Your newsletter for non-halogen fire safety solutions
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pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

FRPM 2023 | EUROPEAN MEETING ON FIRE RETARDANT POLYMERIC MATERIALS
26. – 29.6.2023 ZURICH SWITZERLAND

The 19th edition of FRPM (Fire Retardant Polymeric Materials Conference) www.frpm-23.org was hosted by Empa, Switzerland, 26-29 June 2023. This is one of the world's biggest flame retardant conference, with nearly 250 participants, 69 oral presentations and 70 posters. 185 of the participants were from Europe. 65% were from academia, 35% from industry and other stakeholders. Conference papers will be published in in the Journal of Material Science and Technology or the Journal of Polymer Degradation & Stability. pinfa members were actively present (BASF, Clariant, DTNW, ICL, Lanxess, Sabic, Schneider Electric) and pinfa both sponsored the Conference and specifically offered (for the first time at FRPM) Awards for young researcher presentations.

The 20th FRPM Conference will take place 6th – 9th June 2025 in Madrid, hosted by IMDEA.

As well as presentations on pure and applied flame retardant chemistry research, applications, fire safety trends and regulations, participants enjoyed glorious Swiss weather, a superb gala dinner high above Zurich (sponsored by Clariant), a visit to Empa's experimental green construction building NEST, alpenhorn and yodelling, and many opportunities for networking and discussions.

Most presentations showed laboratory research into possible new flame retardant chemicals or materials (nearly 50 presentations, of which around one third on bio-based chemicals or materials, several on vitrimers, fire behaviour or chemistry modelling …), around fifteen presentations addressed industrial flame retardant applications (more than a third on battery fire safety) and nearly ten presentations discussed policy, regulation and recycling. A number of presentations from China, or coming from cooperation between European and Chinese research organisations showed the extensive range of flame retardant chemistry research ongoing in China. Many of the research presentations of new FR chemistries showed improved LOI (Limiting Oxygen Index) or reduced Heat Release at the lab scale, but did not demonstrate applied industry validation testing (e.g. UL 94).

Of the 140 oral presentations and posters, nearly all of those on new flame retardant technologies or applications centred on PIN FR chemistries (most on phosphorus chemistries, with also nitrogen, sulphur, silica, metal synergists and other inorganics). Presentations on recycling and on regulation considered halogenated flame retardants, because of their legacy presence in today's end-of-life products. Certain brominated FRs pose increasing obstacles to recycling because they are POPs and increasingly tight regulations mean that traces in reprocessed polymers can exclude these from recycling. The conference also noted the EU targeting of brominated FRs as priorities for regulation (ECHA Roadmap).

Photos: Empa organising team, poster session in NEST building.

WHAT WERE THE LEADING THEMES AT FRPM 2023?

New flame retardant chemicals

- especially based on phosphorus PIN FR chemistries: new organo-phosphorus chemicals, often derived from DOPO, reactive PIN phosphorus FRs
- sulphur- and/or nitrogen-based PIN chemicals, as synergists for phosphorus PIN FRs
- ionic liquids to deliver synergist metals (catalysis of char formation)
- inorganic boron and metal synergists, silicon minerals: which can glassify phosphorus chars, so improving fire resistance

Research into bio-based or waste-derived flame retardants

- experimental synthesis and testing of new bio-derived chemicals: presentations showed interesting possible future routes, but without yet information on industrial feasibility: supply, quality consistency, cost.
- research testing of different waste / secondary materials as PIN FR synergists: flue gas sulphur-removal gypsum, power plant fly ash …

Sustainability, chemical safety and recycling

- recycling: use of PIN FRs to ensure fire-safety of recycled materials (necessary for their use in many applications), recycling of flame retarded polymers.
- smoke toxicity in fires, which is often the main cause of deaths and injuries, either directly or by preventing escape (incapacitation, visibility), for example related to nitrogen-containing polymers (cyanide). PIN FRs acting in the solid phase reduce smoke (char barrier layer) but gas phase FR action, whilst being effective in quenching flames, can increase smoke: how to balance these effects?
- water-based FR synthesis or application, e.g. to textiles.
- the question was raised of how to prevent burning-dripping (essential to pass UL 94 V-0 and to prevent fire spread in real life) whilst avoiding the currently-used PFAS anti-drip additive PTFE. But no research presented addressed this.
- both industry and the European Commission (ECHA) underlined the aim to move to Safe and Sustainable by Design chemicals (SSbD), but the majority of presentations proposing new FR chemicals did not consider their compatibility with recycling, nor their possible toxicity and environmental safety.

