

Environmental challenges	2	Oliver Steffen Henze, BASF Polyurethanes GmbH	9
Phosphorus FRs	2	Innovative FRs for textiles and fibre-compounds	9
Research into bio-based PIN flame retardants	4	Recycling flame retardant plastics	10
Researching new FR coating technologies	5	Challenges for FRs in applications and products	11
Fire safety for wood and timber	6	Shuyu Liang, Sika Technology	11
Pasi Virtanen, Teknos	6	Research into new flame retardant solutions	13
Aki Borgentrop, Nordtreat	7	Fire testing and modelling	14
Fire safety for polyurethanes	8	Prizewinning posters	14
Rolf Albach, Covestro	8	Prizewinners' visions for flame retardants tomorrow	15
Nadja Richter, Nima Esmaeili, Huntsman Polyurethanes	8		

FRPM 2019, the 17th conference on Flame Retardant Polymeric Materials, brought together in Turku, 26-28 June 2019, some 220 participants worldwide. The conference showcased a wide range of R&D into novel non-halogenated flame retardant chemicals, as well as other approaches to improving fire safety of materials (barriers, reflective surfaces). Trends shown include development of PIN FRs which can react into polymers, during polymerisation or in processing, to ensure durable fire protection and avoid migration; questions about durability of FR plastics; development of recycling routes for FR plastics; and demand for PIN FR solutions to ensure durable fire safety of wood products used in construction.

The Conference included a site visit to the Meyer shipyard, Turku

The next FRPM conference will take place in Budapest (Buda Castle Royal Gardens), 27th - 30th June 2021.



Carl-Eric Wilén, Åbo Akademi University, Finland, conference organiser, opened FRPM, emphasising the development of wood as a green and renewable polymer resource for building and other applications. This is strategic for Finland, where three fifths of the population live within 200m of the forest and a fifth are forest owners. Increasing use of wood is part of Finland's ambitious climate commitment. Wood however is flammable, and its increasing use requires new fire safety solutions.



Bernhard Schartel, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany, discussed flame retardant modes of action, underlining the use of understanding for evidence-based development. He compared solid phase (char forming) PIN flame retardant mechanisms, to the action of fire fighters: remove oxygen, reduce heat, remove fuel. These FRs act in polymers to store fuel in char, enclose and prevent the release into the flame of flammable gases, form a barrier layer protecting mainly from heat. However, to be effective, such FRs must be specific to the polymer in which they are used, to optimise polymer decomposition reactions and physical qualities of char formation. Solid phase PIN FRs are more effective in plastics where the char formation (pyrolysis) absorbs heat energy (engineering plastics, cellulose) rather than releasing energy (polyolefins). It was discussed whether fire testing reflects real fire conditions, and Dr. Schartel answered: "if you don't believe it, try putting your hand in a cone calorimeter"

Environmental challenges



Steve Hollins, ECHA (European Chemical Agency), suggested that industry should be proactive in substituting chemicals which are flagged as possibly problematic on any of the different ECHA 'early warning' lists, such as PACT (public activities coordination tool), CoRAP, or have been assessed in an RMOA (risk management option analysis). Any chemical on such lists is likely to face restriction in time, or be progressively phased out by users. Substitution should be a business opportunity, including by reconsidering whether the function can be achieved by routes other than using different chemicals. "Regrettable substitution", that is replacing by another chemical which also has potential issues, is an unsustainable way forward for industry. As well as addressing chemicals in products, restrictions under REACH can also directly address emissions, for example a restriction report for formaldehyde proposing limit values for indoor air.



Lara Greiner, Fraunhofer LBF, Darmstadt, explained the possible risk of release of carbon fibre fragments in case of fires involving composite materials, citing the 24th June German Typhoon Eurofighter crash <https://www.sueddeutsche.de/politik/bundeswehr-flugzeugabsturz-mecklenburg-vorpommern-giftgas-1.4503638>. She presented research into PIN FR solutions to address this concern: one-pot synthesis of polymeric acrylamide-DOPO and acrylamide-DDPO. These were tested in epoxy resin RTM6, showing (especially with acrylamide-DDPO) significant delay of production of respirable carbon fibre fragments (low fibre diameter). The delay beyond 25 minutes would be sufficient to protect beyond the time of the jet fuel fire. Analysis suggested that this protection of the carbon fibres was by char production. Combination with a-DOPO ensured effective fire retardancy (by both char formation and gas phase action).



Clémence Rawas, FCBA France (Institute of Technology for Forest-Based and Furniture Sectors), summarised the EMIFLAMME project (national government agency funding: ADEME, ANSES). The project has identified material – flame retardant systems widely used in today's furniture, will develop tests to assess emissions and migration of FRs, will measure emissions into indoor rooms and will model exposure via saliva and sweat (digestion, dermal). Most currently available test data concerns TCP/melamine foam, FR polyester and PVC/polyurethane coverings.

Phosphorus FRs



Sabyasachi Gaan, EMPA Switzerland, presented development of DOPO derivative phosphorus PIN FRs for use in synthetic and bio-based polymers, from research through to industrial production: DOPO phosphonamides (EDA-DOPO = 6,6'-(Ethane-1,2-diylbis(azanediyl))bis(dibenzo[c,e][1,2]oxaphosphinine-6-oxide)), today REACH registered and entering commercialisation by Metadynea; DOPO-PEPA (PEPA = 1-oxo-4-hydroxymethyl-2,6,7-trioxo-1-phosphabicyclo[2.2.2] octane), REACH registration underway, for application in polyester and polyolefins, under development with JET-Aviation for non-halogenated fire safety of wood products for aviation applications; and triazine DOPO, under development with BRUAG. He emphasised the importance of toxicity and ecotoxicity testing at the start of development. Some DOPO derivatives show significant aquatic toxicity or neurotoxicity, and these were discarded from development. Effective dispersion in polyols is also essential to enable processing.

