

<i>ECOFRAM 2018.....</i>	<i>1</i>	<i>Ageing and weather resistance.....</i>	<i>4</i>
<i>PIN flame retardants for 3D-printing.....</i>	<i>1</i>	<i>Lignin and tannin as flame retardants.....</i>	<i>4</i>
<i>Innovative flame retardancy applications.....</i>	<i>1</i>	<i>Ecological flame retardant textiles and composites.....</i>	<i>5</i>
<i>Smoke toxicity.....</i>	<i>2</i>	<i>Fire safety treatment of wood.....</i>	<i>6</i>
<i>Green chemistry and chemical substitution.....</i>	<i>3</i>		

ECOFRAM 2018

ECOFRAM 2018, the second International Conference on Eco-Friendly Flame Retardant Additives and Materials, took place in Metz, France, 28-29 March 2018. The first ECOFRAM conference (2016) is summarised in pinfa Newsletter n°65. Over 70 researchers, companies and experts met at ECOFRAM 2018 and discussed flame retardant solutions for bio-based polymers, fire safety and environmental impacts and smoke toxicity of flame retardants, and bio-based or naturally sourced flame retardants. <https://ecofram2018.com/>

The next ECOFRAM conference will take place in 2020 in Southern France (Nîmes – Montpellier region).



PIN flame retardants for 3D-printing



José-Marie Lopez-Cuesta, C2MA Mines d'Alès, France, outlined the importance of developing performance flame retardants for 3D printing. 3D printed objects show high fire risk, because objects are often thin wall but also because tests show that the 3D printed polymer is itself porous (includes air). Tests have shown lower time to ignition and time to peak heat release but similar total heat release for 3D printed PLA objects, compared to the same object produced by injection molding. To be effective, FRs must be mixable with the polymer pellets used to obtain 3D printing filaments. PIN FR combinations of ammonium polyphosphate, melamine and nanoclays (montmorillonite and sepiolite) showed in tests to improve fire behaviour of 3D-printed PLA, but without achieving UL94 classified performance.

Innovative flame retardancy applications



Alexis Chopin, Eurostar Engineering Plastics, presented radiation-activated cross-linking processes which can improve polymer heat stability and fire performance. In addition to reducing polymer decomposition and improving heat resistance, cross-linking modifies char characteristics. A combination of cross-linking and PIN organo-phosphorous flame retardant in polyamide enabled to achieve UL94-V0 (0.4mm) and EU railway EN 45545 smoke emission R23 HL3. Eurostar now offer PIN-FR radiation crosslinkable polyamide both with and without glass fibre reinforcement.



Severine Bellayer, UMET/ISP Lille, presented tests of sol-gel application to polyurethane foams of phosphorus and silicon based flame retardants (DEP, APTES, TEOS), showing a 1/3 heat release rate reduction. Bio-sourced molecules (adenosine triphosphate, chitosan, cysteine) were tested as replacements for DEP, but showed to be less effective.



Andy Goodwin, First Graphene Ltd., Perth, Australia, presented the company's large platelet graphene product (20-40 μm), mined in Sri Lanka and processed by exfoliation. This graphene has been tested, in combination with inorganic PIN flame retardants, as a fire protection surface treatment for e.g. paper and wood. It functions by generating an intumescent char layer, acting as an oxygen barrier and also limiting toxic gas release in fire.



Bansi Kaul, MCA Technologies, presented the company's triazine products (see previous pinfa Newsletters: 61, 72, 76, 80). He considers that these can act in synergy with various PIN FRs including metal hydroxides, calcium carbonate, kaolin and organo-phosphorus FRs.

Hans-W. Marx, Linseis Messgeräte, presented different methods and equipment for thermal conductivity measurement in fire testing, underlining the need to take into account that thermal conductivity changes in samples with temperature and with polymer decomposition.

Smoke toxicity



Anna Stec, UCLAN (University of Central Lancashire), UK, gave her vision of smoke toxicity from fires involving today's synthetic materials (see summaries of her recent papers in pinfa Newsletters n° 85 and 87). She noted that accidental fires disperse toxicants by three pathways: gaseous molecules, condensing of gas phase pollutants onto soot, and toxicity in residual ash. Smoke toxicity depends on fire development (well ventilated or oxygen deprived conditions), presence of heteroatoms, such as Cl, Br, N, S, Sb in burning materials, and emission of organic toxicants from incomplete combustion. She said that the importance of hydrogen cyanide (HCN) in fire fatalities is often underestimated: HCN is 35x more lethal than carbon monoxide (CO) and rapidly causes unconsciousness. However, HCN is less stable in bodies than CO (so is not identified post-mortem), whereas exposure to CO is measurable after death (as carboxyhaemoglobin).