FR trends, new applications

- reactive and polymeric phosphorus flame retardants, including for example replacing part of epoxy by a P-epoxy
- fire safety challenges of batteries, including battery fire gas toxicity
- flame retardants for polymers for 3D-printing
- new phosphorus-nitrogen PIN FR solutions for textiles
- computer modelling and AI to design new FR chemistries and model toxicity, fire performance

Mechanisms of flame retardants

- combining solid phase (char) and gas phase (radicals) fire performance effects of phosphorus FRs.
- new PIN radical generators for gas-phase fire quenching effects, e.g. amines or silanes.
- link between oxidation state of phosphorus in PIN FRs and fire performance effect: high oxidation state – char generation / low oxidation state – gas phase action.
- synergies between phosphorus PIN FRs and sulphur or silicon compounds.
- synergists to improve char production and structure.
- links between gas-phase action of FRs (fire quenching), smoke emission and smoke toxicity: carbon monoxide, smaller smoke particles, aldehydes, hydrogen cyanamide (nitrogen containing compounds).
- the widespread use of the cone calorimeter for materials fire testing is questioned as not representing real fire conditions. Oxygen supply is generally inadequate in real fires, resulting in smoke toxicity which is not shown with the cone calorimeter, which is well ventilated.

Conference conclusions

The lead organiser of this FRPM Conference, **Sabyasachi Gaan, Empa**, concluded the conference by thanking the organisation team and the conference sponsors, and summarised the themes he saw as emerging at this 2023 19th edition of FRPM:

- sustainability, environment and recycling
- new developments in flame retardant chemistries and synergies
- modelling of fire behaviour and testing
- applications in transport, construction, textiles
- new developments in e-mobility and batteries, 3D-printing

SELECTED FRPM 2023 PRESENTATION HIGHLIGHTS

This small selection does not attempt to represent the rich variety of the 140 oral and poster presentations at FRPM, and should not be taken as a "best of". The presentations summarised may be of specific interest to pinfa Newsletter readers.

SUSTAINABILITY

EU Chemicals Strategy for Sustainability

Martijn Beekman, European Commission, DG GROW

Despite forty years of chemicals regulations in Europe, today sees high levels of citizen concern about chemical impacts on health and on the environment and scientific evidence of widespread impacts of chemicals. The EU Chemicals Strategy for Sustainability fixes the objective of SSbD (Safe and Sustainable by Design) chemicals. For flame retardant chemicals, which need to be robust (to ensure durability of products), this requires to move to chemicals with inherently safe properties.

The European Commission recognises the need for policy visibility and transparency, to enable industry to develop and adapt, and published the Restrictions Roadmap specifying which groups of chemicals will be prioritised for regulation in which timelines (April 2022, see pinfa Newsletter n°138). The ECHA Flame Retardants Strategy (March 2023, see pinfa Newsletter n°147) now clarifies priorities for assessing and regulating flame retardants.

Based on information included in REACH Registrations, some 350 chemicals are registered for use as flame retardants, covering a wide range of different types of chemicals and uses.

ECHA is addressing these with a grouping approach, with a key objective of avoiding the "regrettable substitutions" of the past where banned halogenated FRs were substituted by very similar halogenated chemicals.

This grouping approach has identified as priorities the brominated flame retardants (BFRs), with aromatic BFRs considered to be of general concern as PBT/vPvB (persistent bioaccumulative and toxic, very persistent and very bioaccumulative), and more divers concerns about aliphatic BFRs.

For organophosphorus flame retardants, a number of different groups have been identified. Several groups are considered (based on data available) to be of low concern or unlikely to be hazardous, and for other groups data generation is currently ongoing and should enable further assessment within 2-3 years.

