10 dilution with virgin material was required[60]. Waste poly (ethylene terephthalate) (PET) textiles were recycled into flame-retardant rigid polyurethane foams of lower flammability because the aromatic substituent in the depolymerized products[61]. Polypropylene has been recycled to produce a biocomposite reinforced with plant based kenaf fibre, showing lower flammability and increased biodegradability: further flammability improvement was obtained on addition of a mixture of aluminium and magnesium hydroxides and boric acid[62].

8　Conclusions

The widespread use of synthetic polymers has increased the flammability of our built environment. The demands to improve sustainability by reducing energy consumption, such as replacing traditional building materials with flammable polymeric foam insulation materials, the increasing deployment of large, flammable photovoltaic devices and replacing metal with lightweight materials in transport systems look set to exacerbate the problem. To ensure fire safety, regulations place limitations on the flammability of materials which may be present in prescribed high risk/high hazard situations, such as mass transport, high-rise buildings, furnishings and electrical and electronic equipment. The incorporation of fire retardants into synthetic polymers reduces their flammability; in effect, they allow more inherently flammable polymers to meet the regulatory requirements on flammability for use in such high risk applications.

Some fire retardants, such as hydrated mineral fillers, nanoclays, DNA, lignin or alums are naturally occurring, and have low toxicity. Others, such as ammonium polyphosphate, are also of low toxicity and are rapidly broken down in the environment. Particular problems arise from those which are environmentally persistent, bioaccumulative and toxic (i. e. have PBT properties).

Halogenated flame retardants release hydrogen chloride or hydrogen bromide, which inhibits the gas phase flame reactions delaying ignition, and/or reducing the heat release, while increasing the yields of products of incomplete combustion, such as carbon monoxide, hydrogen cyanide, organoirritants, polycyclic aromatic hydrocarbons and soot. If the item containing the flame retardant was always the only item involved in the fire, and its FR treatment always led to extinguishment, fire would not be a problem. However, most fire deaths result from inhalation of toxic fire effluents, and halogenated flame retardants increase the toxicity of these effluents.

In the future, as petrochemical resources become more scarce, a requirement of a sustainable fire retardant must be that the polymer and FR additive should be able to be recycled, preferably retaining its fire retardancy over several cycles of re-use. At present many fire retardants are incompatible with the recycling processes, and most of the world's stock of polymer recyclate is contaminated with brominated flame retardants and their breakdown products.

It is evident that some of the highest discharges of heavy metals and brominated flame retardants to the environment result from recycling processes in poorest parts of India, the Far East and Africa. Since the largest quantities of HFRs are probably incorporated into products currently in use, unless urgent action is taken to properly enforce regulations such as the European WEEE directive, levels are set to rise before they start to fall, and the legacy of BFRs may be with us longer than the 40 years they have currently been on the planet.

The key goals for achieving sustainability can be summarised：

1. The method of manufacture of polymer and flame retardant should not require significant quantities of fossil fuel.

2. Products should not cause problems at end-of-life.

3. Plastic components can enter recycling stream safely.

4. The fire retardant does not reduce number of re-cycles.

5. Ideally the fire retardant continues to be effective and beneficial.

It appears that many of the technological advances necessary to make step-change improvements in sustainability already exist-what is lacking is the implementation strategy to put these results together and make it happen! In the meantime, researchers will continue to make further breakthroughs so that further improvements in sustainability will be ready to meet future requirements.

Acknowledgements

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