ENFIRO: Life Cycle Assessment of Environment-Compatible Flame Retardants Prototypical Case Study

Newsletter 1

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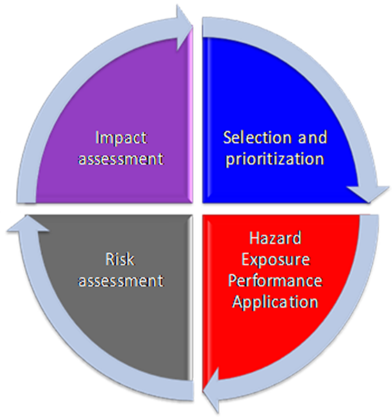
About the project

Flame retardants are applied in a wide range of commercial products, e.g. electronics and plastics, to inhibit or resist the spreading of fire. Due to their persistent nature and their toxicity some brominated flame retardants (BFRs), such as pentabromo-, octabromo-, and decabromodiphenyl ether, need to be replaced by non-toxic substitutes, and will be or are currently being phased out because of their environmental hazard. Less toxic alternative flame retardants appear to be available already but comprehensive information on their possible toxicological effects, exposure and fire performance is often lacking.



Chemical substitution cycle

The ENFIRO project is a research project that evaluates viable substitution options for a number of BFRs for better, safer alternatives. The consortium is a unique collaboration between industries, SME's and universities covering a wide variety of scientific disciplines. A practical approach is followed, based on the chemical substitution cycle in which the alternative flame retardants are evaluated regarding their environmental and toxicological properties, their flame retardant properties, and their influence on the function once incorporated in the product.

The main objectives of ENFIRO

- To deliver a comprehensive dataset on viability of production and application, environmental safety, and a life cycle assessment of the alternative flame retardants (FRs)
- To recommend certain flame retardant/product combinations for future study based on LCA, LCC and risk assessment studies

Which applications and flame retardants are studied?

Three FR/product combinations (e.g. metal-based, phosphorus-based and nanoclay-based FRs) in five applications (printed circuit boards, electronic components, injection moulded products, textile coatings, intumescent paints) are studied for:

- Environmental and toxicological risks
- Viability of industrial implementation
- Fire safety
- Application of the FR into polymers

The information is used for a risk assessment of the alternative FRs. The outcome of that assessment together with socio-economic information is used in a life cycle assessment. The ENFIRO approach and the results are useful for similar substitution studies, e.g. in REACH.

The ENFIRO Stakeholder Forum (ESF) with members representing FR users (e.g. formulators and users of FRs, waste(processing) plants) but also from other institutes like NGOs and policy-related ones, guide this project.

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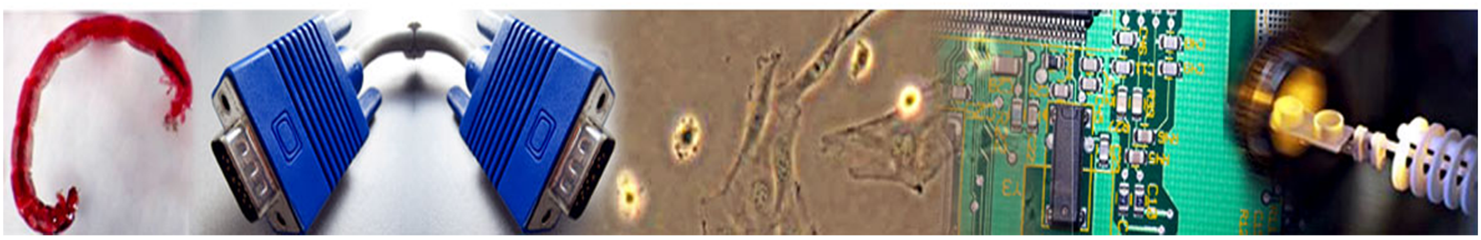

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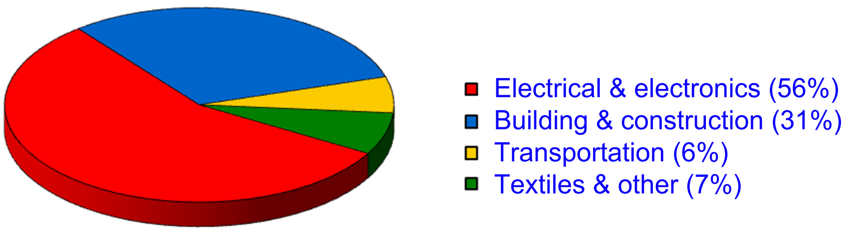
Newsletter 1 & 2