Mr Beekman notes that the Chemicals Strategy for Sustainability also aims to direct EU research and innovation funding towards SSbD chemicals and climate-neutral chemical production, based on identification of key chemicals needed for EU Strategic Technology sectors. The ECHA Flame Retardants Strategy notes that this can include both flame retardants needed to ensure fire safety and also other fire safety approaches such as fire barriers or inherently fire-resistant materials.

EU Chemicals Strategy for Sustainability and FRs

Adrian Beard, pinfa and Clariant

The EU's "Chemical Strategy for Sustainability" (April 2022, pinfa Newsletter n°138) will bring major changes to chemicals regulation in Europe and these are today being initiated, including the recast of the EU chemicals regulation REACH, the concepts of "Safe and Sustainable by Design" (SSbD) chemicals and of "Essential Uses" of certain chemicals, the announced Restriction of all PFAS (as a class of chemicals). The update of CLP includes a new Hazard Category "M" (mobile). The REACH recast is expected to require Registration of some polymer and declaration of all polymers.

The Restriction of PFAS chemicals could pose challenges to formulating FR polymer compounds because it may prevent the use of PTFE as an anti-drip agent, whereas this is currently needed at low doses (generally <0.5%) to avoid flaming dripping which result in failure of UL 94 V-0 and corresponds to a risk of spreading fire in real life.

The Chemicals Strategy for Sustainability will be implemented for flame retardants through the ECHA Flame Retardants Strategy (see above). This identifies a number of brominated FRs as priorities for Restriction, identifies a range of nitrogen and inorganic FRs are requiring no regulatory action and concludes that some groups of organophosphorus FRs are "low or unlikely hazard". Further assessment of other groups of organophosphorus is expected after brominated FRs have been assessed and regulated by 2025 or later.

Clariant is already working to apply the principle of Safe and Sustainable by Design (SSbD) chemistry to the company's FRs using a range of 39-criteria, including comparison to the market standard FR solution. Significant challenges for organophosphorus FRs are the energy requirement for P_4 production and the current use of toxic vector chemicals in the manufacturing chain (PCl_3, PH_3).

Clariant's work on application of Safe and Sustainable by Design (SSbD) chemistry shows that it is very difficult to combine desirable SSbD chemical properties with application requirements for FRs: degradability tends to be contradictory to product durability and to recyclability and non-bioaccumulation to polymer compatibility. Biobased phosphorus FRs are today widely researched, but challenges of thermal stability (compatibility with polymer processing) and water uptake are obstacles to industrial implementation. At the same time, application requirements are becoming increasingly demanding and FRs must be compatible with necessary mechanical performance, miniaturisation, electrical insulation (CTI).

Phosphorus chemistry offers positive perspectives to address these challenges, with high flexibility, fire safety action in both solid (char) and gas (radical quenching) phases, additive, reactive and polymeric chemistries.

Challenges for sustainable phosphorus chemistry

Chris Slootweg, University of Amsterdam

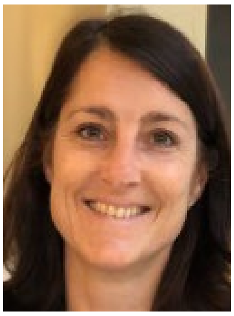
The phosphorus cycle today exceeds planetary boundaries and leads to widespread water quality deterioration (eutrophication). Nearly all phosphorus use is in agri-food (fertilisers, animal feed, human food) and fire safety applications are < 0.5% of global phosphorus consumption. Fire safety should adopt the same Nutrient Circular Economy objectives.

Here in Zurich, in 2013, the population voted 94% in favour of a new sewage sludge incinerator with phosphorus recovery from the sewage sludge incineration ash.

A challenge for sustainable fire safety, without using halogenated chemistry, is that most phosphorus PIN FRs are derived from P_4 ("White Phosphorus" / elemental phosphorus) produced in electro-reducing furnaces, consuming coke, with high energy consumption and greenhouse emissions. Organophosphorus PIN FRs are generally today produced from P_4 using the halogenated intermediate PCl_3. Chris Slootweg is a co-founder of the Amsterdam University spinoff SusPhos. He showed the aim to produce organophosphorus FRs from recovered inorganic phosphate chemicals such as struvite (magnesium ammonium phosphate hexahydrate) precipitated from sewage sludge liquors.

