RISE Guide to sustainable fire protection of plastics and composites

The following document provides a reduced version of our guidelines. For an extended version of the guidelines and support by our experts, please contact us

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Sustainable fire protection of plastics and composites

Flame retardant technologies are traditionally based on halogenated compounds or other hazardous substances. However, various sustainable alternatives have entered the market in recent years. Along with a smart design approach, these alternatives enable the design of sustainable flame retarded products.

The design of a flame retarded product is a challenging process due to complex interactions of thermal degradation products of different flame retardant ingredients as well as the protected material. Moreover, fire protection implies mostly a trade-off between fire performance, mechanical performance, processing properties, sustainability, cost, etc. Careful consideration of all requirements is therefore necessary for each material and each application in order to design a sustainable flame retarded product. Due to the complex chemical processes during fire, it is difficult to predict the fire performance of a flame retardant system in/on a certain material. The development of a flame retardant system is therefore traditionally based on empiric investigations, which are time and cost intensive.

RISE experts can help to reduce development time and cost through our expertise regarding fire retardancy mechanisms, toxicology and cost of different flame retardants, as well as their potential influence on processing, mechanical and other product properties.

For this, the present guidelines include instructions regarding general considerations for developing a sustainable flame-retarded product, along with a collection of relevant information from earlier projects.

Outline

The design of a flame retardant material implies mostly a trade-off between fire performance, mechanical performance, processing properties, sustainability and cost (as well as other requirements). It is therefore important to **define the aimed requirements** regarding all aspects. The most common **Fire regulations and test methods** have been collected to support the definition of requirements. If the structural performance during fire is crucial, **modelling** of the structural response during fire may support the definition of requirements.

Health, Safety and Environmental (HSE) Aspects are the factors that are sacrificed more often than necessary due to lack of knowledge and development time. Therefore, it is our ambition to support our customers with our expertise about flame retardant solutions in their efforts to make more sustainable choices. Basic evaluations of the **toxicology of the most common flame retardants** and **HSE aspects regarding surface protection systems** are provided. For more advanced evaluation of toxicity and life cycle environmental effect, **RISE experts** can provide support.

For a smooth and efficient support, we have created a **team with relevant expertise** and collected our earlier experience in guidelines for efficient choice of protection **approaches** to facilitate future collaborations in the area. Fact sheets for the different technologies summarize their most important features and a list of **commercial products and suppliers** has been compiled. Moreover, information about related **projects** and some **recommended literature** is provided.

Efficient choice of fire protection technologies

The present guidelines support the choice of sustainable fire protection solutions by the input presented in the light blue boxes.

Together with our partners' expertise regarding their requirements and preconditions and our experience in the field, the present guidelines enable therefore an efficient choice of FR promising solutions.

General considerations
Fire regulations
Modelling

Define Requirements

Review Approaches

General considerations
Additives (A)
Surface protection (S)
Inherently FR materials (I)

Potential solutions limited selection

Review potential Solutions

- Technologies & Fact Sheets (A,S,I)
- HSE assessment (list or own)
- Commercial products
- Cost
- Earlier experience, Literature

Potential solutions final selection

Evaluate against Requirements

RISE Processing and Testing Infrastructure and Expertise

Content

Requirements

Fire protection	The requirements regarding fire protection depend on the application and differ largely not only regarding the level of fire retardancy but also regarding other aspects such as smoke production. It is important to ensure that the final solution can fulfil the requirements with some marginal in order to avoid problems arising through variations in manufacturing. However, the solution should not be over-designed regarding its fire performance, as this would in most cases lead to decreased sustainability and mechanical performance as well as increased cost. The most common **regulations and test standards** can be accessed here.
Mechanical properties	The mechanical performance of a material can be influenced by the addition of flame retarding solutions. Most flame retardant additives, especially halogen-free flame retardants exhibit for example a pronounced effect on the impact properties and toughness of plastics. The deterioriation of the structural integrity of a product in a certain fire scenario can be predicted by **modelling**. This approach can support the definition of requirements in certain cases, where the structural integrity needs to be guaranteed for a certain time under exposure to fire.
Processing properties	The processing properties of a material are influenced by the addition of flame retarding solutions. Flame retardant additives, for example, will influence the melt viscosity of plastics. Moreover, it is important to be aware that particulate additives will be filtrated upon infusion of textile reinforcements with thermoset matrices. Surface protection on the other hand will require additional process steps. Further description of the potential influence of additives and surface protection technologies on a production process is included in the respective sections.

