3rd PROGRESS REPORT PUBLISHABLE SUMMARY

Grant Agreement number: 310187

Project acronym: PHOENIX

Project title: Synergic combination of high performance flame retardant based on nano-layered hybrid particles as real alternative to halogen based flame retardant additives

Funding Scheme: Collaborative project targeted to a special group (such as SMEs) FP7-NMP-2012-SME-6

Date of latest version of Annex I against which the assessment will be made: 15/10/2013

Period covered by the Progress report: from month 37 **to** month 48 (January to December 2016)

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[1] The home page of the website should contain the generic European flag and the FP7 logo which are available in electronic format at the Europa website (logo of the European flag: http://europa.eu/abc/symbols/emblem/index_en.htm logo of the 7th FP: http://ec.europa.eu/research/fp7/index_en.cfm?pg=logos). The area of activity of the project should also be mentioned.

PUBLISHABLE SUMMARY

Summary description of the project context and the main objectives

The most conventional fire retardants are halogen-based compounds, due to the low price and the capability to enhance fire-retardancy of polymers without degrading their physical properties, such as impact strength. They have the 30% w/w of the current FR market. However, toxic species such as dioxins and furansi, which are generated during the combustion of halogen-containing composites, could cause serious environmental contamination.

Therefore, developing halogen-free, low-smoke generating, and environmentally-friendly fire retardant composites has become increasingly important in recent years, based on a diverse range of chemicals classified as: 1) Inorganic hydroxides, such as Al(OH)3 and Mg(OH)2, representing 57% w/w of the market, 2) Phosphorus based organic and inorganic phosphates and phosphonates (8% w/w of the market), 3) Nitrogen based: typically melamine derivatives (3% w/w of the market).

In the industry, a combination of them are also employed. However, high levels of loading (30-60 wt%) are required, leading to additional costs, processing difficulties and a decrease in physical properties of polymers. Hence the development of new highly effective, “green” fire retardants has prompted much attention during the last decade.

PHOENIX flame-retardants were produced via a water-based sustainable production method exploiting the capacity to form, by self-assembly technology, “nanoplatellets structures” by a synergic combination of different types of nano-layered nanoparticles, hollow nanoparticles (containing organic phosphonates or melamine phosphate) and modified lignins with different fire retardant mechanism.

To minimize the amount of required FR and to enhance the dispersion of the nanoparticles in the thermoplastic resins, different technologies were investigated and optimized such as Nanodirekt compounding, ultrasound and static mixers in the injection unit and multilayer co-extrusion and co-injection. Moreover, the incorporation of developed FR was also incorporated in epoxy resins, in order to study the compatibilization and content needs for this kind of thermoset materials.

The main industrial sector in which PHOENIX developments will have major impact is the Electrical and electronic (E&E) sector, including housings, wire and cable, and internal parts such as connectors. The E&E is the largest market for flame retardants (FR) in plastics globally; the total EU plastics demand being estimated around 2.6 million tons in 2010. This demand is expected to grow, as the need for FR is increasing due to electronics miniaturization and higher usage temperatures. As E&E parts become smaller and thinner, FRs must withstand higher processing temperatures without compromising the thermoplastic material's flow and mechanical properties. As described in the Impact section, PHOENIX developments on low-voltage electric wires and injected and extruded thermoplastic parts will have impact not only to the E&E sector, but also to all other industrial sectors making use of them, such as household appliances, automotive, computers, white goods, construction, among others.

PHOENIX main **objectives** to fulfil the requested fire safety standards were:

1)**Producing sustainable flame retardant nanoparticles** that can be acceptable in terms of industrial hygiene, consumer safety, and environmental impact. The solvents employed were mainly based in water and the products involved are inorganic salts from natural sources. The synthesis was based in pH changes and the use of templates to model the size and shape of the nanoparticles. The templates employed were non-toxic and natural organic compounds such as lauryl sulphate or urea. Nanoparticles fulfil the safety and health test according the current state of the technique.

