# Next-Generation Halogen Free Flame Retardants Based on Organic Waste

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## Abstract review

### Introduction

Halogen-based flame retardants (HBFR) for polymers are environmentally persistent, bioaccumulate and have chronic toxicity. Many have been banned and others are being phased out according to the San Antonio statement of the Stockholm Convention. Their replacements are often based on compounds with high phosphorus and nitrogen content (PN-FR), commonly called halogen free flame retardants (HFFR) (R. Sonnier et al, 2018). However, phosphorus is considered a critical raw material in Europe (EC, 2020) and hence it would be beneficial to develop flame retardants from renewable and waste sources. This can also provide a beneficial avenue to the valorisation and reuse of waste products. In this context, the European projects DAFIA and KARMA2020 projects were emerged.

#### DAFIA project

The main objective of the **DAFIA project** is to explore the conversion routes of municipal solid waste (MSW), and marine rest raw-materials (MRRM) from the fish processing industries, to obtain high added value products, such as flame retardants, edible/barrier coatings and chemical building blocks (dicarboxylic acids and diamines) to produce biopolymers for a wide range industrial applications.

As part of the DAFIA project, a novel bio-based halogen free flame retardant has been developed. This new flame retardant is based on spend liquor lignin (SSL), a waste product from the pulping industry coupled with bio-based nitrogen sources such as fish gelatine and other materials, such as ground fish bones containing hydroxyapatite as a phosphorus source. It is an effective flame retardant which meets the highest FR standards for the consumer electronics and automobile sectors, while maintaining mechanical properties at a competitive cost.

Beyond the state of the art, DAFIA aims to develop a new range of cost competitive and thermally stabilized flame retardants incorporating nucleic-acid rich waste extracts, using non-polluting routes (free of organic solvents, low temperatures, etc.). These will be used in fire-protection of polymers as an effective alternative to current market leader, *i.e.* commercially used phosphorus-based flame retardants.

#### KaRMA2020 project

On the other hand, the European Union produced 15.2 million tonnes of poultry meat in 2018 with an estimated generation of **3.1 million tons feather waste**. The majority of poultry feathers are currently converted into low value animal food or disposed of in landfills, causing environmental and health hazards. The **KaRMA2020 project** aims at industrial exploitation of this underused waste product to obtain keratin and valorise this as: bioplastics, flame retardant coatings, non-wovens and thermoset bio-based resins.

### Materials and methods

#### DAFIA project

The compounding of the polyamides with the FRs was made using a co-rotating twin screw, loss-in-weight feeders, vacuum degassing, and cooled in a water bath and cut to 3x3mm pellets in a conventional pelletizer. Then the material was injected in an ENGEL VC 200/50 TECH with 50 tons of clamping force and the test bars obtained for their characterisation. Thermal and mechanical tests together with cone calorimetry test were performed.

#### KaRMA2020 project

The keratin based FRs have been obtained by chemical modification of keratin with pulping waste lignosulfonate, amines and phosphates The FR formulation can be composed of >98% bio based material.

The best keratin-based formulations according to lab scale tests were scaled up (see Figure 1) and used at pilot scale (ca. 500m) in solvent based polyurethanes (PU) at 30% w/w for textiles coatings and in 2 component polyurethane paints.

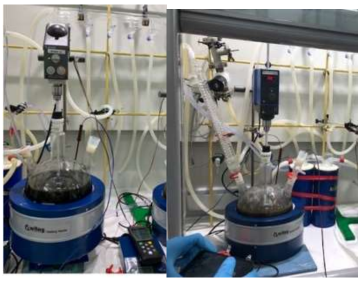

Figure 1: Equipment used for the scale-up of the of the FR at AIMPLAS facilities

The coatings for textiles were tested according to ISO 15025. The keratin-based flame retardants were also dispersed in the polyol component of 2 component PU paints. The polymerized flame retarded PU paint was characterised according to EN13501-2 for architectural market, including the UL-94 flammability test.

**Results and discussion**

**DAFIA project**

Effective bio-based flame retardants can be synthetized from MRRM thanks to the optimisation of the formulation and used in long-chain polyamides. By the proper selection of the smoke suppressant and impact modifiers it is possible to achieve promising FRs for industrial applications from waste, ensuring the lack of competitiveness with animal and human food chain.

**KaRMA2020 project**

The coatings for textiles showed excellent results in flame retardancy and water-fastness were obtained.

The flame-retardant PU paint characterised according to EN13501-2 showed a behaviour equivalent to commercial phosphorous-based flame-retardant PU paints (see Figure 2). Neither of them suffers flame propagation.

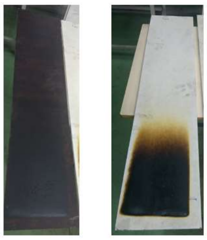

Figure 2. Left: keratin-based PU paint and Right: phosphorus-based PU paint

**Conclusions**

Different waste streams: municipal solid waste, marine rest raw-materials and feather waste from poultry industry, in addition to pulping waste, were valorised to obtain versatile flame retardants that were shown to be effective in a wide range of polymeric materials.

**References**


- R. Sonnier et al. (2018) Chapter 2. Biobased Flame Retardants. Towards Bio-based Flame Retardant Polymers, Biobased Polymers. DOI 10.1007/978-3-319-67083-6_2
- Internal Market, Industry, Entrepreneurship and SMEs <https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en>


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