Requirements

Cost	The cost of flame retardant solutions is almost always higher compared to the cost of plastics/matrices. The cost between different solutions varies largely, not only due to variations in the cost of the materials, but also due to implications regarding processing (see processing).
Toxicity and Sustainability	Flame retardant additives as well as surface protection solutions often have detrimental effects on the work environment as well as on the environment. However, some highly efficient sustainable solutions have entered the market in recent years and decades. Consult the section about **HSE aspects** for further information.
Weatherability and Durability	Durability and weatherability are important requirements for any plastic and composite products. Flame retardant solutions differ in their durability and resistance against water, UV, etc. This is true for additives as well as surface protection solutions and inherently flame retardant materials. It is therefore important to be aware which environment the final product will be exposed to when choosing an adequate solution.
Other Requirements	Aesthetics and surface properties are highly important in almost all products. Flame retardant additives will almost always reduce the glossiness of a plastic surface. One innovative sustainable solution is intumescent systems based on expandable graphite (EG). However, the material or surface will exhibit a dark (grey or black) appearance, thus limiting the use of this otherwise highly promising flame retardant. Also other requirements, such as optical, electrical properties or glueing possibilities may be relevant.

Fire regulations and test methods

Materials and products must be tested and validated with respect to their fire behaviour before entering the market. There are different fire classification standards for different end use applications. The main end use applications are

- Construction products and building elements
- Furniture and mattresses
- Marine applications
- Railway vehicles and
- Transportation such as buses, trucks and automotive

The requirements and test methods for the different branches and applications are described here:

Modelling

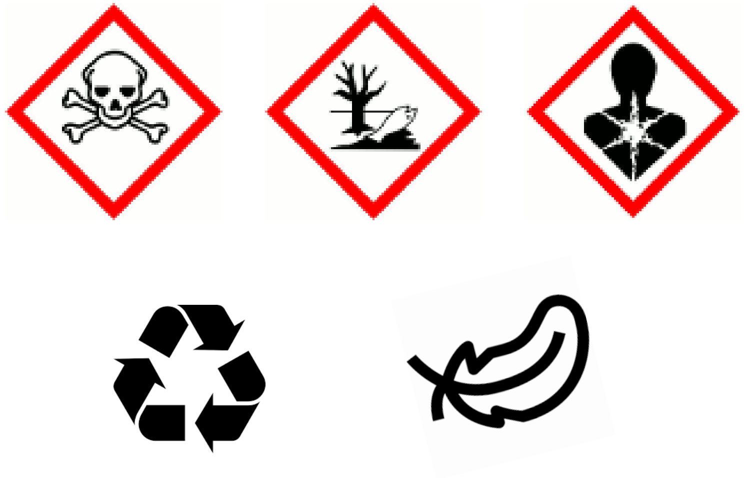
- Composite structures under operational conditions and simultaneously subjected to fire show a very complex response resulting from a combination of multi-physical processes: thermal, chemical, physical and failure processes. Understanding and being able to model the fire structural performance is a critical safety issue as the decomposing resin will result in loss of stiffness and strength (especially when loaded in compression), leading to distortion and possible collapse of the structure.
- Computational modelling of the fire-structural response is a multi-physics problem which can be divided into four steps: modelling of (i) the fire environment, (ii) thermal response of materials, (iii) fire-induced damage and weakening of materials, and (iv) the mechanical response of the structure.

HSE aspects

Flame retardant additives and coatings contain often components that are toxic or detimental to the environment. Here, we provide guidelines on how to assess the health, safety and environmental aspects of different technologies along with a basic evaluation for the most common flame retardant additives. We advise to take expert support for this evaluation.

General HSE aspects:

- Toxicity to human health and the environment
- Recyclability
- Other aspects



HSE considerations for the different approaches:

- HSE aspects regarding fire retardant additives
- HSE aspects regarding fire retardant surface protection

For an extended version of the guidelines, more information and support, please contact us

HSE aspects – Toxicology

Based on the material safety datasheet and the CAS-number, the following websites should be consulted to find out about the toxicity of the component to human health and the environment:

- As a start you should check if your substance is listed on ECHAs candidate list of substances of very high concern: https://echa.europa.eu/sv/candidate-list-table . By searching for the substance in the CLP database you can find information about the compounds hazard classification and if it already is regulated or requiers authorization, https://echa.europa.eu/sv/information-on-chemicals/cl-inventory-database .
- Kemikalieinspektionens PRIO guide provides a tool to identify dangerous substances divided into two categories: phase-out substances and prioritized risk-reduction substances (https://www.kemi.se/prio-start/kriterier/oversiktstabell). By using the CAS-number you can use to search function to see if your substance fulfil the citeras for any of the two categories: https://www.kemi.se/prioguiden/english/search.
- The SIN-list, https://sinlist.chemsec.org/ , is a tool where you can search for hazardous compounds that already are regulated or might be regultated in the near future.
- List of endocrine disruptors by ECHA https://edlists.org/the-ed-lists/list-i-substances-identified-as-endocrine-disruptors-by-the-eu
- List of substances that are under assessment as endocrine disruptors by ECHA: https://echa.europa.eu/sv/ed-assessment
- Search the GreenScreen Assessment tool Pharos: https://pharosproject.net/

If toxicologic data for an alternative is missing, it is important to evaluate potential difficulties that arise with introducing this material to the market in your product. RISE experts can support with an evaluation of the probable risks based on the chemical structure of the substance.

