

Trends in flame retardants markets and regulations	1	Interview: Hellenic Cables	7
<i>Jonathan Crozier, pinfa</i>	1	<i>Dan Masakowski, Marmon Innovation</i>	7
<i>Adrian Beard, Clariant</i>	2	Interview: Marmon Innovation	7
Interview: Gustav Grolman	2	<i>Marco Badalassi, iPool</i>	8
Interview: Wells Plastics	3	Flame retardants and polymer recycling	8
Interview: Beaulieu International Group	3	<i>Arthur Schwesig, MGG Polymers</i>	9
<i>Caroline Braibant, International Antimony Association</i>	3	PIN FR research perspectives	9
<i>Marc Leifer, ICL-IP</i>	4	<i>Rudolf Pfaendner, Fraunhofer LBF</i>	9
Interview: Lubrizol	4	<i>Fouad Laoutid, MateriaNova Belgium</i>	10
PIN FRs reducing smoke emissions	4	<i>Fabienne Samyn, University of Lille</i>	10
<i>Ayaka Katsuki, Adeka</i>	4	<i>S��verine Bellayer, University of Lille</i>	10
Interview: Lehmann&Voss&Co	5	<i>G��nter Beyer, Fire and Polymers</i>	10
<i>Brigit Fassbender, Budenheim</i>	5	<i>Sabyasachi Gaan, EMPA Switzerland</i>	10
<i>De-Yi Wang, IMDEA Materials Institute Madrid</i>	5	Interview: Bekina Compounds	11
<i>Rodolphe Sonnier, IMT Mines Al��s (France)</i>	6	Natural minerals as flame retardants	11
Interview: B��FA Composite Systems	6	<i>P��ter Seb��, Quarzwerke</i>	11
Interview: Biesterfeld Spezialchemie	6	<i>Jochen Wilms, BYK-Chemie (Altana Group)</i>	11
Developments in cables fire safety	7	<i>Alexander Kulichenko, Europiren</i>	11

One of the milestones conference of the year, Fire Resistance in Plastics is always an excellent opportunity to address the Flame Retardants value chain. Latest developments such as the findings in PIN FRs reducing smoke emissions were reported, while an encouraging perspective was shared on recycling of PIN FR polymers. Echoing the hot topics discussed at FRiP 2018, pinfa plans to support research on a smoke toxicity database, strengthening the largest-ever campaign on smoke toxicity, together with its partner Crepim. pinfa has built a long-lasting relationship with the FRiP organizers and usually schedules its own general assembly meeting back-to-back with FRiP, truly making Cologne one of the place to be in December for the pinfa members. The 2018 issue of the event has been successful and we wish all the best to its American counterpart planned in Pittsburgh PA for the forthcoming April. *Jonathan Crozier, pinfa.*

AMI Fire Resistance in Plastics 2018

The 13th AMI Fire Resistance in Plastics Conference, Cologne, 11-12 December 2018, brought together over 190 participants (up from 160 participants in 2017) from nearly 30 countries, from the polymer, compounding and plastics additives industries as well as scientists and downstream user industries. This pinfa Newsletter Special Edition summarises presentations relevant to PIN fire safety and presents interviews with a selection of companies present. Previous AMI FR conferences are summarised in pinfa Newsletters n  s 61, 76, 80, 88.

The next AMI flame retardant conferences will take place in [Pittsburgh](#) 2-3 April 2019 and in [Cologne](#) 3-5 December 2019.

Trends in flame retardants markets and regulations

Jonathan Crozier, pinfa

summarised trends in flame retardants requirements as seen by pinfa member companies (input collected under anti-trust rules), and market tendencies indicated by different experts and studies, in particular [Markets&Markets](#) who kindly allowed to use this data for the event presentation. He underlined that both regulatory requirements and industry voluntary product specifications are pushing towards better levels of fire safety worldwide, whilst at the same time regulations are increasingly banning conventional halogen flame retardants. Labels such as [EPEAT](#) (widely used for public purchasing) limit the use of brominated and chlorinated flame retardants, and propose to use health and environment evaluation systems for substitutes (such as [GreenScreen](#)).