See J. van Dijk et al., Chemosphere 296 (2022) 134050 DOI.

Fire and smoke from cross-laminated timber



Gaëlle Fontaine, Centrale Lille France

Tests assessed smoke and fire behaviour of cross-laminated timber under different oxygen concentrations. Cross-laminated timber is a sustainable building material made from dried wood sections bonded by adhesive. Tests used ISO 5660-5 equipment, which enables reduced oxygen atmospheres, and 40 mm thick, 100 mm squares of spruce - polyurethane glue plywood. Results showed that reduced oxygen concentrations did not impact time to ignition and did not significantly reduce peak heat release rate down to 15% oxygen at 50 kW/m². Below that level, no ignition occurs but smoke production significantly increases. Carbon monoxide was much higher with non-flaming (smouldering) decomposition, as were volatiles from incomplete combustion (acetaldehyde, formaldehyde) and smoke particles were less numerous but much smaller (<0.03µm).

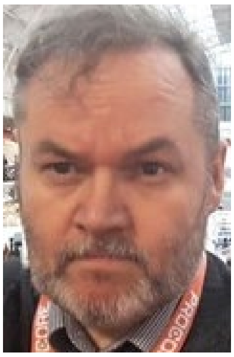
NEW FIRE SAFETY CHALLENGES AND SOLUTIONS

PIN FRs and electric vehicle battery pack fire safety

Lei Chen, SABIC

A key challenge to Electric Vehicle (EV) battery pack design is the battery pack structure which includes battery cooling and cell separation to prevent propagation of the whole battery pack in case of failure of one cell. PIN FR performance engineering polymers structures enable this, whilst ensuring lightweight and electrical insulation. The FR performance of the battery pack structure is key to passing China and UN battery fire safety standards which test the whole battery pack in abusive thermal events.

SABIC's PIN FR glass fibre reinforced polypropylene compounds can prevent fire spread from thermal runaway of one cell, with a 2mm thickness between 18650 lithium ion cells. When used as battery pack enclosure materials, 4mm FR polypropylene and other engineering thermoplastics compounds can also withhold the abusive temperature and pressure exposure in the UL2596 thermal runway test. Such polymer-based solutions enable lightweight and mechanically effective EV battery pack design.



Polyphosphonates for performance fire safety

Richard Clay and Stephen Blair,
Polymer Compounders Limited (PCL)

Based in the UK, PCL supply several thousand tonnes per year of performance thermoplastic polymer compounds to a broad range of customers in automotive, healthcare, industrial, white goods and electrical, including Tier 1's and large OEMs (original equipment manufacturers), in particular ABS (acrylonitrile butadiene styrene), ASA (acrylonitrile styrene acrylate), PC (polycarbonate), PC/ABS and PC/ASA. Innovative, phosphorus polymers, developed by FRX Polymers, deliver phosphorus fire performance in low toxicity, low mobility polymeric molecules, compatible with certain polymers without deteriorating mechanical performance.

In particular, polyphosphonates offer a preferable alterative to brominated FRs in PC/ABS for performance applications in e.g. automotive. UL 94 V-0 can be achieved at 0.8 mm, as well as UL-V5, GWI 825°C (resistance to ignition) and aerospace low smoke, low smoke toxicity requirements. Density is c. 5% lower for comparable mechanical performance, so weight saving. Successful mechanical recycling (one reprocessing cycle) of PC/ABS with polyphosphonate PIN FRs has been shown, with fire resistance and mechanical performance maintained. An outstanding challenge is that the PFAS chemical PTFE is today used to avoid flaming dripping.

Innovative liquid PIN FRs for foams

Claudia Vogt and Edwin Kroke (Technical University Bergakademie Freiberg, TUBAF), with Tobias Wagener and Alexander König (BASF), Carl-Christoph Höhne and Jennifer Limburger (Fraunhofer ICT).

Non-halogenated flame retardant solutions are needed for polyurethane and polyisocyanurate (PUR, PIR) foams for applications such as sound and heat insulation in buildings. Different symmetrical and asymmetrical substituted s-triazine phosphonates were synthesised from alkyl phosphites. These phosphorus-nitrogen PIN FRs are liquid, so compatible with foam manufacture. DIN 13501 class E test was achieved in both PUR and PIR at 5 – 7.5% FR loading.