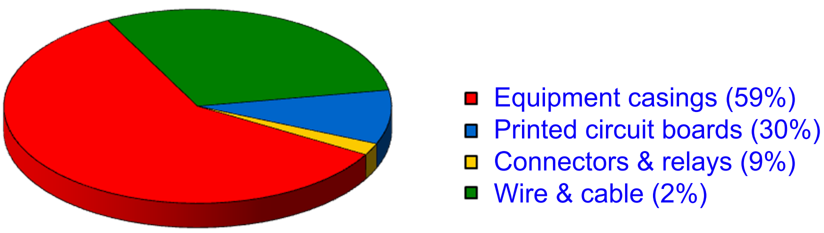
Choice of flame retardants, polymers and products

Recent regulatory and environmental pressures have led to increasing demands for safer flame retardants, particularly as alternatives to certain brominated additives, which find extensive use particularly in the electronics industry. Less toxic alternatives appear to be available already, but comprehensive information on their possible toxicological effects and environmental impacts are lacking. The ENFIRO project seeks to evaluate substitution options for the main types of brominated flame retardants in key application sectors.



EU Brominated Flame Retardant Use by Industry Sector. From European Plastics News Conference, Flame Retardants for Electrical Applications, Brussels on 5th - 6th March 2003.

The choice of flame retardants, host polymers and target end applications is based on a comprehensive review of technical and market literature. A range of commercially available halogen-free flame retardants, including systems based on phosphorus, nitrogen and various inorganic fillers and synergists, are being evaluated alone and in combination, in order to optimise cost – performance characteristics when compared against conventional brominated systems.



EU Brominated Flame Retardant Use in the Electronic Sector . From European Plastics News Conference, Flame Retardants for Electrical Applications, Brussels on 5th - 6th March 2003.

Polymers selected in the ENFIRO study represent the main types that currently utilise brominated flame retardants – engineering plastics such as PC/ABS and PPE/HIPS, both widely used in equipment casings, glass-fibre reinforced thermoplastics (PA66-GF and PBT-GF) for electrical switches, sockets and connectors, and epoxy resins, where brominated variants are the mainstay of laminated printed circuit boards and encapsulants for electronic components. Alternatives to brominated flame retardants are also being assessed in a typical cable insulation compound (EVA) and in textile back coatings.

Key end application prototypes will be subjected to a comprehensive technical evaluation and will be compared with performance given by traditional bromine-based systems. The applications selected for this study are printed circuit boards, electronic components, injection moulding products and textile coatings, all of which are major uses of brominated flame retardants at the current time.

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Results of the primary selection study of viable non halogated flame retardants in possible commercial future applications

The primary selection and prioritization of HFFRs was based on the ability of these HFFRs to make the actual polymer manage current fire requirements in addition to how the selected HFFRs affect the material's characteristics of the polymers that are flame retarded. Such characteristics include compatibility, electrical properties, and various ageing properties in addition to already available data on intrinsic toxicity, exposure risks and the environmental fate. Three common commercial brominated flame retardants (BFrs), TBBP-A, DecaBDE, and brominated polystyrene are reference substances in comparison to the HFFRs selected in this primary phase of ENFIRO.

Selected HFFRs

- Three common commercial aryl phosphates were initially selected as alternatives to BFRs in HIPS and polycarbonate (PC/ABS): these HFFRs were triphenylphosphate (TPP) , resorcinol bis (biphenyl)phosphate (RDP) and bisphenol A bis (biphenyl) phosphate (BDP). Due to identified hazardous intrinsic properties in the literature review of TPP, it was used as a hazard reference compound but was excluded for the fire performance and application studies.

- For epoxy resins used for printed circuit boards, dihydro-oxaphosphaphenantrene oxide (DOPO) and m-phenylene methylphosphonate (Fyrol PMP) were selected as HFFRs. These are used as a reactive constituent and regarded as the major building block used to make phosphorus containing epoxy resins.

- Aluminium-phosphinate belongs to a relatively new class of HFFRs, the so-called metal-phosphinates, that are well suited for glass fibre reinforced polyamides and polyesters. They can be used for rigid as well as flexible printed wiring boards (PWBs) and similar applications in this area since they are not hygroscopic and have very low solubility in water, which is important for electronic applications since water uptake is unacceptable in these applications. The selected HFFR application consist of aluminium-phosphinate together with melamine polyphosphate or zinc borate, anhydrous (Zn2B6O11) or zinc stannate (ZS), that act as synergists. Also melamine cyanurate is tested in reinforced polyamides.