The global flame retardant market is expected to grow at >6% per year through to 2025, with growth >5% for all types of flame retardants and the highest growth rate for phosphorus-based PIN FRs. The largest and fastest growing market is Asia, in particular for electrical and electronics goods (E&E). Construction is also a major driver of demand for fire safety. Needs for flame retardants are expanding with development of a wide range of polymers, including products for epoxies, ABS, unsaturated polyester resins, PVC, polyolefins.

The pinfa product selector <https://www.pinfa.eu/product-selector/> enables to identify and find information on PIN flame retardants for different polymers and applications and is open to both pinfa members and non-members.

pinfa is the non-halogenated phosphorus, nitrogen, inorganic flame retardant association (a sector group of Cefic, the European chemical industry council). The presenter thanked for input the MarketsandMarkets flame retardants report – global forecast to 2021 <https://www.marketsandmarkets.com/Market-Reports/flame-retardant-chemicals-market-686.html>



Adrian Beard, Clariant

outlined the **fire safety challenges posed by electric vehicles (EVs)** and the resulting needs for new flame retardant solutions. Over 3 million EVs were sold worldwide in 2017, expected to rise to 40 million by 2030. This implies radical changes for the whole car industry, e.g. the drive system of EVs has only 200 parts compared to 1200 in a current car. EVs bring specific new fire risks, with high energy concentration in batteries and risk of thermal runaway, difficulties to extinguish, and high voltages in drive and charging cables, components and connectors, including charging stations. Consequently, manufacturers are trending to demand fire resistance specifications, such as UL94-V0 (vertical test) and limiting the risk of short circuiting by high current tracking index (CTI) values. These requirements must be combined with weathering and temperature, water, UV and chemicals resistance, as well as aesthetic quality (including the specific “signal” orange for charging cables and connectors). Advanced phosphorus-based PIN FRs (e.g. phosphinate based) can ensure these demanding specifications, including reactive phosphorus PIN FRs which can ensure minimal fogging and VOC emissions. He concluded with the opportunities for PIN flame retardants: “orange is the new black”.



Interview: Gustav Grolman

Nils Rickertsen emphasised the added value provided by the distributor, due to a portfolio of solutions, including service to customers, R&D and expertise, and loyalty to suppliers to ensure reliable cooperation. Markets for flame retardants and for FR polymers are increasing in general, and customers are often looking for alternatives to halogenated products. Many solutions exist, in particular a broad variety of different ATH-based flame retardant products with particular added-value, and also some synergists, which can enable lower loadings for mineral-based FRs. Trends are towards using combinations of PIN FRs, and also the modification of well-known PIN FRs, e.g. by special surface treatments, in order to improve the FR-performance without sacrificing the mechanical properties. Distributors can propose innovative and tailored solutions by combining products from different suppliers. Specific areas of development include e.g. adhesives, which need to be FR when used in fire risk assemblies. Electric vehicles are leading to new demand for flame retardant materials, where sometimes performance is key, but sometimes only cost-effective alternatives are needed. Also, further research is still important to better understand the mechanisms of different PIN flame retardants, especially in combination with each other.

Gustav Grolman Group is an international distributor of specialist chemicals since 1855, with technical teams and logistics installations in all European countries. Grolman provides a wide range of additives, fillers, pigments, binders and flame retardants. Customers include producers of compounds, cables, coatings, adhesives, sealants, elastomers and thermoset materials. <https://www.grolman-group.com/>



Interview: Wells Plastics

Gary Ogden sees new opportunities for flame retardants in the expanding markets and new applications. Demand for fire safety can be expected to continue to tighten in sectors such as construction films, wire and cable, automobile and E&E, where innovative synergies with different additives can enable improved performance with cost-effectiveness in these applications. High performance FRs can find added-value niche markets for specialist applications, such as different technical fibres. R&D suggests that novel flame retardant solutions may be developed in coming years. One significant potential sector is flame retardancy of bio-based polymers and fibres, including in fibre-polymer composites. These are growing markets, and customers are looking for non-halogenated bio-based flame retardants, or PIN flame retardants with positive environmental profiles conform to the 'green' image of such materials.