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HSE aspects – Recyclability

Thermoplastics and thermoplastic composites can generally be mechanically recycled, which is the most straightforward and cheapest process of recycling. Thermoset composites are recycled by thermochemical methods.

Additives: Flame retarding additives in the thermoplastic matrix will have an influence during recycling especially on the processing temperature. For each individual product, it needs to be evaluated empirically if different streams can be combined in a new material, as any additives (FR or not) may not be compatible and react with each other. Components containing additives with an “onset temperature” for a certain type of reaction must be processed below this temperature in order to consider safety aspects for personnel and equipment. The mechanical properties are often influence by flame retardants which means that experiments should be made that verify the possibility to include a recycled fraction and still obtain a useful material. Also other aspects need to be considered: BDP for example, is not recyclable as it lacks hydrolysis stability.

Surface protection: Conventional mechanical recycling includes size-reduction by shredding or milling of the recycled plastics. Painted or surface coated parts that are milled will be contaminated by the paint. The consequence is commonly reduced mechanical properties. The paint residues mixed into the matrix will result in spots on any processed surfaces that provides less good adhesion if a new coating is applied. Recycling of painted parts therefore starts with paint removal.

More information:

For an extended version of the guidelines, more information and support, please contact us

Fire protection approaches

A short introduction regarding combustion and fire protection mechanisms is provided here:

The approach that needs to be taken for fire protection of a certain product is mostly determined by preconditions regarding processing and material properties. It is often not viable (neither economically nor environmentally), to change the value chain, production processes or design of a product. However, if the approach is not limited by these preconditions, other aspects can be the driving factor in this decision. In this case, potential technologies may be compared on a life cycle perspective without limiting the possible approaches.

In general, three approaches can be adopted to provide fire protection to plastic or composite products: additives, surface protection or inherently fire-retardant materials.
Additives are mostly dispersed into the plastic or matrix material but can also be applied to fibre reinforcements (e.g. SAERTEX LEO). The addition of additives into a material influences its processing and mechanical properties and potentially also other relevant properties (surface properties, electrical and optical properties), depending on the plastic and additive. This means that the material composition needs to be optimized.
Surface protection allows the introduction of a protective layer onto an existing material or structure without influencing the material's bulk properties. However, it requires in most cases an additional process step.
Inherently fire-retardant materials often exhibit a large fraction of aromatic cycles and heterocycles, which provide rigidity and stability to the material. Such polymers form char upon combustion, thus protecting the underlying structure and decreasing the formation of combustible gases.

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Fire protection approaches

Approach	Advantages	Disadvantages
Additives	• Provides protection even after the fire breaches the surface • Only components that contribute to fire protection need to be added (no binder or solvents as for e.g. coatings)	• Requires optimization of the material and process • Often requires larger amounts of flame retardants compared to surface protection. • Influences the properties of the bulk material
Surface protection	• No need to change existing process /design • Inhibit surface flame spread efficiently • Protects locally where the fire first reaches the structure (surface)	• Additional process step required • If the fire breaks the surface protection, the structure is not protected any more • Often requires additional potentially detrimental components to form coatings
Inherently fire-retardant materials	• No or less fire-retardants required • Fire-retardancy throughout the material	• Limited choice of materials, processes and properties

Moreover, a combination of two or several of the above-mentioned approaches may be considered if a high degree of fire protection is required. Moreover, combinations of different technologies that fall under the same approach may be considered.

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Additives – Introduction

Additives are components that are added into the bulk of the material as opposed to surface protection, which is applied to the surface. These components can be ‘additive’ or ‘reactive’. Additive FRs do not react with the constituents of the plastic material and are thus prone to leaching and often lead to decreased mechanical performance of the materials. On the other hand, additive FRs are cheaper and easier to use compared to reactive FRs.

Reactive FRs are mainly used for thermosets such as epoxies, polyesters and polyurethanes. They exhibit functional groups that allow incorporation into the polymeric structure upon curing. This approach leads therefore to an ‘inherently’ flame retardant material. The drawbacks of this approach are the higher price as well as the necessity for adapting the processing (especially curing) conditions.