2)**Nanotechnology approach.** Self-assembly molecules (SAM) technology was used to functionalize nano-layered FR particles and form ordered nanostructures, as a new approach to develop functional nanocomposites with enhanced FR properties.

3)**New FR additives from renewable source** based on modified lignins with synergic effect with proposed nano-layered FR particles. Lignin were modified to incorporate non-polar groups (to improve polyolefin compatibility) and various phosphorous- and boron-containing reagents to increase their fire retardancy capacity. Base lignin was a by-product of the paper industry.

4)**Reduction of FR content.** A maximum 15% w/w FR content compounds produced thanks to the use of different types of nano-layered particles and organic phosphonate placed in ordered structures. The synergy is achieved by a combination of silica encapsulated phosphonates with different fire-action nanoparticles (metallic hydroxides and graphenes). This reduction of FR needs will be also achieved by innovative processing technologies (objectives 5, 6 and 10).

5) **NanoDirekt Process** contributes to improve nano-layered flame retardant dispersion without aggregation because water removing is not required for twin screw extruder feeding. This new technology contributes to a cost reduction compounding process and a reduction of the necessary amount of FR additives to fulfil the proposed requirements.

6) **New module for *Ludovic* software** was specifically developed to simulate nanofilled FR thermoplastic compounds.

7) **Good processability in conventional plastic production equipment,** thanks to the particular characteristics of the self-assembled nanoparticles that will provide a suitable matrix-nanoparticle interaction and the capacity to improve the nanoparticles dispersion of standard machines by using ultrasound devices and static mixers.

8) **Competitive cost, less than 20% cost increase regarding current HFR compounds** and cost competitive in comparison with currently available non-halogenated FR, but improving the final properties

9)**Processing routes using multilayer co-extrusion** (in wire and thermoformed parts) and co-**injected** (housing parts) **structures,** to create a protective layer by maximizing the amount of the FR additives in the skin layer and reducing the percentage in core, depending on the application**,** without reduction of FR and mechanical performance of the final part**.**

10) Development of a **stable epoxy pre-pregs** containing FR nanoparticles that fulfil the fire requirements in the electric-electronic industry (mainly household appliances). Commercial fireproof halogen free formulations of epoxy resins are based on ammonium polyphosphate, organo phosphorous and Aluminium hydroxide.

11) **Increase mechanical and thermal properties in comparison with HFR by at least 10%** for the selected materials.

12) **Fully recyclable compounds**, up to a 30% of recycled materials will be added to the virgin material without significant loss of mechanical properties (less than 10%).

13) **Methodology development and standardization** of quick or in-line test to evaluate the fire resistance of develop compounds.

14) **Positive environmental impacts** (by a LCA preparation in accordance with the ILCD handbook), in comparison with non-halogenated flame retardants formulations.

15) **Technical, performance, health, environmental and economic factors** must be duly considered in the justification of the choice of the optimum novel flame retardant material for the selected applications.

Description of the work performed since the beginning of the project and the main results achieved so far.

WP1

Task 1.4 is active during the whole project. The objective consist of evaluating the technical risk and prepare a contingency plan if needed. WP leaders revised the risks before the last general assembly.

WP2

The main objective of WP2 is the development of suitable halogen-free flame retardant (FR) systems for different thermoplastic and thermoset resins selected in the project. To achieve this aim, new procedures and technologies for the production of new, green and economic feasible nano-sized materials and different functionalized substances on the basis of lignin are being established.

The work done has been divided in three blocks, which are related with the specific objectives proposed at the beginning of the project: a) synthesis of nanoparticles with flame retardant properties, b) functionalization of those nanomaterials with self-assembly processes and c) preparation of FR lignins. All partners involved in WP2 (AIT, TUD, FhG-LBF and ENSCL) have been working on those tasks during this period M37 – M48, specially focusing on working at big scale, to obtain enough quantity of the requested products.