Wells Plastics has over 30 years experience in specialist masterbatches and compounds, with a high commitment to R&D at the global level. The company is specialised in tailor-made and technically advanced polymer based masterbatches and compounds for polymers, such as anti-microbials, flame retardants, processing aids, biopolymers and oxo-biodegradables. The company drives research and innovation to support the plastics industry and its chemicals suppliers. <https://wellsplastics.com/>



Interview: Beaulieu International Group

Femke Faelens notes increasing need for fire safety treatment of floor covering and textile products, in particular in markets such as automobile, commercial premises and hotels, and in higher end markets. Customers are tending to push for non-halogen products, in order to achieve low smoke requirements in regulations, or because this is demanded by environmental labels such as Cradle to Cradle or Ökotex. Important challenges are to find flame retardant solutions for polypropylene or polyamide fibres, with low loadings and compatible with processing of thin fibres (fine dispersion needed), which do not compromise mechanical performance and aesthetics of fibres and which are cost-effective. New FR additives, and particularly their combination with innovative synergists may enable these objectives with low addition levels. The AMI FRiP conference enables to meet suppliers of these different products and experts to better understand what is today available and how different PIN FRs and synergists function.

Beaulieu International Group, headquartered in Belgium, employs more than 5 000 people worldwide with 27 production sites and distribution centres in 16 countries. The company is a world leader in floor coverings, and has business units in polypropylene polymers and engineered fibres and textiles. www.bintq.com



Caroline Braibant, International Antimony Association

presented the increasing regulatory pressure on antimony trioxide (ATO), which is widely used as a synergist for halogenated flame retardants. ATO is currently classified as carcinogenic category 2 by inhalation and STOT cat. 2 (Specific Target Organ Toxicity – lung) but classification as carcinogenic category 1B for all routes could be proposed on the basis of the recent US National Toxicology Program ([NTP Report on Carcinogens – Antimony Trioxide](#) Oct. 2018) carcinogenicity study unless Industry completes the existing toxicological evidence and describes the current occupational exposure situation. Also, Germany has now applied a very low workplace limit of 0.006 mg respirable Sb per m³ (since [May 2018](#)), whereas the current limit in many countries is 0.5 mg inhalable Sb per m³ ('respirable' concerns smaller particles, generally < 10 µm versus < 100 µm for 'inhalable'). Japan has implemented a 0.1 mg per m³ inhalable antimony limit in 2017. i2a is deploying a product stewardship program aimed to address all scientific questions which

could explain what adverse effects could be caused by exposure to antimony substances (trivalent and pentavalent), and identify the workplace exposure levels able to ensure safe production and use of antimony. Producers and users of antimony substances are invited to participate in the generation and reporting of workplace exposure data through a dedicated 2-year campaign starting in 2019.



Marc Leifer, ICL-IP

outlined his vision of flame retardant trends in automotive and E&E, both growing markets for FRs. In automotive, mobility, connected vehicles and safety standards push for more electronics, more cables and connectors, and more demand for flame retardants to ensure fire safety. Similarly in E&E, smart homes, the internet of things and safety standards will also lead to increased demand for FRs. Materials will have to ensure demanding dielectric properties and low conductivity, heat and chemical resistance, whilst enabling miniaturisation which requires improved processing flow. Increasingly Glow Wire 775°C (3 mm) and UL94-V5A (2 mm) will be demanded. Expected trends include continuing growth in the use of and need for flame retardant solutions for performance polymers (ABS, HIPPS, polyamides, epoxies) and a move to substitute ATO (antimony trioxide).

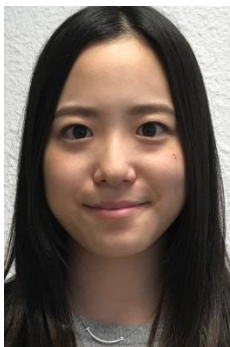


Interview: Lubrizol

Lola Guerra sees that the market is looking for polymer additives solutions with preferably no toxicity profiles for the future. Combinations of phosphorus and nitrogen based additives and synergists with minerals can ensure fire performance while improving mechanical characteristics in materials such as thermoplastic polyurethanes (TPU) for wire and cable. A challenge is that no flame retardant does everything, and new PIN FR products or combinations are needed to improve, in particular, tensile strength and elongation in different polymers. Electromobility is a demanding new market, implying increased use of polymers in vehicles with specific performance requirements, such as electrical and chemical resistance, and weatherability. Future standards are not yet defined, but trends are evident towards higher fire safety requirements than in today's vehicles and growth of non-halogenated solutions.