Manfred Döring, Fraunhofer LBF, summarised developments in chemistry and applications for DOPO derivatives as phosphorus based PIN flame retardants. DOPO (DOPO = 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) mainly acts in the gas phase, by releasing phosphorus radicals which inhibit the flame, but chemical modifications of DOPO can increase the solid phase



(char formation) fire protection effects. The reactive P-H bond in DOPO is reactive, enabling versatile chemistries and the development of molecules with specific properties. For example, DOPO containing hardeners have been developed for epoxies, thus reacting the phosphorus PIN FR into the epoxy polymer, or modifications of DOPO and incorporation of other molecules or atoms can improve impact of DOPO addition on polymer performance, improve char generation or improve thermal stability and so processing compatibility.

Roland Krämer, BASF, presented results from micro-scale flame calorimeter testing of nearly 200 samples of polyamide and PBT with phosphorus-based PIN FRs, with the objective of understanding which loadings of these flame retardants are necessary to achieve required levels of fire performance (UL94-V0, 0.8 mm and 1.6 mm). Although single fire properties (e.g. heat release) were statistically correlated to UL94-V0 pass, single parameters show a too high scattering for practical predictions. However, by using several fire properties determined by calorimetric techniques, robust limits for pass/fail can be determined.

Yuan Hu, China State Key Laboratory of Fire Science, Anhui, presented synthesis of polyphosphazenes (indifferent nano-forms), with integration of silicon, cobalt and copper, and used for micro-encapsulation of ammonium polyphosphate. These nano-form PINs were tested as additive FRs in epoxies at up to 10% loading. Results showed significantly improved fire performance (e.g. heat release rates) and reduced emissions of both smoke and toxic gases (carbon monoxide, hydrocarbons, aromatics, carbonyls), probably because the PIN nano-composites were acting to catalyse redox reactions to complete oxidation of partial combustion gases.



Alexander Morgan, University of Dayton, USA, presented tests of phosphorus hydrazides as reactive PIN FRs in epoxies. These react into the epoxy during epoxy polymerisation, so providing non migrating, in depth fire protection, by both charring and nitrogen release. Tests showed that this reactive PIN FR solution significantly reduced smoke emissions. Objectives are also to enable compatibility with epoxy electrical performance (printed circuit boards) and with corrosion resistance, and prevent re-ignition after fires (epoxies retain heat). A challenge may be scale-up of production, because the hydrazines can interfere with epoxy polymerisation and both chemistry and processing may need some adaptation.



Johannes Lenz, Leibnitz Institute for Polymer Research, Dresden, presented a new proposed phosphorus-based PIN FR, the cyclic phosphonate BPPO and derivatives (dibenzo[d,f][1,3,2]dioxaphosphaphine 6-oxide). BPPO can be simply synthesised in one step from three-component condensation. The substance's aromatic ring is highly reactive, enabling a gas phase FR action. Phosphorus content can be increased in BPPO derivatives, by reactions with acrylates and diesters. These were tested as a PIN FR in rigid PUR/PIR foams, showing good dispersion, no significant impact on foam characteristics and fire performance comparable or better than conventional FR foams (TPP triphenyl phosphate) at comparable phosphorus contents.

Andrea Toldy, Budapest University of Technology and Economy, presented testing of two phosphorus-based PIN FRs (APP and RDP) in carbon-fibre reinforced epoxy resin, at phosphorus loadings of 0 – 5%, showing synergistic flame retardancy effects. A challenge was the dispersion of solid APP, with tendency to accumulate in upper layers of the composite produced by RTM (Resin Transfer Molding), which led to lower pHRR and higher residue during Mass Loss Calorimeter tests.



Research into bio-based PIN flame retardants

Xin Wang, University of Science and Technology of China, presented proposed PIN FRs derived from bio-based cardanol, tested in epoxies, including by reaction with organic phosphorus chemicals such as phosphaphenanthrene or benzoxazine, with zirconium phosphate, in combination with boron graphene nanosheets and in layered double hydroxides. The chemical properties of cardanol enable functional modification and contribute to improve hardening of epoxies. 6% loading of a zirconium phosphate – cardanol derivative reduced total heat release of the epoxy by nearly 50% and total smoke emission by over 25%.



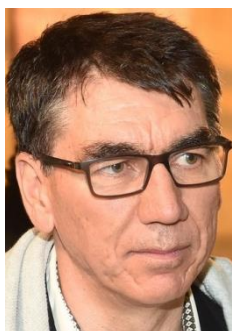
Gyorgy Marosi, Budapest University of Technology and Economics, claimed that to address public and regulator concerns about “plastics”, the objective should be to develop recycling and use of bio-based polymers. He presented a number of innovative applications of bio-based materials integrating fire safety, including phosphorylation of chemicals extracted from organic materials to produce bio-sourced flame retardants, use of bio-sourced fibres, including production of carbon fibres from cellulose and nano-fibres from bio-sourced cyclodextrin or chitosan. Some of the examples referred to materials approved for pharmaceutical purposes. The health and environmental safety of other synthetic organic molecules and nano-fibres were not addressed, whereas the use of bio-sourced materials gives no indication of safety of derived chemical.



Yun Liu, Qingdao University, China, showed studies of flame retardancy of alginate fibres. Alginates are water-soluble polysaccharides and bio-based fibres can be produced by wet spinning of sodium alginate solution, extracted from marine algae, into solutions of e.g. calcium chloride. These fibres show inherent fire resistance, and tests showed that blending with cotton fibres improved fire performance (lower peak heat release rate, longer time to ignition).