- For polyethylene/ethylene vinyl acetate (PE/EVA) alloys used as a mantle polymer for cables and wires, the HFFR system selected was aluminium trihydroxide (ATH) together with nanoclay (organo clays based on montmorillonite) as smoke suppressant and additionally zinc hydroxy stannate (ZHS) or zinc stannate (ZS) or zinc borate (ZB) as synergists.

- An intumescent system was selected in ENFIRO for coated textiles and painted HIPS as alternatives to BFRs. Good intumescent systems are efficient to reduce flammability and the exposure of fume gases. In this specific ENFIRO case, the intumescent system consists of ammonium polyphosphate (APP), pentaerythritol (PER) and melamine polyphosphate.

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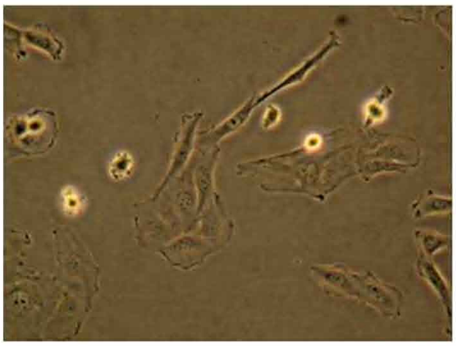

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Fire performance of alternative fire retardants

Brominated fire retardants widely used in polymers are known to a) produce excessive toxic gases in a fire and b) cause dispersion of toxic compounds to the environment upon disposal of polymer products. ENFIRO (FireSERT) examines experimentally and numerically the fire performance of polymers utilising alternative fire retardants in comparison with those utilizing brominated fire retardants. The novelty of our approach lies in determining intrinsic flammability properties that can be applied in modelling of fires in real and large scale situations which is not currently possible to do from LOI and UL94 tests. For this reason, the thermal stability and fire performance is investigated by a) thermogravimetric analysis (TGA) coupled with Fourier transform infrared radiation (FTIR) of gaseous products in microscale (mg quantities) and b) ignition and burning in the cone calorimeter in mesoscale (hundred gram quantities). The experimental plan and analysis has been completed for glass-fibre-reinforced poly(butylene terephthalate) (PBT/GF) materials retarded by a) brominated polystyrene combined with antimony trioxide and b) a phosphorus based flame retardant, aluminium diethylphosphinate (Alpi), with/without nanoclay (nano-MMT).

Experimental results

The extensive experimental results show that Alpi with nano-MMT has the best performance: a) it leaves twice as much residue in the TGA compared to brominated polystyrene, b) it emits fewer toxic compounds compared to brominated polystyrene as measured in FTIR and c) it achieves similar reduction in the heat release rate (HRR) as brominated polystyrene, but with much less smoke and carbon monoxide production. Currently, work continues with glass-fibre-reinforced Nylon 6-6.

Evaluation of test methods

We have also shown that LOI and UL94 results do not allow reliable and credible comparison of the burning and toxicity magnitudes for the examined fire retarded formulations of PBT/GF. For example, all fire retarded formulations achieve V0 rating in the UL94 test and LOI ratings that are inverse to the detailed burning characterisation from the TGA/FTIR/Cone analysis in our work. To probe the underlying physics of LOI and UL94 tests, numerical modelling work has also been carried out to (i) understand the mechanisms of UL94 and Limited Oxygen Index (LOI) tests and (ii) predict the burning intensities and toxicity of polymer materials in real and large scale tests. A novel approach based on extinction theory has been developed to predict the LOI values of the examined materials using their flammability properties as deduced in the present work such as critical mass loss rate at extinction or heat of combustion. For understanding and predicting the UL94 test, computational fluid dynamics (CFD) simulations were performed using the fire dynamics simulator (FDS), which will also be used for prediction of real and large-scale tests. One of the key challenges in CFD simulations is the determination of intrinsic flammability properties of real materials. This is done in this project by performing systematically well-instrumented experiments and using optimising techniques such as the genetic algorithm (GA).

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ENFIRO consortium:

VU University Amsterdam (coordinator), University of Ulster, Clariant Produkte (D) GmbH, IRIS Vernici s.r.l., Procoat, IVAM, Stockholm University, IRAS Utrecht, Swerea IVF AB, University of Amsterdam, Callisto Productions, and ITRI Innovation Ltd.

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