The Lubrizol Corporation, a Berkshire Hathaway company, is global specialty chemicals company with more than 55 years of experience. Lubrizol Engineered Polymers offers a broad portfolio of engineered polymers including resins that are flame retardant, chemically resistant, bio-based*, light stable, adhesive and fast cycling. www.lubrizol.com/Engineered-Polymers

PIN FRs reducing smoke emissions



Ayaka Katsuki, Adeka

underlined the need to find substitutes to brominated flame retardants because these generate dense black smoke and carbon monoxide in fires. Tests with PIN FRs, acting by intumescence (solid phase) in polypropylene show burning with nearly no smoke. Using the ISO 5659-2, as required by European railway regulations EN 45545-2, polypropylene shows only one sixth of smoke emissions when treated with phosphorus flame retardants than neat polymer, whereas brominated flame retardants with antimony result in higher smoke density. Adeka has achieved the first ever “UL Verified” label for functional polypropylene, for samples with PIN FR propylene UL94-V0 classification (1.6 mm) “99% less smoke density and 89% less carbon monoxide” compared to brominated flame retardant with antimony. In combination with appropriate antioxidant additives, the material also shows durability of flame retardancy and mechanical properties under heat and ageing treatments.



Interview: Lehmann&Voss&Co

Ines Dumsch, underlined the high level of innovation in non-halogenated flame retardants, both in research and in applications in user industries such as construction and automotive. Customers are looking for new additives for new polymer applications and to move away from halogenated flame retardants, but performance and price must be comparable. In her opinion, it would be desirable to move towards polymeric flame retardants in order to avoid issues of migration out of polymers (blooming) and to improve polymer compatibility, but with price remaining a key objective. Another issue is that of corrosion in applications such as cables and electronics, in the case of migration of acid-generating molecules out of FR polymers. “Low smoke” products are demanded, but this can raise questions of what this claim means, how it should be tested and of complexity of impacts on smoke emission of combinations of additives: further information is needed.

Lehmann&Voss&Co. was established in 1894 as a trading company in Hamburg and is today a trader and distributor of chemical additives and a producer of masterbatches and compounds, with more than 20 years of experience in developing and supplying non-halogenated flame-retardant masterbatches for customers in different applications. In 2017, Lehmann&Voss&Co. was recognised as a Top Innovator company by www.top100.de. Lehmann&Voss&Co with its subsidiaries (LEHVOSS Group) has nearly 600 staff worldwide. www.lehvoss.de



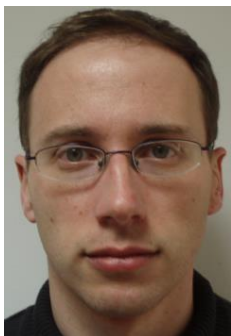
Brigit Fassbender, Budenheim

noted that flame retardants (FRs) represent around one third of polymer additives, and pointed to market tendencies towards FRs with lower smoke emissions and positive toxicity and environmental profiles. Intumescent PIN FRs act by forming a barrier which prevents oxygen entering into contact with flammable gases released from polymers, insulates against heat and also reduces emission of smoke. They do not generate black smoke by pyrolysis in the gas phase of combustion. However, challenges are to prevent migration to the polymer surface over product life (blooming: “dashboard” test), to avoid water uptake and to minimise loss of polymer mechanical properties resulting from FR loading. Budenheim has developed improved formulations of the recognised and effective PIN FR, ammonium polyphosphate, using a new coating which does not contain formaldehydes. Such coated APP based systems improve processing, prevents migration and water uptake and improves thermal stability. UL94-V0 (1.6 mm) is achieved in polyolefins and mechanical performance is maintained (tensile modulus and strength) or improved (elongation at break) compared to standard intumescent FR



De-Yi Wang, IMDEA Materials Institute Madrid

summarised different investigations underway looking at different novel mineral flame retardant and smoke suppression synergists: boron nitride nanosheets, iron hydroxide nanoparticles and functionalised halloysite (an aluminosilicate clay mineral), nanotube (HNT), graphene (used for structural strength), copper and iron compounds (e.g. in nano-form ferrocene), combined with nano-structures (layered double hydroxides). These were tested in epoxy resins, thermoplastics, elastomers and thermosets. In some cases, time to ignition was increased or heat release reduced. In particular, reductions of smoke emission were achieved, including at low doses of metal compounds. The mechanisms of smoke suppression are discussed, included catalysis of aromatic carbon compounds to form linked, stable structures in chars (so making a barrier to smoke emission), the reduction of polyaromatic carbon compounds in fire and the catalytic degradation of soot.