WP3

ENSCL, AIMPLAS, FhG-ICT, Bada and ALFA worked on the development of new flame retardant systems to evaluate phosphorylated lignins and graphene and synergist of commercial ammonium polyphosphate aiming to achieve better performance and lower content of flame retardant in the final material. Polymers studied were HDPE, PP, HIPS and ABS.

AIMPLAS produced cable formulations for Revi and ALFA produced compounds for Revi, Artic, Akumplast and Arcelik.

WP4

WP4 work for the last period of the project consisted of demonstrated that the US equipment developed was suitable to improve the dispersion of FR nanoparticles within the polymer matrix. This work was carried out by FhG-ICT and A&E.

AIMPLAS and FhG-ICT worked in the co-extrusion and co-injection trials with new developed compounds to validate the good result previously obtained with commercial materials. Monolayer and bilayer sheets extruded at AIMPLAS were sent to ENSCL for MCL testing. FhG-ICT produced the compounds and co-injection trials are being performed in September.

Regarding pre-pregs developments, Vonroll worked in the optimization of the FR formulation and production method to optimize the properties of the pre-pegs.

WP5

WP5 aim for the last period of the project consisted on the industrial validation of the FR materials producing demonstrators by the industrial partners. The demonstrated were analyzed to compare the properties achieved with the requirements involved in each application.

REVI, Arcelik, Akumplast, Polyraz and Artic worked on this tasks. The interaction with the previous WPs was very important in order to transfer the knowledge from research centers and compounders to the final material producers.

WP6

The aim of the WP6 in the PHOENIX project is to conduct an environmental and economic impact study of the new selected nanostructured materials and modified lignin's FR and processing throughout each stage of development to ensure compliance with legislation and to maximise market acceptance and to study the environmental suitability of the FR compounds by a Life Cycle Assessment (LCA). To assess the economic viability of the product, and to ensure that the new material and their processing technology fulfils related legal requirements, a technical and economic evaluation will be developed to establish innovations and economic viability and to demonstrate that PHOENIX developments, comply with Health and Safety. Regarding the regulatory analysis for the last period of the project, AIMPLAS studied the compliance of new FR materials with REACH regulation. FhG-ITEM worked on completion of characterization and testing of the (geno)toxic and pro-inflammatoty potential of the five technologically most promising flame retardant (FR) (nano)materials. As cell culture models primary rat alveolar macrophages (AM) and the primary human lung fibroblast cell line MRC-5 were used to look for cell type-specific difference in biological response. For the least (Mg1) and most biologically active (GR1) nanomaterials, concentration-dependencies were investigated. As phosphorylated lignin (LigninP) seemed to exhibit promising FR potential, the (geno)toxic potential of LigninP was also investigated in AM, although not originally planned, together with uptake experiments in AM.

WP7

WP7 aim during the last period of the project was focused on ensuring the technology transfer from RTDs to industrial partners to ensure the future industrialization of PHOENIX materials. The second PHOENIX workshop has been organized. This workshop is going to be focused on the applications of the materials developed. Therefore, it was decided to wait until next year and join a flame retardant conference organized by AIMPLAS. Even there is no funding for 2017 PHOENIX partners will do the workshop as it was not possible to find a good forum to show our developments at the end of 2016.

Final version of the PUDF has been prepared.

Technology watch for aspects related to PHOENIX has been active during this period. Although limited because of the results' achievement, partners have been actively performing different dissemination.

Expected final results and their potential impacts and use

The PHOENIX workplan was focused on providing solutions to the real needs of the Industry regarding flame retardants (FR): finding a true alternative to existing halogenated FR which allows simultaneously a significant improvement of mechanical properties, currently hindered with the existing non-halogenated flame retardants available in the market.

A strong interaction between the whole SMEs partnership/industries and research organisations ensured the complementary fields involvement along the project implementation. The participation of end-users guaranteed high impact and the wide dissemination & exploitation of the project results at National and EU level. The achievement of the results represented a significant advantage to the SME and End User participants demanding halogen-free FR materials to manufacture high-performance parts.