Ravi Mosurkal, US Army Combat Capabilities Development Command Soldier Center, Natick, MA, explained that the Army is working to ensure fire safety of soldiers clothing both in combat and day-to-day. Current solutions (e.g. using FRACU Flame-Resistant Army Combat Uniform and Nomex) are expensive and pose durability issues and the army wishes to find FR solutions for nylon-cotton blends. A combination of bio-based tannic acid and phytic acid has been tested as coating. Both of these are widely available from plants and are recognised to be safe for health and the environment. The tannic acid provides a carbon source and phytic acid provides phosphorus, together generating intumescent char, resulting in effective fire protection, reducing heat release by around 37%. Fabric properties were not significantly reduced. Unfortunately the fire performance is lost after only one wash, apparently not because of loss of the coating, but because of chelation by metal ions in laundering cycle and loss of phosphorus. Work is underway to find a solution for durability.



Laurent Ferry, C2MA Alès, France, presented work looking at use of tannins extracted from regional Cévennes chestnut tree wood by-products. Tannins are polyphenolic compounds. Gallic acid and ellagic acid, can be purified from chestnut tannin. These chemicals (industrially supplied) were reacted with boric acid, because this chemical is widely used in wood preservation. The resulting boron tannin derivatives were tested as flame retardants in DGEBA/IPDA epoxy. Promising results for fire performance were obtained, including a 2/3 reduction in peak heat release rate. Work is underway to improve extraction and purification from chestnut wood by-products and to generate small particles for better dispersion in polymers.



Sheng Zhang, Beijing University of Chemical Technology, China, summarised research into use of different phosphorylated derivatives of bio-sourced chitosan as a flame retardant in TPU (thermoplastic polyurethane). Chitosan is the only naturally occurring alkaline polysaccharose. Chitosan was modified by reaction with organic chemicals (Schiff-base, with the objective of improving thermal stability), with phosphonates and with montmorillonite clay, and these were tested in combination with APP, AlPi, melamine polyphosphate, including layer-by-layer. 19% APP plus 6% modified chitosan, or 9% AlPi plus 1% combined chitosan / phosphorus / montmorillonite, both achieved UL94-V0 (3.2 mm).

Researching new FR coating technologies



Bartosz Weclawski, University of Bolton, UK, presented research into use of plasma technology based on an atmospheric pressure plasma and high power UV laser. Multiplexed Laser Surface Enhancement (MLSE from MTIX Ltd., UK) can bond fire retardant precursors physico-chemically and even covalently into a fabric, followed by plasma/UV, so avoiding the conventional wet processing cycles. Using this technology, the nylon 6.6 (PA66) component of the nylon 6.6/cotton blends (type Nyco, commonly used for US Army personnel uniforms) was flame retardant functionalised. Results of tests of formation of covalent bonds with reactive flame retardants like DOPO were presented. Thermal degradation and flammability studies on functionalised nylon 6.6 fabrics were discussed.

Jaime Grunlan Texas A&M University, presented research into layer-by-layer coating application of PIN flame retardants to textiles, to wood and to flexible polyurethane foam. Application uses aqueous solutions of combinations of clay minerals, ammonium polyphosphate, melamine compounds, poly(allyl amine) and sodium hexametaphosphate. Such coatings showed to provide effective fire performance at around 20% w/w (textiles, self-extinguishing) or 6% w/w (wood). Some applications have been licenced and patents are pending. Work is currently underway to improve durability of treatments (to date, textiles only washed five times).



Federico Carosio, Politecnico di Torino, also presented water-based layer-by-layer and one step application of PIN flame retardants to flexible polyurethane foam to cover the foam 3D structure. Application of a combination of graphene nanoplatelets, phosphorus-based compounds, alginate and nanoclays (e.g. montmorillonite, sepiolite) at a total loading of 30 to 70 % w/w achieved self-extinguishing, no melt-dripping and also smoke emission reduction of up to 75%. The foams could resist penetration of an 800°C flame, retaining thermal insulation properties. Mechanical performance of the treated foam was acceptable after 50 compression cycles and testing with 2 000 cycles is underway.



Sophie Duquesne, University of Lille, France, presented a one-step process being researched for surface application of PIN flame retardant coatings to polycarbonate. A combination of two polymers (epoxy and silicone) with PIN FRs is applied and is optimised to self-stratify, because of incompatibility of the polymers. This self-stratifying process enables in one pass to obtain a good adhesion (epoxy) to the substrate (polycarbonate) whereas the top layer (silicone) containing the FRs brings both weather resistance and fire retardant performance. A 200 µm layer containing minerals (e.g. iron oxide or calcium carbonate) enabled to achieve UL94-V0 (3 mm) and to increase the LOI from 27 (neat PC) to 35.



Anne-Lise Davesne, University of Lille, France, presented studies of thin metal coatings on polymers, as radiant heat reflectors contributing to fire resistance. 500 nm metal/dielectric coatings were deposited on polypropylene and polyamide 6, using physical vapour deposition (pulsed DC magnetron sputtering of pure metal targets). This metal layer alone increased ignition time, reduced heat transmission, but did not reduce heat release. Combination with a PIN FR intumescent, expandable graphite (for PP), and Exolit Clariant OP1311 (for PA6), showed extended ignition time (8 minutes vs. 40 seconds in neat PP, and 15 minutes vs. 1 minute in neat PA6) and peak heat release rate (PHRR) reduced by around half.

Fire safety for wood and timber



Pasi Virtanen, Teknos

In the wood and timber sectors, Teknos' industrial customers today are looking for 'green' coating and treatment solutions: water based, VOC emissions free, non-halogenated and if possible bio-based. In the construction sector, demand for fire safety treatments is increasing, especially for public buildings, with today also demand for low smoke (Euroclass). Customers want flame retardants to be non-halogenated, and to not be subject to Hazard labels. "Nano" materials are also beginning to raise questions in some markets. Challenges include ensuring stability of raw materials (in order to reliably achieve precise customer product specifications), the need to ensure repeatable results in fire testing, the complexity of fire testing (several different tests for the same product for different applications) leading to large product portfolio and the development of more "efficient" fire safety treatments. That is, products which achieve fire safety with lower loadings, for example by using targeted synergists. Teknos is constantly screening new fire retardant solutions to offer sustainable coating solutions to customers.