Anna Stec summarised tests showing high toxicity from polyamides and polyurethanes (PUR and PIR) in under-ventilated fires, because nitrogen in the polymer generates HCN. Presence of brominated flame retardants increased this toxicity (in PA6) more than did the PIN FR tested (AlPi). Also in tests in cables, PIN FR cables showed lower smoke toxicity than halogen-containing cables. Anna Stec also summarised recent studies showing skin contamination by chronic smoke toxicants (e.g. poly aromatic hydrocarbons) under fire fighters' protective clothing, after exposure in fire interventions.

For these reasons, she considers that smoke toxicity regulation should be introduced in Europe for construction products. She notes that in the recent EU study on this question (for the Construction Products Regulation CPR, see pinfa Newsletter n°89) five countries replied to EU questions stating that they already have existing regulations on the toxicity of smoke from construction products (Belgium, France, Lithuania, Poland and Sweden). This report recognised the need to address the issues associated with fire toxicity of smoke produced by building contents when toxic smoke is leaking into or being generated in areas that are considered to be escape routes or safe zones.

pinfa editor's comment: to our understanding, of the five countries stating to have construction products smoke toxicity regulation, the information in the report suggests that two regulate smoke toxicity (Lithuania = ISO13387, Poland = PNB-02855) and the other three limit smoke emission or corrosivity. The report also notes that London Underground Fire safety performance requirements 1-085 refer to the toxic fume test B2 in Annex B of BS 6853.



Green chemistry and chemical substitution



Jonathan Crozier, pinfa Sector Group manager, Cefic, and **Chris Thornton**, consultant, explained that PIN flame retardant fire safety solutions are essential to support EU objectives of bio-economy, sustainability (especially sustainable construction materials), circular economy and social inclusion. PIN FRs can be sourced from natural materials, from bio-sourced or from recycled materials. Selection of PIN FRs with optimal health and environmental profiles can limit obstacles to future plastics recycling currently posed by “legacy” halogenated FRs.



Manfred Döring, Fraunhofer LBF, outlined how “green chemistry” principles can be applied to bio-based flame retardants. Base natural materials should preferably be hydrophobic, thermally stable and enable bonding of functionalities. Bio-molecules such as tartaric acid, phytic acid, glycerine and pentaerythriol have such characteristics. Bio-polymers can offer stable, non-migrating solutions which are compatible with material polymers. He presented tests using DOPO (phosphorus PIN FR) reacted onto bio-based acrylate polymers in polyamide.



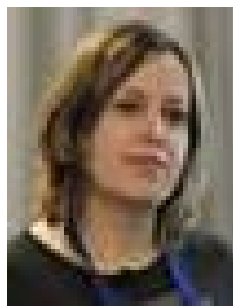
Ine De Vilder, Centexbel, presented the LIFE-FLAREX project (see pinfa Newsletter n°90) which is assessing alternative flame retardants for textiles, compared to brominated FRs, with and without ATO (antimony trioxide). The project has selected, amongst others, a number of phosphorus-based PIN FRs and will assess the technical performance (application to textile, impacts on textile properties) and toxicity (skin absorption), enabling comparative risk assessment. Furthermore, a LCA study will be performed on all FR treated textiles.



Hakan Kanli, Etimine SA, Turkey, outlined challenges for the future of borates as flame retardants. Borates are natural, mined minerals: sodium borate (tincal), colemanite (calcium borate) and sodium-calcium borate (ulexite). Boron is on the EU list of Critical Raw Materials (CRMs) because it is essential for certain industries (i.e. 73% of boron use is in glass and ceramics, 15% in fertiliser) and Europe is dependent on imports. Around ¾ of global boron reserves are in Turkey. Most of the borate chemicals used in flame retardants - except zinc borate, which is not today classified - are included in the list of SVHC (Substance of Very High Concern), due to their harmonised classification as Cat. 1B for reproductive toxicity. Industry however considers boron compounds should be classified only as Cat. 2 for reproductive toxicity. There is no restriction for borates for industrial and/or professional uses and there is also possibilities for consumer uses through the specific concentration limits assigned to borates individually. Borates have been “postponed” from the REACH Annex XIV Priority List because of the complexity of dispersive uses and consequent difficulties to define Authorisation procedures.



Rodolphe Sonnier, IMT Mines d’Alès, France, presented studies of smoke emission for different polymer / flame retardant combinations, plotting the smoke production rate versus the heat release rate. He shows that smoke emission is related to the aromaticity and to the carbon fraction in the polymer. In EVA, the inorganic PIN FRs ATH and MDH show lower smoke production per kg polymer consumed compared to neat EVA. In polyethylene, smoke production per kg consumed is higher with DOPO (phosphorus-based) and TBBA (brominated) FRs.



