FR GREENSI Report Summary

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Final Report Summary - FR GREENSI (New Si-based halogen-free flame retardants for greener plastics)

The use of low-cost, bio-based and highly flammable organic polymers is increasing in all product classes and is one of the major contributors to the increase in fire growth rate nowadays. This is leading to an overall greater use of flame retardants in polymer formulations. Growing pressure for increased product safety and health and environmental impact reduction is driving the development of innovative halogen-free flame retardant additives to replace the widely used brominated and in general halogen-based additives. This technical challenge is focused at flame inhibition, anti-dripping phenomenon, low smoke generation, low toxicity and corrosion when plastics are exposed to fire.

Currently, burning of polymer-based products is responsible for 25% of fire-caused injuries and property damage and for 40% of deaths. One of the major contributors to the increase in fire growth rate today is the difference in modern furniture and construction materials compared to those of 40 years ago. The total market for flame retardants in the United States, Europe and Asia in 2007 amounted to about 1.8 million metric tons and was valued at around 4.25 billion USD. Growing pressure for increased product safety complying with RoHS and REACh regulations and for health and environmental impact reduction, e.g. carbon footprint reduction, is driving the development of innovative HFFR additives, to replace the widely used brominated and, in general halogen-based FR additives.

This technical challenge is focused at flame inhibition, anti-dripping phenomenon, low smoke generation, low toxicity and low corrosion when plastics are exposed to fire. This Marie Curie Intra European Fellowship project 'New Si-based halogen-free Flame Retardants for Greener plastics' was focused on development of silicone based halogen free flame retardants for polycarbonate and polyamide matrices which are two of the most important, widely used thermoplastics in many commodity products and other applications.

Polycarbonates (PC) are a particular group of thermoplastic polymers. Polycarbonates received their name as they are polymers containing carbonate groups (-O-(C=O)-O-). A balance of useful features including temperature resistance, impact resistance and optical properties position polycarbonates between commodity plastics and engineering plastics. They have been used in electronic applications, construction materials, data storage, automotive, aircraft and security components and medical applications. Polyamide is a widely used engineering plastic containing monomers of amides joined by peptide bonds. Polyamides grouped in three main families according to their main chain as aliphatic polyamides, semi-aromatic polyamides and aromatic polyamides. Mostly used polyamides are aliphatic polyamides and the most common two members of this family are polyamide 6 ([NH-(CH2)5-CO]n) made from (epsilon)-caprolactam and polyamide 66 (NH-(CH2)6-NH-CO-(CH2)4-CO]n) made from hexamethylenediamine and adipic acid. They have been used in automotive parts, electrical/electronic devices (E&E), mechanical components, and many other industrial applications. Commercial applications of PAs in E&E include circuit breakers, relay switches, bobbing, and electronic parts for surface mounting technology (SMT) (connectors, jacks, switches, and power supply terminal), etc.

The first focus was the development of the halogen free flame retardant additives for polycarbonate matrix. Silicone resins and formulations based on them were developed in order to meet the new railway transportation standard EN45545 Fire Protection for Railway Vehicles, which will be replacing the individual railway standards of the each member state of EU and will be the only valid standard throughout the EU. EN 45545 standard will bring a set of tests to be performed for different components of railway transportation vehicles like high speed trains, conventional trains, metros and trams. One of the stringent test of this standard is concerning the measurement of MAHRE (Maximum Average Heat Release Emission) value via Cone Calorimeter. Also smoke density measurements Ds at 4min and VOF4 according to ISO-5659-2 are stringent requirements to meet. In order to meet the requirements of this standard, silicone resins having Si-P-X functionality in the form of white fine powder were produced.

These resins have a vinyl silane in combination with phosphorous functionality and presence of X element which could not be disclosed due to confidentiality and IP reasons. Different amounts of P and X was incorporated to the silicone resin and detailed optimization trials were performed. As a result, when used standalone, developed Si-P-X resin reduces the MAHRE value of polycarbonate 39% at 50 kW/m2 irradiation level when compared to neat PC. Besides this improvement, smoke density requirements of the standard were also met. These resins were also tried by a global polycarbonate producer in Netherlands, in combination with their current solutions for flame retardancy to observe whether there was a synergy and improvement or not. Promising results and good synergy was observed with their trials which confirm that these kinds of resins could be efficient and greener alternative flame retardants to be used for production of polycarbonate components which are meeting the EN 45545 standard.

The second focus of the project was developing silicone based flame retardant additives for glass filled polyamide 6. For the moment main halogen free flame retardants for polyamide are almost all phosphorous based additives. Although those additives are very effective, they have some drawbacks like, reduction of mechanical properties, corrosion of processing equipment due to formation of phosphoric acid species, bad performance in some of the electrical tests like CTI. So, phosphorous free solutions are also in wide interest. Even though there are some phosphorous free solutions available, high amount of loadings required to have a desired flame retardance performance. Polyamide 6 is widely used in electric and electronics applications and one of the main benchmark of these applications is the Underwriter Laboratories (UL) UL-94 test. This test measures the flame retardance performance of a rectangular prism sample at different thicknesses, placed vertically and exposed to flame from the tip and based on the timing of the self-extinguishment and dripping of the material. There are several ratings available for different behavior of the material when exposed to flame.

The best rating is the V0 rating at which the material extinguishes after the both of the flame applications and also no dripping will be observed. Currently, V0 rating at 1.5 mm thickness could be achieved by using 15-18%wt. of aluminum diethyl phosphinate based solutions in the market. The drawbacks of the phosphorous based additives were mentioned above so while a new additive for glass filled polyamide was being developed, we avoided incorporating phosphorous to the formulations. Various silicone based additives were tried standalone and in combination with synergists and co-additives like talc, zinc borate, melamine cyanurate, organically modified clays, etc. Different functionalities were incorporated to the silicone. After a long set of trials firstly a V1 UL-94 rating at 1.5 mm thickness and then V0 rating at same thickness was obtained at 30% glass filled PA6.

The chemical composition of the silane could not be disclosed for the moment due to the confidentiality and on-going patent filing procedure. The silane loading was 15%wt. Co-additives were talc, zinc borate and melamine cyanurate. The total loading of the additives including silane were 25 %wt. Throughout this project, the aim was to develop halogen free greener flame retardants based on Si for two widely used thermoplastic matrices. There are very few studies on silicone as a flame retardant material and we hope this study could be a valuable contribution to the literature and the results would be a light for future studies and commercially available products which could make a positive impact for the EU's incentive to usage of greener materials for the future of Europe and the World. The policy makers and governments should continue supporting the activities for greener materials for a sustainable development and cleaner future.

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