Teknos is a global coatings company with operations in more than 20 countries in Europe, Asia, and the USA. It employs approximately 1,700 people and its net sales for 2018 was EUR 408 million. The company's strategy is based on sustainability, innovation, knowledge and people. Sustainability objectives are based around life cycle analysis of the whole product and production chain, the objective of low VOC emissions, non-halogenated and sustainable raw materials, including developing the use of secondary raw materials, and also integrate social responsibility today and for future generations www.teknos.com



Richard Hull, University of Central Lancashire, UK, outlined some of the challenges associated with working with inhomogeneous natural products, such as wood, and discussed various methods for quantifying the effectiveness of fire retardant treatments. Construction applications of timber range from structural beams and panels to facades and balconies, and even fire barriers, to protect more flammable components, such as insulation foams. New products, such as thermally treated wood, are resistant to microbial attack and therefore have low maintenance requirements rendering them suitable for use on tall buildings. However, little work has been reported on the fire performance and potential fire retardation of thermally treated wood. At least one major fire disaster (Barking, London, June 2019) resulted from the flammability of thermally treated wood. Moreover studies have shown dramatic decreases in the effectiveness of fire retardant timber treatments over time after external exposure*. Professor Hull highlighted the urgent need to develop new, sustainable, resilient fire retardant treatments for timber for construction products

* See: Östman & Tsantaridis, 2017, *Durability of the reaction to fire performance of fire-retardant-treated wood products in exterior applications – a 10-year report* (2017), *International Wood Products Journal*, 8:2, 94-100)



Gilles Labat, French Technical Institute for Wood in Construction and Furnishing, presented the development of a bio-based and biodegradable, non ecotoxic flame retardant for wood. The product LIGNOFLAM is based on chitosan polymer and talc, with surfactants to improve adhesion to the wood fibres. The product is an aqueous solution, application is by spraying resulting in a surface coating which does not modify wood colour nor wood thermal performance. After formulation optimisation, the product has shown to improve fire classification of wood insulation boards (density 200 kg/m³) from M4 (untreated) to M2 (application of 800 g/m² spraying wet weight). SBI tests with 160 kg/m³ panels showed an improvement from Euroclass E to C. Work underway shows that fire performance of particle board is also improved.



Aki Borgentrop, Nordtreat

The use of wood products in building is growing, for sustainability reasons and for cost-performance, but fire safety is a major challenge. A conventional solution is to cover wood by non-combustible materials, both interior and exterior. Today, however, both architects and building end-customers, want to have wood visible because it has a positive ecology image and is recognised as contributing to an attractive work and living environment. Wood products which will be visible in interiors need flame retardant treatments with low VOC emissions, aesthetic finish and colourings and resistance to chemicals and cleaning. These FR treatments must be compatible with recycling of construction wood products (e.g. into packaging pallets or by energy combustion). They must be non-toxic, to enable renewal of fire safety treatment, because wood construction products are designed to last for a building's life, not just for a few decades. Challenges today are that fire tests for wood products are complex and sometimes incoherent. Industry should take a responsible role to inform about wood product fire risks, explain testing methods and enable architects and developers to implement wood products in attractive, sustainable buildings in which local regulatory specifications are respected and in which fire safety can durably be ensured.

Nordtreat is a North European innovation SME, established in 2015 to develop and market fire protection solutions for wood. The company today operates two manufacturing facilities in Finland and Estonia, as well as supporting sales offices in Germany and Norway. The company offers flame retardant formulation, sales and services for wooden interior and exterior panels, engineering wood and structural timber products. Nordtreat's products are based on food-grade raw materials, water-based and non-halogenated, following the slogan "Transparent by Nature". They can be surface or vacuum applied. The company today offers the only water-based, translucent fire safety coating for wood with EN 16755 "EXT" durability (exterior use). www.nordtreat.com



FRPM conference dinner 2019, Turku castle

Fire safety for polyurethanes



Rolf Albach, Covestro

Covestro sees fire safety as an increasing challenge in all applications of plastic foams, in particular in buildings, where such foams offer the best insulation performance, cost effectiveness and adaptability of materials available. At this FRPM conference, ECHA showed early warning flags for chlorinated flame retardants, suggesting some risk of future regulation. Covestro has global R&D capacities and is developing its own chemistries to ensure non-halogenated fire safety in polyurethane. Part of this has been shown at the FRPM conference in collaboration with the IPF Dresden. Non-halogenated replacements for TCPP are today available, but the objective is to develop new chemistries with even better fire and foam material performance, and to ensure full compatibility with Covestro's customers' processing equipment (no corrosion or abrasion in extrusion and foaming). Tomorrow's solutions will tend to be integrated into the foam polymers, to improve processing and performance, and to minimize issues with FR emissions from foams. Covestro's aim is to provide chemistry expertise to support customers (foam producers), including combining fire engineering and materials fire performance to achieve fire safety most efficiently.

Covestro, www.covestro.com is a world leading polymer manufacturer, offering a range of application solutions. The company has 30 sites in Europe, Asia and the Americas. Covestro produces polyurethane (PUR), polyisocyanurate (PIR) and polycarboxylate rigid foams, as well as flexible foams for furniture and bedding.