Rodolphe Sonnier, IMT Mines Alès (France)

summarised over 80 smoke emission tests of polymers, with and without flame retardants, using a cone calorimeter, and comparing smoke density (by laser) to heat release rate (HRR). The relation between smoke and HRR is not always linear, particularly towards the end of tests. In these test well-ventilated conditions, polyolefins generate little smoke at low HRR whereas aromatic polymers generate more. Mineral flame retardants ATH and MDH reduce smoke emission, but this seems to be mainly related to the reduction in HRR. The brominated flame retardant TBBA and the phosphorus PIN FR DOPO did not increase the ratio [smoke release per energy released] in polyethylene, but did cause smoke production to start at a lower HRR.



Interview: BÜFA Composite Systems

Peter Kornas considers that fire safety requirements will continue to tighten in some sectors, with at the same time increasing demands on smoke toxicity. Standards such as EN45545-2 (railways), CPR EN13-501 (building) or IMO FTP Code 2010 (shipping) already require very high levels of fire resistance, which can be achieved by PIN (zero halogen) flame retardant systems. More demanding requirements are liable to also come into place on toxicity, such as calculation of survival impact in a given space for railways, or smoke toxicity specifications for construction products. Also, infusion (closed mould) processes will develop to avoid emissions in production workplaces. An important challenge for PIN FR systems is water resistance and related issues with weathering and durability of polymer surface characteristics. Combinations of novel coated PIN FRs and innovative polymer – FR – additive systems can be developed to address these challenges, whilst making fire protection more stable, lighter and safer.

The BÜFA Group was established in Germany in 1883 and today operates in chemicals, composites and cleaning products. The company is committed to innovation, environmental chemistry and targeted products for demanding industries and specific applications. BÜFA Composite Systems supplies in-house developed FR solutions, especially to the automotive, rail, commercial vehicle, energy and construction sectors, with a main focus on non-halogen systems. <https://www.buefa.de/en/composites/>



Interview: Biesterfeld Spezialchemie

Peter Kumpf emphasised the role of the distributor in advising customers, including both users of polymers and related products as well as formulators, supporting definition of requirements and material selection, providing expertise on applications and ensuring supply. In applications where halogenated flame retardants are under pressure Biesterfeld is offering halogen free alternatives. Challenges include fire performance, material performance and increasingly concerns about smoke density and smoke toxicity. There is no single solution for low smoke, with specifications depending on the testing method. Customer pressure is moving towards substitution of antimony trioxide, with concerns about developing regulatory constraints. Also, a trend towards reactive and polymeric flame retardants is expected, to minimise migration and exposure risks. The polymer and application specificity of these substances will reinforce the need for distributor support and expertise to customers.

Biesterfeld Spezialchemie, part of the Biesterfeld group, distributes chemical specialities in Europe, with divisions covering life sciences, health care, nutrition, performance products, CASE (coatings, adhesives, sealants and elastomers) and polymer additives. The latter distributes flame retardants for all thermoplastics as well as polyurethanes, coatings, adhesives, textiles and other applications. www.biesterfeld-spezialchemie.com

Developments in cables fire safety

Interview: Hellenic Cables



Fotini Karkantelidou and **George Dritsas** note that an important challenge today is the Construction Products Regulation. Demanding CPR specifications are increasingly specified by customers, both for low voltage cables in construction and for medium and high voltage cables. Innovative solutions to achieve these specifications, including low smoke and prevention of flaming dripping, being implemented by Hellenic Cables, include use of ammonium polyphosphate and silicates as PIN flame retardant components and synergies with specific smoke reducing additives. Also, changes in polymers used for low and medium voltage cables can be expected. Hellenic Cables is already implementing recycling of production losses at its sites, and remelt and reprocessing of PIN FR cable compounds is effective, although sometimes with downgrading to less demanding applications.