The impact of PHOENIX project affects nanoparticles producers (synthesis and functionalization), compounders, thermosetting parts manufacturers, sheet extrusion, thermoforming, software & machine manufacturers and injection moulders.

The expected impacts regarding to different segments of the value chain directly represented in the project are:

- Nanoparticles producers (AIT): Production of graphene as FR synergist for thermoplastic compounds, technology that can be adapted to new markets in order to optimize their adhesion to different plastic matrices. Production of PH1 mod encapsulated particles for thermoset resins and low temperature thermoplastic polymers (HDPE)

- Compounders and thermoset formulations (ALFA, BADA, VONROLL): Production of graphene as FR synergist for thermoset and thermoplastic composites. Use of PH1mod for thermoset resins and low temperature thermoplastic polymers (HDPE)

- Plastic processors (AKUMPLAST, POLYRAZ, REVI): will develop an optimized process to produce more innovative and environmentally friendly products with better properties production of FR synergist for thermoplastic compounds and competitive price. Reduced costs, sustainable products and an increased and differentiated portfolio will result in a higher turnover. Using FR material at the skin of the co-injection and co-extrusion processes; this results with

- Compounding simulation Software: LUDOVIC manufactured by SCC is adapted to new FR materials

- End users (ARCTIC, ARCELIK, REVI, AKUMPLAST, POLYRAZ): will be able to differentiate from competitors by introducing a new line of products employing sustainable FR plastics with better properties. They will improve their environmentally-friendly image by using the new materials containing lignin from biowaste, helping them to increase their business.

- Academic and Research centers (ENSCL, FhG-LBF, TUD): further research is also available with the promising results of the FR behavior in ABS and ,phosphorylated lignin at lab scale.

The sector addressed in PHOENIX project was E&E appliances.

The developed PHOENIX materials may be suitable for other application sectors.

Taking this facts into account, PHOENIX partners have identified the following applications in which the developed compounds could be competitive:

1. Transport
2. Building and construction
3. Upholstered Furniture and Textiles
4. Electrical and Electronic Devices

Figures:

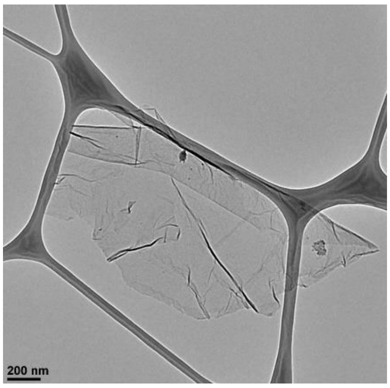
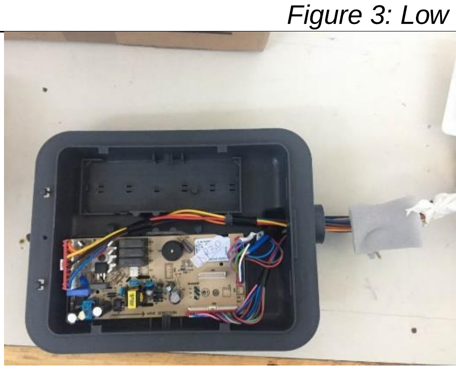
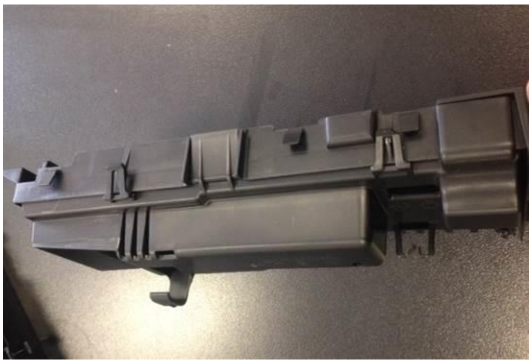


Figure 1: Graphene monolayer

Figure 2:Optimized dispersion of graphene compounds (compression moulded discs)

Figure 3: Low voltage extruded cable

 *Injected card box*	 *Injected battery box*

 *Card holder for washing machine*	 *Card holder for refrigerator*