Nadja Richter, Nima Esmaeili, Huntsman Polyurethanes

Huntsman considers that polyurethanes offer one of the most cost efficient solutions for achieving high performance insulation – be it to improve the energy efficiency of buildings or reduce noise vibration harshness and increase thermal management and acoustic control in demanding transport and automotive applications. Huntsman is working on developing new flame retardant solutions for polyurethanes which can deliver better long-term fire safety performance and reduce the risk of fire retardants migrating out of end products. Huntsman is also looking closely at the reduction of smoke emissions in line with new EU Construction Products Regulation “Euroclasses”. Currently, solutions are available, but pose challenges of

price and of compatibility with existing processing (foaming) techniques. Innovative new solutions may combine several technologies, but must be realistic - bringing to market products that are compatible with current manufacturing methods and end-of-life recycling. To meet these challenges it's essential to ensure quality and consistency of materials by controlling production, and to work closely together with foamers and end users to develop product specifications that meet specific processing, performance and regulatory requirements.

Huntsman Polyurethanes is a global leader in MDI-based polyurethanes, serving over 3,000 customers in more than 90 countries from production facilities in the US, the Netherlands and China, as well as 30 downstream formulation facilities worldwide. Applications include insulation, timber products, coatings and adhesives, footwear, automotive, bedding and furniture and thermoplastic polyurethanes suitable for extrusion and injection molding. <http://www.huntsman.com/polyurethanes/>



Oliver Steffen Henze, BASF Polyurethanes GmbH

TPU (thermoplastic polyurethanes) are high performance elastomers used in extrusion (e.g. cables, films, tubes) and injection moulding applications (e.g. plugs, electronic connectors). Formulations are tailor-made, often in low volumes, for customers' specific components and uses. BASF supplies only non-halogenated formulations of flame retardant TPU for over twenty years. Customers' requirements are increasingly demanding, covering fire safety performance, mechanical and aesthetic properties and processing requirements. Trends include increasing specification for low smoke and low toxicity of combustion gases, and sustainability criteria. Increasingly demanding fire safety requirements in combination with high mechanical requirements are opening opportunities for replacement of other materials by TPUs. BASF sees future flame retardants in TPUs as additive, because processing is easier than for reactive compounds and additive FR packages enable the rapid tailor-made formulation response needed for specific customer product demands. The FRPM conference provides information about FR innovation which could provide new fire safety solutions for tomorrow, such as synergist additives and novel PIN flame retardants.

BASF produces a range of polyurethanes, including both tailored systems and basic products (polyether polyols, polyester polyols, MDI and TDI) for manufacturing cellular PU foam materials and compact polyurethanes, including elastomers: thermoplastic polyurethane (TPU) and microcellular elastomers. BASF provides not only polymers and compounds, but also service to customers to help define appropriate compounds, implement processing, as well as appropriate R&D and testing.
http://www.polyurethanes.basf.com/pu/solutions/en/content/group/Arbeitsgebiete_und_Produkte/Products

Innovative FRs for textiles and fibre-compounds



Jelena Vasiljević, University of Ljubljana, presented tests of three DOPO derivatives as additive PIN FRs in polyamide 6 fibres. The FRs were added in the caprolactam melt before polyamide polymerisation. Only PHED proved compatible with the melt extrusion process (0.35 mm) and with dyeing (transparent) and at 15% loading achieved self-extinguishing and no flaming drip with ASTM D6143 (filament and textile) and UL94-V0 (1.2 mm woven textile). However, tensile strength was reduced by around 50%. The objective is to avoid compounding, by a one-step polymerisation – FR addition – melt-extrusion.

See also Vasiljević et al. *Polymer Degradation and Stability*, vol. 166, August 2019, pp 50-59
<https://doi.org/10.1016/j.polymdegradstab.2019.05.011>

PHED = bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide

Comments from conference participants also referred to developments of one-step polyamide processing using additive PIN FRs. *pinfa* NOTE: for example, see the EMPA - Litrax process now commercialised by [Aquafil](#).

A prizewinning poster by **Marija Čolović, National Institute of Chemistry, Slovenia**, presented similar work, but where the DOPO was reacted into the caprolactam monomer of polyamide 6 (not additive) – see summary below.



Yu-Zhong Wang, Sichuan University, Chengdu, China, summarised different approaches to improve fire safety of fibre-reinforced composites where fibres are used to reinforce plastics. Such composites can be problematic in fire because of the “candle wick effect” of the fibres. Two approaches can be combined: treatment of the fibres, and flame retardancy of the plastic matrix. For epoxy resin matrix, studies of a polymeric phosphorus compound (PBHDDP) were presented. For carbon fibres, improvement of the fibre – epoxy resin interface was achieved by phosphorus-containing electrolyte soaking of the fibres before composite molding, resulting in a reduction in peak heat release rate of nearly 50%. For composites of polypropylene reinforced with natural ramie fibre (Chinese nettle), a novel polymeric PIN FR (EPA-APP) was added, showing effectiveness both via bulk flame retardation and by interfacial effects achieved by selective dispersion onto the surface of ramie fibres during processing of the composites.

PBHDDP = poly [4,4-bis(6-hydroxyhexyloxy)biphenyl 9,10-dihydro-10-[2,3-di(hydroxylcarbonyl) propyl]-phosphaphenanthrene-10-oxide

Recycling flame retardant plastics



Jürgen Troitzsch, Fire and Environmental Protection Services, summarised the opportunities for the circular economy for plastics and implications for flame retardants. World demand for polymers is continuing to grow exponentially, but also to grow more slowly in Europe. On the other hand, only just over 1/5 of Europe's total material needs are met by recycling. However, a range of EU regulations are pushing to improve recycling: the Waste Framework Directive (with obligations for increasing waste collection and recycling), landfill, packaging, end-of-life vehicle, batteries legislations, and WEEE (Waste Electrical and Electronic Equipment) Directive. Plastics can be valorised by mechanical recycling, chemical processing back to feedstock, energy or use in energy production. A number of FR/polymer combinations have been shown to be compatible with mechanical recycling, but POPs restrictions, REACH SVHC classifications and RoHS prevent this for plastics containing certain brominated FRs (PBDEs, HBCD, with discussions underway on antimony trioxide, TBBPA, chlorinated paraffins and chlorinated phosphate esters) and RoHS requires removal of any plastic containing brominated FRs. Chemical recycling will be possible for plastics containing these problematic FRs.