PIN FRs AND RECYCLING

Several presentations and posters at FRPM addressed recycling:

Jiuke Chen, Empa, presented tests recycling of PET fibres (two re-extrusion cycles, without ageing) containing phosphorus PIN FRs (DOPO derivate, phosphinate) – see Poster Awards above.

Valeria Berner, Fraunhofer ICT, presented recycling of epoxy vitrimers (with an amine hardener containing disulfide bonds) with different commercially available phosphorus PIN FR Vitrimers are innovative polymers which act like thermally-reversible thermosets, see pinfa Newsletter 139. After one reprocessing cycle at 220°C results showed deterioration of fire performance after reprocessing in some cases, but maintained performance in others. Poster online here: https://publica.fraunhofer.de/handle/publica/445003

Marcos Batistella, José-Marie Lopez-Cuesta, IMT Mines Alès, Constantinos Xenopoulosc, Holcim, presented tests using specific grades of fly ash from a thermal power plant as an engineering filler in PIN FR systems (ammonium polyphosphate and melamine polyphosphate) for several different polymer systems.

Marcos Batistella, Dylan Seigler, José-Marie Lopez-Cuesta, IMT Mines Alès summarised tests of reuse of non-sintered polyamide-12 3D-printing powder in LSL printing (Laser Sintered Layer), with and without added PIN FRs. In SLS, layers of powder are deposited, then in each layer the shape is created by laser melt-bonding the polymer, then removing the remaining non-sintered powder. Non-sintered powder was reused in the SLS process for four cycles (total five builds). Addition of ammonium polyphosphate in PLA resulted in changes in the sintering temperature window. Addition of zinc borate showed agglomeration of the FR in reprocessing, probably because it reacts with the laser frequency.

Hai-Bo Zhao, Sichuan University, China, presented laboratory development of chemically recyclable PIN FRs. An experimental phosphorus-siloxane polymer fabric FR coating (wash resistant) could be reversibly redissolved using ethanol. An experimental tannin plus DOPO PIN FR in polyurethane foam could be redissolved out for recycling.

Richard Clay, Stephen Blair, PCL, showed successful mechanical recycling (one reprocessing cycle) of PC/ABC with polyphosphonate PIN FRs (see above)

Dániel Gere and Katalin Bocz, Budapest University of Technology and Economics, presented tests of APP (ammonium polyphosphate) and MMT (montmorillonite) as a PIN FR and synergist in recycled polyethylene (HDPE) reprocessed from post-consumer bottle caps. The objective was to produce a material for outdoor building decorative panelling, so a UV stabiliser was also included (8 hydroxy-benzophenone). Hot pressed samples achieved UL 94 V-0 with 25% APP and 1.5% MMT (the recycled HDPE was UL 94 non-rated without PIN FR addition).

Lein Tange, ICL, summarised the challenges to recycling E&E and technical plastics. Only 6-7 % of post-consumer collected plastics are technical polymers, so sorting and recycling are very uneconomic. A further challenge is the sorting of black plastics, for which Near Infra Red (NIR) laser sorting cannot be used to efficiently separate individual polymers. Consequently, heavier weight polymer plastics are currently in Europe mainly going to incineration or co-combustion in smelters (recovery of precious metals from circuit boards and from other components): HIPS, ABS, PC, PVC, polyamide. Where technical plastics are collected, up to three quarters can often not be recycled because of contamination with other materials or mixing of polymers. Technical polymers have long service lives (several years for E&E, seventeen years on average for automotive, up to half a century for construction materials) so that collected materials are contaminated by “legacy” additives. An increasing proportion today contains chemicals designated as POPs, such as legacy brominated FRs or PFAS, for which the new limit for recycling of 75 ppm for HBCD / 500 ppm for POP PBDEs will be a major obstacle for mechanical recycling but is possible with solvent based purification recycling. The key economic driver for recycling of E&E remains the metal content (copper, silver, gold, rare earths).

Frederico Ulisse, Padova University, presented testing in compression moulded polypropylene of flue gas desulfurization gypsum (main constituent: calcium sulphate dihydrate) with PIN FRs (melamine cyanurate, phosphate ester – the latter also providing plastification. UL94-V2 (3.2 mm) was achieved. The gypsum inhibits fire by releasing water with heat and contributes to char glassification.