Hellenic Cables group, part of Viohalco SA, is specialised in cables since 1950, and includes Fulgor and Icmec Ecab. The group has six production plants in three countries in Europe, producing extra high, high, medium and low voltage cables, submarine cables, thermosetting cables, cable compounds and enamelled wires. 80% of the company's production is exported outside Greece (Europe and Worldwide). www.cablel.com

Dan Masakowski, Marmon Innovation

presented development of new materials and their testing to meet demanding fire safety and smoke emission standards for cables for railway and metro control cables. Non halogenated materials are needed to achieve smoke limitations. Use of electron beam radiation to ensure cross-linking of cable polymers has enabled to achieve UL94- VW-1 test, with a LSZH (low smoke zero halogen) polyol based cable formulation, which offers a longer time to ignition and lower peak heat release than conventional halogenated flame retardant cable, whereas smoke emission is down to nearly one tenth (passing FT-4 tray burn smoke test).



Interview: Marmon Innovation

Dan Masakowski notes the overall trend towards zero halogen, low smoke cables, in many applications, although this is moving faster in Europe than in the USA. A key driver in this trend is the low corrosivity of smoke emitted in fires, both because of the impact on people (preventing escape) and the impact on electrical safety and communications systems. Overall, low combustibility remains however more important than smoke emissions: carbon monoxide emissions are above all related to the quantities of materials burning. Cable trends include moves to cheaper polymers, such as cross linked polyethylene, but the flame retardant systems are similar to conventional cross linked ethyl propyl rubber. A challenge for PIN flame retardant solutions is that intumescent do not function in cross linked polymers, which are increasingly used in cables. Future solutions may include developing higher performance thermoplastics, and using fire protective coatings over the whole cable tray to reduce requirements applicable to the cable materials themselves.

Marmon Innovation was established eight years ago, to provide R&D support for the Marmon Engineered Wire & Cable group (a Berkshire Hathaway company), which as 15 wire and cable companies worldwide, providing basic research and support to the companies on product development. Marmon Innovation has a platform specialised in zero halogen materials. <https://marmonewc.com/innovation/>

Marco Badalassi, iPool

summarised trends in cables flame retardancy. The EU Construction Products Regulation brings new requirements for smoke density, non dripping and smoke acidity. Developments to achieve this cost-effectively are based in PIN flame retardants, including combinations of different mineral fillers (e.g. with calcium carbonate), coating of natural minerals, better particle size specification of minerals, coupling agents (e.g. silanes) and additives / synergists.



Flame retardants and polymer recycling

A panel discussion on recycling was organised by pinfa, with **Raquel Llorens Chiralt, AIMPLAS**, **Kathrin Lehmann, Evonik** and **Rudolf Pfaendner, Fraunhofer**, chaired by **Adrian Beard, President of pinfa**.

The panellists noted that EU policy is strongly pushing towards obligations for polymer recycling, with mandatory [objectives](#) fixed for recycling rates in the Circular Economy Package: 65% sorting and recycling of municipal waste, 55% recycling of plastic packaging waste, zero landfill of potentially recyclable materials by 2030.

Brominated flame retardants (BFRs) are identified as a significant challenge to recycling, because of the obligation to separate out these materials.



Opportunities identified include

- **potential for mechanical recycling of thermoplastics, including when containing PIN flame retardants**
- **possibility to downcycle** to products with less demanding technical requirements: industries producing such lower value products are mostly today not operating in Europe, so this offers an opportunity to relocalise jobs into Europe
- **increase the use of recycled polymers in new products**. New composite materials can combine recycled materials (polymers or fibres) with new polymers.
- **industry actions**, such as the automobile CARE Initiative (objective recycling of 80% of cars)

Panellists and conference participants however pointed to challenges:

- need to considerably **improve collection and sorting**, to ensure supply of recyclable materials, including legislation to define who is responsible for organising and funding this (in particular for imported products)
- **difficulty of recycling thermosets**: need for chemical recycling
- need for research to ensure **material quality and mechanical properties** with repeated recycling
- an alternative to mechanical recycling is chemical recycling, where the polymer/compound is broken back down to chemical building blocks for chemical reprocessing, see for example the PSLoop industrial pilot plant <https://polystyreneloop.org/>
- currently over 2/3 of WEEE (electrical and electronic goods waste) **leaves Europe**, so preventing development of industrial scale recycling in Europe
- **flame retardants used today should have positive environmental and toxicity profile** in order to prevent issues with their presence in polymer recycling in the future
- a **stable legal framework** is needed to enable industrial investment in recycling and development of operational markets between recyclers and polymer users