Lein Tange, ICL, considers that the actual challenge is that mechanical recycling of plastics is only possible if end-of-life plastics are collected and precisely sorted, in order to generate secondary streams of consistent and compatible materials without hazardous impurities. Recycling is only feasible if such sorted input streams are represent industrially significant quantities. Additionally the price of plastic articles alone does not today cover the end-of-life costs (collection + sorting + recycling). He presented the [CreaSolv®](#) Process developed by Fraunhofer IVV and the Polystyrene Loop Cooperative ([PSLoop](#)), with the aim of physical purification of end-of-life polystyrene containing “legacy” brominated FRs (HBCD) back to purified polystyrene polymer and recovery of bromine. A demonstration plant of 3 000 t/year is now planned (cost over 10 M€). Other processes at development scale work are super heated solvent recycling of HIPS and ABS in the [PLAST2bCLEANED](#) project and the CreaSolv® Process in the [CLOSEWEEE project \(both EU funded\)](#).



Elke Metzsch-Zillingen, Fraunhofer LBF, Darmstadt, Germany, presented results of tests of mechanical recycling of PIN flame retardant polymers, funded by pinfa. Tests covered widely used polymer / FR combinations, with polypropylene, polyethylene, polyamides and polycarbonate, and PIN FRs: APP, pyrophosphate, ATH, DEPAL, melamine cyanate, non-halogenated phosphate ester. For 9 out of 10 combinations, after multiple re-extrusions, and after accelerated ageing, flame retardancy was retained, but for many combinations, material properties deteriorated – but this is considered to be mainly related to impacts on the polymer and on glass fibres, not related to the PIN FR. The overall conclusion is that mechanical recycling for widely used polymer / PIN FR combinations is possible, subject to careful reformulation with appropriate additives to correct polymer deterioration and use of appropriate extrusion equipment. An important comment is that the prerequisite for mechanical recycling is that collection and sorting systems for end-of-life plastics must be in place and effective.

Challenges for FRs in applications and products



Shuyu Liang, Sika Technology

Flame retardants are of increasing interest to Industry, in response to a worldwide increase in fire safety and environment awareness. Sustainability is a key requirement in fire safety, meaning environmentally friendly products, based on green chemistry, green production, and compatible with recycling. Some sectors, such as shipping and marine, already have demanding fire safety specifications, requiring innovative products and solutions. Sika today drives the needs of using sustainable solutions in constructions in response to today's new materials and new building designs. The commitment to achieving up-to-date fire norms should be expected in all fields. New processes such as 3D-printing will need new solutions for fire safety. Industry should provide a full package for fire safety, integrating design, materials, flame retardants and application services. This integrated approach can facilitate innovation and can reduce overall costs, which remain a key challenge for green fire safety approaches.

Sika Technology is a fast growing Swiss-based company, innovating for over 100 years in products and services in sealing, bonding, damping, reinforcing and protecting, in building and construction and today in industry and automotive. Sika has over 20 000 staff and 200 factories worldwide. <https://www.sika.com/>



Serge Bourbigot, University of Lille, outlined the challenges for flame retardants in 3D-printing, noting that fire performance of 3D-printed materials depends on variables such as printing direction, printing parameters, infill pattern and geometry for 'solid' items and printer quality (which influence porosity of final article). This can make fire testing results variable and inconsistent. Innovative fire safety enabled by 3D-printing include integration of a fire resistant outside layer into the print, new design of biphasic materials, as well as use of novel PIN FR combinations and synergists, such as glass microbubbles and nanoclays.



Marcos Batistella, C2MA Alès, discussed 3D-printing using SLS (Selective Laser Sintering) technology with polyamide 12, as increasingly used industrially for production of parts for industries such as aerospace which require high levels of fire performance. Commercially available PIN FRs (APP, cyanurate melamine, phosphite ...) were tested, looking both at the fire performance of the 3D-printed parts and at impacts on processing parameters (sintering temperature range, coalescence in printing). Conclusions were that some but not all of the PIN FR combinations could achieve both fire performance and 3D-printing quality in these PA12 tests.



Petri Moisio, Meyer Turku Shipyard, explained the importance of fire safety onboard during the cruise ship construction process. The shipyard, which the conference visited, is today constructing top-range cruise ships, currently a 1 800 m² floor surface liner (the size of a modern hospital). Sections of the ship are built onshore, then transported (1 200 t crane) and welded onto the vessel under construction in dry dock. There is a major risk of fire being started onboard by “hot works” (welding, etc) taking place near flammable materials. Four minutes of fire are estimated to cost a million euros. The shipyard has some 150 hot works per day on a cruise ship under construction, and each one is specifically identified, authorised and monitored using a real-time online / mobile device system. Fire risk is further reduced by requiring flame retardant materials for packaging of construction materials and equipment to be installed, and flame retardant specifications for protective films and other materials. Flammable materials are as far as possible removed from the ship during construction but the metal structure of the ship is only around 10% of its value, with 90% being electrical and electronic equipment, furnishing and decoration. These must all respect maritime fire performance requirements.