The nature and thus the mechanisms involved in flame retardancy for additive and reactive flame retardants vary and overlap for both approaches. Halogen-, phosphorus- and nitrogen-based FRs are available as additive as well as reactive components. Inorganic flame retardants, such as minerals, nanoparticles or graphite are only available as additive FRs.

The flame retardancy mechanism and efficiency for any FR depends on the decomposition temperatures of both the FR and the matrix. FR additives need therefore to be chosen to match polymer processing and pyrolysis specifics. There is therefore not one FR system that is universally applicable, but each FR influences the properties of different polymers in a different way.

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Additives – Technologies and Fact Sheets

Fire retardant	Fire retardancy mechanism	Representative chemicals/materials	Fact Sheets (links)
Mineral	• Decompose endothermally, absorbing energy and releasing non-flammable molecules that dilute combustible gases • The remaining inorganic residue forms a protective layer	• Metal hydroxides, e.g. $Al(OH)_3$ and $Mg(OH)_2$ • Hydroxycarbonates, e.g. hydromagnesite • Borates, e.g. zinc borate	- Mineral-based FRs - SAERTEX LEO
Halogens	• Eliminate highly reactive free radicals, H· and OH· generated during thermal decomposition of the polymers during combustion, slowing down further decomposition	• Tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), DECA • Halogenated monomers and copolymers	- Halogenated FRs: additive and reactive
Phosphorus	• Produces phosphoric acid that condenses to give phosphorylated structures and release water. This results in a carbonaceous protective layer • Can volatilize into the gas phase, to form active radicals and act as scavengers of H· and OH· radicals	• Red phosphorus • Inorganic phosphates • Compounds based on organic phosphorus • Intumescent systems together with a charring agent and a blowing agent	- Ammonium polyphosphate - Metal phosphinates - Organphosphorus FRs: additive and reactive - Intumescent FRs
Nitrogen	For more detailed information, please contact us		
Silicon			
Nanoparticles			
Other			

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Surface protection – Introduction and Considerations

Surface protection is often used for materials where the inclusion of FR additives is not desired due to their detrimental influence on the mechanical performance or processing properties. This approach is therefore mainly adopted for composites rather than plastics.
Different variations of surface protection technologies exist, ranging from coatings to mats that are included within the top layer of the material. The surface protection solutions rely on the same protection mechanisms and include the same additive systems that are also described in the section 'additives'. The main difference being that those additives are not included in the bulk of the material, but rather concentrated on the surface of the structure. This leads to a lower required total amount of additives, but also limits the flame-retarding effect to the surface, providing no protection once the fire has breached the surface.

For the protection of plastic and composite structures in general, the most straightforward protection systems are those that have been developed or optimized specifically for plastics and composites (inorganic-organic coatings, intumescent mats for co-infusion, gelcoats). For the other systems, the following challenges need to be addressed:

- Surface preparation to ensure good adhesion of coatings that are not intended for use on composites: especially water-based coatings with low organic binder content may exhibit poor adhesion to the polymeric substrates.
- Investigation of the protection properties of the coating regarding the failure temperatures of the composite structure. Often the protection potential for steel or wood structures is given as a time span until the structure collapses. A composite structure, however, will collapse at a different temperature (and thus after a different time interval) than a steel or wood structure.

For an extended version of the guidelines, more information and support, please contact us

Inherently flame retardant materials – Introduction and Considerations

The intrinsic fire resistance properties of polymers depend on their (i) stiffness, (ii) presence of polar groups and (iii) hydrogen bonding. Most inherently flame retardant polymers contain aromatic cycles and heterocycles, which provide rigidity and stability to the material. Such polymers form char upon combustion, thus protecting the underlying structure and decreasing the formation of combustible gases.

Examples for polymers with good intrinsic fire protection are polyimides (PI) or poly(furfuryl alcohol) (PFA). Moreover, materials such as phenolic resins and polycarbonate exhibit rather good fire performance.
The range of available materials and properties is rather limited for this approach and most of these plastics exhibit rather high cost. A general juxtaposition of price vs. fire hazard of polymers has been presented by Lyon et al [1].
However, inherently flame retardant plastics can be combined with other plastics to provide a compromise between fire performance, mechanical performance, cost and sustainability. The suitability of such approach needs to be assessed in comparison with other potential approaches and technologies.

Plastics with good intrinsic flame retardancy properties are not automatically classified as fire-resistant. The fire behaviour of plastics can vary on continuous a spectrum where the plastics listed below are among the best performing. However, it depends on the application and the associated requirements, whether these materials can be used in their pure form or if additional fire protection is required.