Sophie Duquesne, Lille University, tested whether post-consumer recycled polymers could achieve fire performance standards (PEPSIr project, funded by EcoSystem). HIPS from large household appliances, as being the most available post-consumer EEE polymer (25% of arisings), was considered. Commercially recycled HIPS (rHIPS), with addition of brominated flame retardants (at supplier recommended loadings), was not able to achieve the same levels of fire performance under the glow wire GWFI test as virgin HIPS. Full characterisation of the rHIPS was carried out to identify additives and contaminants resulting from various stages of the first life of the material including inherited substances as well as sorting errors. Deterioration of the HIPS polymer itself was found to be limited. Further studies with model materials are in progress to link the ability of recycled materials to be flame retarded with these additive and contamination aspects.

PINFA YOUNG RESEARCHER PRESENTATION AWARDS

These pinfa Awards are the first time such prizes have been offered for presentations at FRPM. A total of 14 candidate oral presentations by young researchers were graded for scientific content, presentation quality and oral delivery by experts from fire research and industry.

- **pinfa Award 1st Prize** (1500 CHF): **Iben Hansen Bruhn, BCE Austria** - Comparison of fire retardant timber treatments
- **pinfa Award 2nd Prize** (1000 CHF): **Weronika Tabaka, BAM Germany** - Bench-scale fire stability testing of carbon fibre reinforced polymer laminates with protective layers
- **pinfa Award 3rd Prize** (500 CHF): **Marie-Odile Augé, Centrale Lille France** and **Daniele Roncucci, Empa** – Ring-opening polymerisation of L-lactide with phosphorus containing compounds

Comparing coated and impregnated FRs in plywood

Iben Hansen-Bruhn, Aarhus University, Denmark, and University of Central Lancashire, UK

Two different ammonium phosphate based PIN flame retardants were applied to 12 mm pine plywood: vacuum impregnation of aqueous mono ammonium phosphate solution and intumescent surface coating of ammonium polyphosphate based. Both resulted in total heat release significantly lower than for untreated plywood (-34% and -20% respectively), in both cases achieving Euroclass B-s1, d0 (versus D-s2, d0 for untreated plywood). Peak smoke toxicity was however three times higher with impregnation compared to coating in under-ventilated fires (smoke from FR coated plywood was similar to untreated). The conclusion is that fire protection by intumescent PIN FRs, which generate char, can be effective in reducing heat release without significantly increasing smoke toxicity.

Protecting carbon fibres from fire in laminates

Weronika Tabaka, BAM Germany

Fire stability of carbon fibre – epoxy resin laminates with protective interlayers was tested at bench scale (120 mm x 120 mm) with simultaneous application of mechanical load and direct flame (butane burner). Six different combinations of two fire protection systems were tested: titanium foil, thermoplastic foil, ceramic layer, basalt fibres, kenaf fibres, rubber isolation mat. Protective systems significantly enhance the fire stability and increased time to failure by 3 to 10 times. Thicker specimens showed longer resistance time, however CFRP laminate with ceramic layer and titanium foil presented outstanding results and the best performance. The protection with Kenaf and basalt fibres offered a natural fibre solution with also good fire resistance performance.

See also previous work testing protective coatings: W. Tabaka et al. Bench-scale fire stability testing – Assessment of protective systems on carbon fibre reinforced polymer composites, Polymer Testing, Vol. 102, 107340, 2021
https://doi.org/10.1016/j.polymertesting.2021.107340

Reactive phosphorus PIN FR for poly(lactic acid)

Marie-Odile Augé, Centrale Lille, France
Daniele Roncucci, Empa / ETHZ, Switzerland

The bio-sourced polymer poly(lactic acid) (PLA) is highly flammable and requires flame retardants to reduce fire risks. A new phosphorus PIN flame retardant DDPO (a phosphorus-containing PIN compound, produced by reacting diethyl phosphite with neopentylene glycol) was incorporated into PLA by copolymerisation, in a one-pot reaction with (*L*)-lactide (the cyclic dimer of lactic acid) and a tin salt catalyst. The objective was to overcome the challenge that phosphorus monomers tend to inhibit polymerisation, including of PLA. Over 90% of lactide was polymerised, but only around 50% of the DDPO monomer was consumed. The resulting copolymer with c. 1% P content, is amorphous compared to neat PLA but showed lower molecular weight and was somewhat gel-like. Peak heat release rate was reduced and delayed. This initial work has so far been carried out at the 1g synthesis scale and UL94 fire performance not yet tested, as this is the initial stage of the research. These polymers could be used as adhesives where fire protection is needed and could be post-functionalized by reactions with the P-H moiety.