Sebastian Eibl, German Army, underlined that the end-customer does not know which flame retardants are being used in products. The only solution for the end-customer is chemical analysis. He presented examples of deterioration with ageing of polyurethane camouflage nets. The army's chemical analysis showed that the problem is related to appearance of phosphoric acid, with the low pH then breaking down the polyurethane polymer. Further analysis identified red phosphorus, RDP, a sulphur-phosphorus compound and melamine (which may or may not come from melamine polyphosphate). Analysis showed deterioration with age irrespective of different phosphorus-based FR chemicals identified and that deterioration was related to folding for storage, leading to humidity. Modelling suggested that in humid conditions, 50% of the phosphorus FRs in the plastic can be decomposed. Also, with PIN FR polyurethane, antimony was identified to be accessible (water soluble on the surface) posing potential health concerns.

Xuebao Lin, BAM Germany, presented tests of weathering resistance of PIN FR polymers for E&E applications. The fire protective barrier effect of mineral FRs (ATH or boehmite in EVA) showed in some cases to improve with ageing, possibly because of surface agglomeration of the minerals. In TPU (thermoplastic polyurethane) with melamine cyanurate, however, polymer degradation after ageing led to deteriorated melt-dripping and fire spread. A self-developed cable module test (to simulate at bench scale the full-scale vertical test) showed to provide good indications of fire spread behaviour.



Mauro Zammarano, NIST, described a reduced-scale test aiming to predict full-scale fire performance of upholstered furniture. Despite reductions in smoking, upholstered furniture remains the biggest cause of home fire deaths in the USA. At the same time, some States are limiting the use of some flame retardants (California, Maine). NIST has therefore carried out fire testing of fire barrier materials in full-scale chair mock-ups, and reduced-scale testing (10 cm cube of material + barriers). In full-scale tests, the best fire barrier materials can reduce the peak heat release rate (PHRR) by a factor of about three and increase time to PHRR from 3 to around 25 minutes. After this time, liquid pyrolysis products produced by the foam percolated through the barrier and caused a rapid increase in heat release rate. The reduced-scale test was able to predict the time to PHRR and the plateau heat release rate before PHRR observed in full-scale tests.

Gabrielle Peck, University of Central Lancashire, presented the results of four, reduced height (5 m) BS 8414 facade fire tests, in which both the heat release and smoke toxicity had been quantified. Three of the facades used non-combustible aluminium composite material ACM A2, while the fourth used a polyethylene (PE) cored ACM. These were used alongside three insulation products, mineral wool, PIR foam (for both ACM A2 and ACM PE) and phenolic foam. The 3 megawatt wood crib fire was sufficient to destroy the ACM panels above it, exposing the insulation,

which burnt almost completely. Where the ACM had failed, the combustible insulation products also burnt away. As may be expected, most of the toxicity in the main exhaust resulted from the 3 MW wood crib, predominantly a mixture of CO₂ and CO. The toxicity in the cavity between the ACM and the insulation was significantly greater, with hydrogen cyanide being the major toxicant from PIR, suggesting possible risks if the effluent were to blow in through a vent or broken window.

Research into new flame retardant solutions

De-Yi Wang, IMDEA Materials Institute, Madrid, presented different approaches to develop specific nano-materials and architectures as PIN flame retardants in different polymers and the complexity of understanding the mechanisms involved. These include using layered surface materials (LDH) to improve char behaviour by including metal compounds (e.g. iron or nickel) between layers, nano-encapsulation of PIN FRs in MOF (metal organic framework) nano-structures, using nano coatings to improve interface between inorganic flame retardants and polymer matrices.

Gaëlle Fontaine, University of Lille, France, presented studies of thermal degradation of three high performance polymers: PEEK = polyetheretherketone, PI = polyimide and PBO = Poly(p-phenylene-2,6-benzobisoxazole). These polymers are inherently fire resistant, with decomposition temperatures above 600°C and show significant char generation under nitrogen.

Nima Esmaeili, Huntsman, presented tests of zinc and tin stannate as replacements for antimony as synergists for polymeric brominated flame retardants in polyamide 6,6, concluding that zinc stannate offered better performance. Inclusion of zinc stannate (7% loading) and acrylate polymeric brominated flame retardant (15% loading) showed that this limited the reduction in the thermal stability of the polyamide induced by the brominated FR, modified the release of aromatic compounds and generated char formation in fire.

Mark Beach, DuPont, presented a brominated polymer product used for flame retarding polystyrene foams, to replace the brominated flame retardant HBCD which is indicated to be PBT (persistent, bioaccumulative, toxic). The brominated polymer is not B or T. Ongoing tests show that it is stable with no detectable or extremely slow biodegradation, hydrolysis, thermos-oxidative degradation. Installation and handling instructions should ensure very little exposure to light and tests show that UV degradation impacts only the foam surface.

Teija Tirri, Åbo Akademi University Finland, presented studies of sulphenamides as PIN synergists for phosphorus flame retardants in polystyrene, polypropylene, epoxy and TPU. These sulphur containing, thiyl releasing molecules include aromatic rings (benzothiazoyl, phenyl), giving improved thermal stability. At low loading of 1-3% they show a strong synergy with phosphorus flame retardants, improving fire performance by acting in both the solid and gas phases, and reducing smoke emissions. For example, 2% sulphenamide and 8% spirocyclic phosphate ester achieved UL94-V0 (1.6 mm) in polypropylene. 2.5% sulphenamide alone achieved ISO 11925-2 in polystyrene.



Rashid Nazir, EMPA Switzerland, presented research into synthesis of bridged phosphorus compounds (alkyl sulfoxide based) and their application as additive flame retardants for polypropylene (PP) and flexible polyurethane (PU). Aromatic bridged compounds were suitable for flame retardation of polyolefin, because of higher thermal stability, and the aliphatic compound was more suitable for application in rigid PU foams.