[1] R. E. Lyon, M. L. Janssens in *Encyclopedia*

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RISE experts

Name: Angelika Bachinger
Relevant expertise:
Fire-retardant additives – esp. phosphorus-based,
Fire-retardant surface protection
Projects: LightSURF, FRIPs, HFFR ABS
Contact: angelika.bachinger@ri.se,
+46 10 228 49 67

Name: Guan Gong
Relevant expertise:
Fire-retardant additives – esp. Nanoparticles
Inherently fire retardant polymers
Projects: POLYWALL, HIPWOOD, Demo-Up
Contact: guan.gong@ri.se, +46 10 228 49 49

Name: Karin Lindqvist
Relevant expertise:
Fire-retardant additives for plastics
Formulation and compounding of plastic products
Projects: HFFR ABS, industrial assignments
Contact: karin.lindqvist@ri.se, +46 10 228 47 74

Name: Anna Sandinge
Relevant expertise:
Fire regulations and testing, Ageing of fire-retardant properties
Projects: HFFR ABS, FRIPs, LightSURF, RAMSSES, Mat4Rail
Contact: anna.sandinge@ri.se, +46 10 516 59 73

Name: Anna S Strid
Relevant expertise:
Toxicology and life cycle environmental impact of flame retardants
Projects: HFFR ABS
Contact: anna.s.strid@ri.se, +46 10 228 48 37

Name: Erik Marklund
Relevant expertise:
Modelling of structural response during and after fire exposure
Projects:
Contact: erik.marklund@ri.se, +46 10 228 49 72

Related projects – recent examples

Project	Description	Funding	Contact person RISE	Duration
FIRE-RESIST	Improved fire behaviour of composites	EU FP7	Anna Sandinge	2011-2015
POLYWALL	Nanoclay for improved thermal stability of wood-plastic composites	Eureka via Vinnova	Guan Gong	2013
Mat4Rail	Fire resistance composite materials for rail applications	EU Shift2Rail (Horizon 2020)	Anna Sandinge	2017-2019
RAMSSES	Advanced material solutions for sustainable and efficient ships	EU Horizon 2020	Anna Sandinge	2017-2021
HIPWOOD	Advanced high-performance material based on wood	Vinnova UDI	Guan Gong	2019-2020
FRIPs	Fire-resistant interior parts for buses	Vinnova FFI	Angelika Bachinger	2019-2021
LightSURF	Surface protection of composites against fire in aerospace, marine, building & infrastructure	SIP LIGHTer (Vinnova, EM, Formas)	Angelika Bachinger	2019-2022
HFFR ABS	Halogen-free flame retardants for ABS	Swedish Center for Chemical Substitution	Angelika Bachinger	2020
Demo-Up	Fire retardant foam from fibre-reject from pulp&paper recycling waste stream	RISE SVI	Guan Gong	2020
KOMPIS	Development of new bio-based, fire-restricting composite materials	Västra Götalands regionen	Anna Sandinge	2020
CEFIMA	Cost-efficient fire restricting materials	Maroff (Norway)	Anna Sandinge	2020-2023

Further reading – recommended books and reviews

Description of mechanisms and commonly used solutions for different plastics:

- Fire retardancy of polymeric materials. Wilkie C.A and Morgan A.B. CRC Press, Taylor and Francis Group 2010. ISBN: 978-1-4200-8400-9.

Commercially available FRs for different plastics and their influence on material properties:

- Flame retardants for plastics and textiles, Weil E.D and Levchik S.V. Carl Hanser Verlag, Munich 2009. ISBN 978-3-446-41652-9

Description of recent developments mainly regarding halogenated and phosphorus-FRs:

- Advances in fire retardant materials, Horrocks A.R. and Price D. Woodhead Publishing Limited 2008. ISBN 978-1-84569-262-9.

Phosphorus-FRs:

- Velencoso et al. Molecular Firefighting—How Modern Phosphorus Chemistry Can Help Solve the Challenge of Flame Retardancy. Angewandte Chemie, International Edition 2018, 57, 10450 – 10467. DOI: 10.1002/anie.201711735.

Fire protection of composites:

- FIRE PERFORMANCE OF FIBRE-REINFORCED POLYMER COMPOSITES - A Good Practice Guide. Royle T., Keen N., Job S. by National Composites Center & Composites UK.

For further reading, we refer to the References in our reports and literature reviews.

We recommend a focused literature and market review prior to any new challenge.

The information you are interested in is included in our extended guidelines.

Please contact our Team for more information and support

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