Arthur Schwesig, MGG Polymers

presented the company's activities as an 'urban miner' of waste materials, specialised in post-consumer E&E wastes. Recycling is complex, because E&E wastes contain over 150 different polymers, containing a wide range of additives. Brominated flame retardants are a significant problem, because plastics containing them must be separated and incinerated, with high costs. OEMs are looking for polymers made of recycled materials to respond to requirements of public purchasing (EPEAT, GPP) or labels. MGG offers Blue Angel certified recycled polymers (EuCertPlast). Successful examples include Nespresso coffee machine, Trodat stamp using recycling ABS and Orange 'box' using recycled PC/ABS. As an example, Mr. Schwesig presented the development by MGG of a new recycled polymer from 100% post-consumer lighting PC, which is transparent so allowing all colours for the manufactured PC/ABS. OEMs do not want brominated substances, so a phosphorus FR is used, completed by additives for anti-dripping and cooling (preventing afterburn). Development requires identifying and organising the stream of appropriate secondary materials, testing different additives to ensure UL94-V0 (1.6 mm) and GWIT 800°C as well as mechanical and electrical properties and reliable colour. UL CRI (Certification Requirement Investigation) is then implemented to establish the reliable testing of quality and characteristics for the yellow card listing.

PIN FR research perspectives



Rudolf Pfaendner, Fraunhofer LBF

presented investigations into oxymides as a possible new class of PIN flame retardant synergist, acting in the gas phase by releasing radicals which quench oxygen. These nitrogen containing aromatic carbon molecules release nitrogen containing radicals and alkyl or alkoxy radicals in fire. They can be engineered to enable high temperature processing or to produce polymer forms and can be functionalised with phosphorus or sulphur. Used at loadings of 2-5% with 5-15% phosphonate (phosphorus PIN FR) they have shown to achieve UL94-V0 (1.6 mm) in polypropylene and polyethylene. Synergy has also been demonstrated with melamine cyanurate. This gas phase mechanism does not generate smoke acidity and is not expected to increase smoke toxicity. Further development is underway with an industry partner.



Fouad Laoutid, MateriaNova Belgium

presented testing of industrial plasma technology for coating different materials with flame retardants. Such technology is today widely used in industry, for example for coating articles with metals (such as drill bits). Plasma coating equipment is today available for coating powders, films, fibres or cables. The plasma reactor technology has been tested for various materials including vegetal lignocellulose fibre insulating panels, polyamide sheets, polyester fabrics. Plasma coating of DEP (diethyl phosphate) and tri ethoxysilane, with a 5-10 µm deposit, reduced peak heat release by around one third for polyamide sheets and rendered polyester fabric difficult to ignite and self-extinguishing.



Fabienne Samyn, University of Lille

presented testing of innovative PIN flame retardant solutions for polyamide (PA6). Guanidine sulfamate, which can be derived from bio-sourced DNA in food processing wastes, and MPP (melamine polyphosphate) were tested at 2.5% + 2.5% loading, showing synergy in fire performance, and enabling UL94-V0 at 1.6 mm. The mechanism was thought to be generation of aromatic carbon structures, so increasing the molecular weight (and so reducing the flammability) of gases released from the polymer during fire. The implications of this for smoke toxicity were not discussed. In other tests, vinyl silane surface treated MDH (magnesium dihydroxide) was tested in PA6, again enabling UL94-V0 at 1.6 mm but Glow Wire Ignition of only 700°C (instead of 750°C requested). Water uptake and blooming which are known issues with mineral FRs in polyamides were not yet investigated.