Fire testing and modelling



Richard Lyon, US Federal Aviation Administration (FAA), presented work underway by an FAA/industry working group to use milligrams of sample in a microscale combustion calorimeter to compare the fire performance of components (e.g., adhesives, films, potting compounds, fibers, etc.) used in aircraft cabin materials. A new combustion parameter was derived for this purpose that combines ignition and burning characteristics, called the Fire Growth Capacity/FGC, having units of J/g-K. The FGC is a reasonably good predictor of pass/fail fire and flame test results of a single component (polymer) at bench-scale, but cannot be expected to predict fire test results of multi-component constructions and laminates. However, because of its accuracy, repeatability and specificity, the milligram-scale FGC parameter may prove useful for comparing components of constructions, quality control of incoming materials, or product surveillance.

Work on fire modelling was presented by **Joshua Swann, University of Maryland, USA** (characterisation of pyrolysis and combustion of polycarbonate), by **Louise Speitel, US Federal Aviation Authority** (effect of fuel to oxygen ratio and temperature on polymer combustion products) and by **Yan Ding, University of Maryland, USA** (flammability model for polymers containing the PIN FRs: MPP and DEPAL).

Prizewinning posters

From the more than 70 posters presented at FRPM 2019, the scientific committee designated three prizewinners, summarised below:

- 1st prize: Marija Čolović et al., National Institute of Chemistry, Slovenia (P47)
- 2nd prize: Weronika Tabaka et al., BAM, Germany (P35)
- 3rd prize: Nick Wolter et al., Fraunhofer IFAM, University of Bremen, Germany (P58)

Poster P47 (1st prize): Novel flame retardant polyamide 6 copolymer. **Marija Čolović et al., National Institute of Chemistry, Slovenia**, presented work testing the reaction of the phosphorus PIN FR, DOPO, into the caprolactam monomer of polyamide 6. This proved compatible with polymerisation and melt extrusion and retention of material properties of the polyamide polymer. 10% DOPO loading enabled to achieve UL94-V0.



Poster P58: Manufacturing of fiber reinforced polybenzoxazine with advanced fire, smoke and toxicity properties. **Nick Wolter et al., Fraunhofer IFAM, University of Bremen, Germany**, studied flame retardancy of basalt fibre reinforced polybenzoxazine, using RDP (phosphorus PIN FR). 10% loading RDP enabled achievement of UL94-V0 at 3.7 mm (already achieved by the neat polymer-fibre compound) and showed high potential to fulfil EU railway standard HL3 (Hazard Level) for external application and HL2 for internal application, but also improved processing in terms of decreasing viscosity and increasing pot-life of the resin. Furthermore, RDP influences the reaction to small flame behaviour by preventing a delamination of the composite.

Poster P35: Bench-scale fire stability testing – assessment of protective coatings on carbon fibre reinforced polymer composites, **Weronika Tabaka et al., BAM, Germany**. Fire safety is a major challenge for carbon fibre reinforced polymers (CFRP) in applications such as aviation, maritime and buildings. Protective coatings were tested at bench scale for fire performance and ultimate load failure, for a composite of carbon fibres in epoxy resin. At this scale, different coatings showed



to be effective in providing thermal insulation and prolonging time to structural failure: cellulose nanofiber/clay coating, vermiculite with different PIN flame retardants, intumescent based on expandable graphite.

Other posters included:

- **Dan Meng, Beijing University** (P32) integrated phosphorylated chitosan into exfoliated montmorillonite, showing that this was an effective synergist to AlPi in TPU, achieving UL94-V0 (3.4 mm) and significant smoke reduction.
- **Gustavo Schinazi, Case Western Reserve University, USA** (P34), tested eight different bio-based and PIN FRs in ABS (tannic acid, phytic acid, fish gelatin, DNA, melamine poly(magnesium phosphate), MDH, ATH, melamine) showing optimal fire performance with tannic acid plus phytic acid or tannic acid plus fish gelatin due to synergy with the ABS matrix.
- **Jens Reuter, Fraunhofer LBF, Darmstadt, Germany** (P39), showed synergies between the PIN FRs ATH and zin phosphinate or aluminium hypophosphite in unsaturated polyester resins, achieving UL94-V0 (3 mm) with 37% ATH and 8% phosphorus PIN FR.
- **Roberto Spogli, Probalin & Tefarm, Italy** (P69), presented studies of biodegradable PIN FRs in elastomeric polymers, within the EU-project PolyCE (GA No 730308 www.polyce-project.eu) showing that a 5% loading of hydrotalcites and zirconium phosphates reduced heat release rate by 50% and smoke by 60%.



Prizewinners' visions for flame retardants tomorrow

Pinfa asked the poster prizewinners at FRPM to express their vision of challenges for fire safety and for flame retardants for tomorrow.

Weronika Tabaka

Interest in environmental protection will push demand for recycled and bio-based flame retardants but also to reduce flame retardant loadings. Also, fibre-reinforced composites will continue to develop to reduce the weight of products. The challenge is to develop flame retardants which meet these objectives without impacting mechanical performance, especially for aviation and automotive. Resulting needs for more fire testing may meet obstacles of cost, laboratory capacity and personnel. To meet tomorrow's fire retardancy challenges, better collaboration is needed between regulators, industry and research. Problems with flame retardants or deviations from fire standards must be reported and addressed.

Marija Čolović

Sustainability should be tomorrow's driver. Life Cycle thinking will drive new competitive solutions, beyond current technologies. For fire safety, the challenge is to develop efficient, durable and recyclable fire retarded materials with reduced environmental impact. New scientific knowledge, transferable into technology, can take this forward. Polymers which integrate flame retardant functionalities (chemically bonded as chain side groups) are a solution to the problems of emissions and leaching. However, development of such polymers is very demanding, in order to retain materials physical and mechanical properties. The specific FR mode of action for each particular FR – polymer combination should be the leitmotif for new flame retardant systems. The ideal FR system should provide efficient flame retardancy, low smoke emission and low smoke toxicity. Also, FR synthesis must be sustainable and low toxicity