POSTER AWARDS

Poster and Travel Awards were offered for the first time at FRPM, by the **Ingeborg Foundation Germany**, for posters from young researchers (51 candidate posters). Summaries below.

For doctoral students:

Poster 1st Prize (500 CHF):

- **Jiuke Chen, Empa** - Mechanical Recycling of PET Fibers containing Phosphorus Flame Retardants

Posters 2nd Prize (300 CHF) – jointly:

- **Hannah Flerlage and Steven Beijer, University of Amsterdam** - Safe and sustainable by design: redesigning flame retardants using a computer-aided framework

and

- **Natalie Vest, Texas A&M University -** Bio-sourced intumescent nanocoating

Posters 3rd Prize (200 CHF) – jointly:

- Marie-**Odile Augé, Centrale Lille France** - Improvement of PLA fire properties with autopolymerizable additives

and

- **Alessandro Beduini, University of Milan** - Polyamidoamines derived from natural α-aminoacids as effective flame retardants for cotton

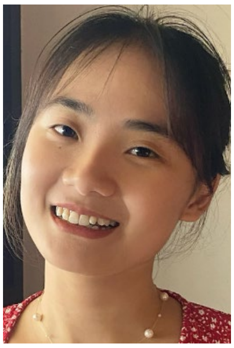
For early-stage researchers (post doc.):

Poster 1st Prize (500 CHF)

- **Daniela Gödderz, Fraunhofer Institute for Structural Durability and System Reliability LBF**, Combination of optical diagnostics and pyrolysis fragment analysis to investigate flame retardant mode of actions.

Travel awards were also made to Alessandro Beduinia, Università degli Studi di Milano, Kata Decsov, Budapest University of Technology and Economics, Hannah Flerlage, University of Amsterdam, Francesca McKenzie, University of Bolton UK, Caleb Ojo, Charles Darwin University Australia, Jovana Petkovska, Cyril and Methodius University North Macedonia, Natalie Vest, Texas A&M University USA.

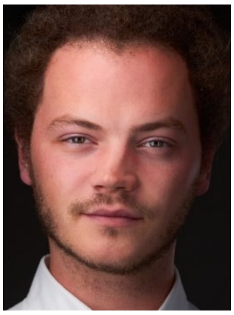
The Poster Prize winners.



Recycling PIN FR PET fibres

Jiuke Chen, Empa

Extruded PET (polyethylene terephthalate) fibres neat or with two different phosphorus PIN FRs (DOPO derivate DOPO-PEPA, phosphonate compound) were tested for mechanical recycling, with twin-screw extrusion – quench – spin-melt – reprocessing cycles (without ageing, total 3 extrusions). The neat PET showed little deterioration of properties with multiple extrusions. The phosphonate reacted with the PET during reprocessing causing cross-linking and brittleness. This, deterioration of the PET was mitigated by the DOPO derivate, which stabilised the recycled PET. A combination of these two PIN FRs showed compatibility with mechanical PET fibre recycling.