Carine Chivas-Joly, LNE (French National Laboratory of Metrology and Testing), presented tests of incineration of EVA cables containing mineral nanoparticles: aluminium oxide hydroxide (boehmite) and alumina. The tests show that nanoparticles are present after incineration in both soot and ash, but that the form is modified: particle size increases in soot and decreases in ash. Also, boehmite, which is non cyto-toxic as used initially, develops low levels of cytotoxicity after incineration, and cycto-toxicity of alumina also increases in fire.



Toussaint Barboni, University of Corsica Pascale Paoli, summarized studies of smoke toxicity from forest fire smoke. Among the compounds emitted during a forest fire, there are gases, VOCs and aerosols. The major compounds emitted are CO₂, H₂O, CO, NO_x and aerosols. The main tars component is levoglucosan, from cellulose degradation. Soots are small particles smaller than 1 µm and penetrate deep into the bronchi. Toxicants compounds include: benzene, polyaromatic hydrocarbons (PAH), phenol, alkanes, aldehydes (formaldehyde and acrolein), ketones and alcohols, as well as gaseous toxicants including nitrogen oxides and carbon monoxide.

Ageing and weather resistance



Jean-Luc Gardette, Clermont-Auvergne University, France, discussed the challenges of ensuring that weathering, and in particular ultraviolet radiation (UV), does not deteriorate the properties of flame-retarded polymers. Deterioration is generally related to the polymer itself rather than to additives. Interactions with UV absorbers, anti-oxidants and catalyst-deactivation also need to be verified. PIN effervescent FRs have been shown not to deteriorate polypropylene (PP), nor to interfere with HALS (UV stabilisers). On the other hand, certain nanoclays showed to accelerate PP deterioration, probably because of metal impurities present in the grades tested.



Rémy Mangin, Lorraine University, France, demonstrated the difficulties of developing reliable formulations with PLA (poly lactic acid). Testing included combinations with PMMA polymer (poly methyl methacrylate = Plexiglass) and PIN FRs (ammonium polyphosphate and sepiolite nanoclays). Flame-retarded PLA shows deteriorated physical and fire properties after a few weeks of humidity ageing. This is significantly mitigated in a 50%/50% PLA/PMMA blend, showing a positive effect of incorporation of PMMA in PLA.

Lignin and tannin as flame retardants



Fouad Laoutid, Materia Nova, Belgium, presented tests of several bio-based FRs in PLA (poly lactic acid). Lignin grafted ammonium phosphate groups enabled to achieve V0 (3mm) but lignin poses challenges because of high variability between different plant origins and different extraction methods. Phosphorus-grafted tannic acid (1.75%P) in PLA (polylactic acid) reduced peak heat release rate by 1/3, but poses issues because it can decompose the polymer. Phytic acid, a liquid bio-sourced molecule containing phosphorus, could not be used in PLA because of migration issues. A new FR agent, based on a combination of polyethyleneimine – tannic acid and phytic acid has been developed and enables overcoming the problems induced by these compounds when used separately. Its incorporation in PLA generated an intumescent, porous char and reduced PHHR by around 50%. Analysis showed that the phosphorus remains in the residue and is not lost in the fire gases.



Valeriia Karaseva, IMT Mines Alès, France, presented tests of using tannins and their borate derivatives in epoxy resin. The latter are produced by the reaction of gallic and ellagic acids with boric acid. The incorporation of these molecules in epoxy resin helps to increase char content and reduce peak of heat release rate by 30%.

Benjamin Chollet, IMT Mines Alès, France, tested different lignins as flame retardants in PLA (polylactic acid). Micro size lignin particles showed better char production (up to 11.5%) and better total heat release THR decrease (up to 19%) than nano scale, and phosphorus functionalised lignin did not show significantly better fire performance.



Stéphane Giraud, ENSAIT-GEMTEX Roubaix, France, presented experiments using zinc phosphinate and alkali draft lignin as additives in polyamide PA11 fibres. Comparatively to neat PA11 fibers, mechanical performance of composite fibers (at 20% loading) was preserved. The fire reaction of textile with the composite fibers is improved with the increase of time to ignition regarding PA11 textile but without any significant decrease of heat release. This demonstrates the complexity of finding effective PIN FR – polymer combinations with bio-sourced materials.