Computer modelling to propose safer FRs

Hannah Flerlage and Steven Beijer, University of Amsterdam

SSbD (Safe and Sustainable by Design) is applied to redesign P FR for reduced environmental hazard using a computer-based approach, starting from the existing PIN phosphorus flame retardant Tri-iso-butyl phosphate (TiBP). This PIN FR has been identified as a preferable alternative (Hendriks & Westerlink, pinfa Newsletter 56) but is widely detected in the environment, with a half-life in abiotic conditions of a few weeks (van der Schyffel et al., pinfa Newsletter 146). QSAR computer modelling of biodegradability (aerobic, anaerobic), mobility, bioaccumulation and different toxicity endpoints suggest that Tris (2-hydroxyethyl) phosphate (TEHP) could be an environmentally preferable alternative to TiBP and to other FRs such as the halogenated FR Tris(2-chloroethyl) phosphate (TCEP) which is classified as substance of very high concern (SVHC). The phosphate centre of the molecule is unchanged, but the branched alkyl chains are modified to unbranched chains with terminal hydroxy groups. Reduced ecotoxicity of THEP was demonstrated in acute and chronic experimental tests. Further work is now needed to verify the expected degradability of the THEP molecule, to verify whether it is suitable for use as a flame retardant and also to look for synthesis routes which do not involve the chlorinated vector $POCl_3$ and make use of renewable phosphorus from waste.

Bio-based intumescent PIN FR coating for NYCO

Nathalie Vest, Texas A&M University

Nylon-cotton fabric (NYCO) was multi-layer coated with phytic acid, chitosan and tannic acid, achieving self-extinguishing with 17% weight added. NYCO is widely used in military uniforms and workwear, but has high flammability because of interaction between the two fibres in fire. 50/50 NYCO was primed with polyethylenimine to impart a positive charge then soaked in solutions of bio-based phytic acid (PA), chitosan (CH) and tannic acid (TA), then soaked with repeated quadrilayers CH-PA-CH-TA, rinsed between each treatment. After 15 quadrilayers the textile was dried at 70°C. This resulted in a c. 17% weight increase, nearly six times higher than with 30 bilayer coatings of CH-PA or CH-TA. This high deposition rate, and colour change with the three components suggests chemical reactions between them. The 15 quadlayer PA-CH-TA coated NYCO was self-extinguishing in the 12s Vertical Flame Test and showed >50% reduction in peak heat release rate compared to control (uncoated), 8% lower than CH-PA coated.

Polymeric PIN FR for PLA

Marie-Odile Augé, Centrale Lille France

A self-polymerising commercial additive was compounded into poly lactic acid (PLA) using a twin-screw extruder operating at 185°C. The flame retardant was is able to polymerise under heating. Screw compounding of 20% loading of the FR into the PLA resulted in a c. 10% reduction in peak heat release (cone calorimeter), whereas the reduction in peak heat release rate increased to -43% when the compound was cured at 150°C for 80 minutes (-36% when cured for 120 minutes). The addition of the PIN FR and the curing had little effect on the transition (melt) temperatures of the PLA. The authors conclude that the fire protection effect is a combined result of increased char generation and gas phase action.

Bio-derived PIN FRs for cotton

Alessandro Beduini, University of Milan

Polyamidoamines, synthesised from a bisacrylamide (MBA) and natural amino acids, soaked into cotton, significantly improved fire performance. Nine different α-amino-acids, with hydrophobic, neutral, acidic or basic side-chains, were reacted with N,N'-methylenebisacrylamide. The resulting polyamidoamines (PAAs) were impregnated into cotton by soaking in aqueous solution then drying at 100°C, resulting in 5%, 7% or 10 % weight added. The PAAs from all of the amino acids prevented horizontal burning of the cotton fabric at 7%, with those based on *L*-glutamine or *L*-glutamic acid achieving this even at 5%. The PAAs reduced peak heat release by up to 33% compared to untreated cotton. Fire protection was identified to be by char formation with a stable carbonaceous structure.

Analysing gas phase action of different PIN FRs

Daniela Goedderz, Fraunhofer IBF

Action of the modes of action of PIN flame retardants, gas transport, flame topology and gaseous pyrolysis products, by a combination of optical diagnostics (planar laser-induced fluorescence spectroscopy of OH-radicals) and pyrolysis fragment analysis (TGA-FTIR). In collaboration with the RSM institute (TU Darmstadt), four different commercially available PIN FRs (APP, ATH, DEPZn and a spirocyclic organophosphonate) were tested in polypropylene. Different sample geometries (micro-sized particles and sticks) were compared and the OH-radical concentration was visualised during the combustion process. The use of optical diagnostics revealed peculiarities of the flame retardants used, such as small additional flames emerging from the surface of the sample. The aim is to improve understanding of how different PIN FRs act in the gas phase and to enable more efficient FR design and formulation.

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