Ecological flame retardant textiles and composites



Marc Vanhoomissen, Veramitex SA, Belgium, presented the LIFE-FARBioTY project: Fire and Ageing Resistance Biocomposite for Transportation industry (see pinfa Newsletter n°83). This project aims to develop new composite materials based on renewably-sourced flax fibres. Epoxy and polyester resins are being tested with flax fibres and THPC + ammonia treatment for flame retardancy. This is a classical textile process, in which the chlorine is removed in the process, leaving a phosphorus-nitrogen flame retardant treatment. Results to date show that treated flax can achieve M1 fire performance, similar to glass-fibre based products. Besides, the impregnation of resins is much easier after flame retardancy treatment. Further testing of ageing, weathering and UV resistance are underway.



Giulio Malucelli, Politecnico di Torino, presented experimental studies of bio-based PIN materials as flame retardants for cotton fibres. Bio-based materials tested include dairy-derived whey proteins and casein protein (S+N), chitosan protein (C, N), hydrophobin proteins produced by filamentous fungi (S+N) and nucleic acids (C, P, N). Tests show that low molecular weight nucleic acids (which are less expensive) are effective. LBL (layer-by-layer) deposition of 20 alternate layers of chitosan and nucleic acids rendered cotton textile self-extinguishing, including after washing (durable), without deteriorating fibre mechanical properties. This is considered to be because chitosan is negatively and nucleic acids positively charged, enabling LBL deposition, and chitosan reacts to a 3D network ensuring durability. Scale up is now being studied to reduce costs. See also pinfa Newsletter n°84.





Sebastian Rabe, BAM Germany, summarised research testing of a Novamont thermoplastic starch – polyester blend polymer with various natural fibres as filler material (industrial processes wastes from various Mexican industrial sectors): keratin fibres from bovine skin hair during leather tanning, coconut, blue agave and henequen agave fibres. These were tested with different PIN FRs: ATH (aluminium tri hydrate), APP (ammonium polyphosphate), expandable graphite. In some cases, the fibre showed synergistic fire performance with the PIN FRs. 10 wt.-% APP and 20 wt.-% fibre achieved UL94-V2 (3.1 mm) and achieved a lower PHRR and THE in cone calorimeter than 30 wt.-% APP alone.



Roland El Hage, Lebanese University, presented experiments on PIN fire safing of a mixture of bio-sourced miscanthus fibres and recycled textile fibres, intended as sustainable construction insulation materials. Chitosan polysaccharide based binder and aluminium hydroxide (ATH) PIN flame retardant were tested, showing good surface adhesion to the fibres and achieving Euroclass E (“non flammable”) with 3.5% total fillers loading. No significant deterioration of mechanical properties were observed and good thermal insulation values were achieved.



Maude Jimenez, University of Lille, France, presented experimental development of a single-step coating method to fire protect polycarbonate, to replace the current coating methods usually involving three layers: adhesive, base and topcoat. Spray-on self-stratifying epoxy resin / silicone coatings were tested with the PIN FRs: RDP (bis(diphenyl phosphate), iron oxide Fe_2O_3 and calcium carbonate. Presence of iron oxide and calcium carbonate, which probably modifies the structure of the silicon network, allowed achieving UL94-V0 (3mm) at 2.5% FR loading (within a 50µm coating). Fire performance showed to be resistant to UV and ageing. Life cycle analyses of this one pot process and of the three-layers processes were compared, showing improved environmental impact for the one-step process.



Raymond Hajj, Lebanese University / IMT – Mines Alès, presented experiments in binding phosphorus FRs to flax fibres by impregnation and radiation fixing. Vinyl phosphonic acid showed to be effective, using water as the impregnation solvent. Radiation breaks the compound’s carbon double bond, so fixing into the flax fibres. Flax fibre textile was rendered self-extinguishing with > 0.5% phosphorus loading, but the temperature of thermal degradation of the fibres was significantly reduced.



Fire safety treatment of wood

Laia Haurie, Universitat Politècnica de Catalunya, presented tests of resin-impregnation of wood, with the objective of developing flame retarded wood-plastic composites. Two phosphorous flame retardants were added to an unsaturated polyester resin and compared with a chlorinated unsaturated polyester resin. Wood samples were impregnated in a vacuum and pressure process in an autoclave and cured by means of gamma-radiation. The wood plastic composites tested exhibit an improvement in some properties, such as mechanical behaviour. The phosphorous-based resins promote charring, but their fire performance is lower than for the chlorinated resin. Both resin-impregnated woods showed higher smoke emission than non-impregnated wood, with higher smoke production from the chlorinated resin.



Osman Emre Özkan, Kastamonu University, Turkey, presented testing of a process to fix inorganic PIN FRs in wood to reduce leaching in outdoor construction applications. Pine wood was impregnated with aqueous solution of the FRs (diammonium phosphate, borax, boric acid) and glucose, then heated at 120-180°C for fixing by polymerisation. Results show that the fixed PIN FRs slow the decomposition of wood in fire, and reduce leaching of phosphorus.