Séverine Bellayer, University of Lille

presented research into substitution of SVHC (substances of very high concern) brominated flame retardants in flexible polyurethane foams by sol-gel surface application of phosphorus – silicon compounds (see pinfa Newsletter n°91). For some combinations, with a surface coating thickness of around 100 nm, significant reductions of pHRR (peak heat release rate) and of carbon monoxide emission and UL94 self-extinguishing were achieved. Application on wood has also been tested. Mechanisms are thought to be production of a silicon – oxygen – phosphorus linked char and release of DEP (diethyl phosphonate) acting as a radical scavenger in the gas phase. Testing underway with bio-derived materials (cysteine from DNA, chitosan) has so far not given reliable results. Tests suggest that the treatment is physically but not chemically bound to the foam surface, but is not released in mechanical tests.



Günter Beyer, Fire and Polymers

discussed research underway into flame retarding of silicone based polymers and use of silicones in flame retardant systems in other polymers. Silicone elastomers are growing 7% per year. Different minerals can improve fire performance of these polymers, including ATH, MDH, calcium minerals (e.g. wollastonite), silica, coatings of metal hydrates, by mechanisms including release of flame diluting water or carbon dioxide, production of ceramic-like char. Platinum is also effective at ppm levels, probably by inhibiting degradation of the polymer backbone. Silicone polymers can contribute to flame retardancy in other polymers by generating silica residues contributing to char barriers.



Sabyasachi Gaan, EMPA Switzerland

presented innovation in DOPO-derived (phosphorus based) PIN flame retardants. Products already developed include a DOPO-derivative for polyamide (PA6), now industrialised by Litrax for use in carpets. This is effective at <10% loading. A DOPO-PEPA (pentaerythritol phosphate derivative) is being developed with Metadynea for use in polyester-based technical textiles and films, which can be mixed directly during spinning, has low water uptake and inhibits oxygenation of the polymer so facilitating recycling. Research is underway to develop a DOPO derivative (DVVPO with vinyl bonds) which can be reacted or polymerised during extrusion, so ensuring

durability and no migration. All of these DOPO derivatives have been tested and show good toxicity profiles: absence of cell toxicity, inflammation or effects on DNA or reactive oxygen in cells.



Interview: Bekina Compounds

Peter Uytterhaegen explained that Bekina produces and sells an innovative non-halogen fire safety solution, using a rubber-like polymer for injection molding or extrusion to provide protection from extreme fire (Cellulose fire ISO 834-1, hydrocarbon ISO 834-3 and even jet fires). Applications include offshore and petrochemical installations, but also safety cable protection in construction and transport systems (alarm, communications, control cables). More on-shore applications will be developed based on the successful experience in off-shore. The material absorbs heat, expands about 100% and ceramifies in fire, producing a low heat conductivity, highly mechanical and chemical resistant protective volume around sensitive elements, with stability up to 1500°C. Release of water from compound OH groups at 200-250°C and endothermic (heat absorbing) ceramic transition at 700-800°C contribute to limiting temperature increase behind the protective barrier.

Bekina Compounds produces compounds and masterbatches, specialised in natural and synthetic rubbers. It is part of the Bekina groups which also manufactures natural rubber, synthetic rubber, polyurethane and TPE (thermoplastic elastomer) products by extrusion and injection molding, including the footwear, which was the company's first activity in 1962 boots. www.bekina-compounds.com

Natural minerals as flame retardants



Péter Sebő, Quarzwerke

presented developments with kaolin (a mined aluminium silicate mineral) and wollastonite (a calcium silicate). Kaolin can be optimised by specification of grain size, coating or calcination. It offers advantages of white colour, low abrasion and improvement of impact strength. Tests showed that use of amine-coated kaolin with phosphinate in polyamide enabled reduction in loadings of flame retardants needed to achieve UL94-V0 (0.8 mm). Wollastonite with a chain/needle structure can possibly replace glass fibre, to provide both flame retardant and mechanical properties.

Jochen Wilms, BYK-Chemie (Altana Group)

Showed developments in use of natural and modified clay minerals as PIN flame retardant synergists, based on mined bentonites (montmorillonite, smectite). Functionalisation with amines enables exfoliation of clays in processing, improving dispersion of platelets into the polymer. These platelets, with a high aspect ratio (surface area/thickness) can inhibit gas movement through the polymer in case of fire, prevent dripping, stabilise char and also improve polymer mechanical properties and scratch resistance. The clays can also be delivered in a concentrate with a special grafted polymer. The use of coupling agents brings in general polarity, so improving the effects of the clay.



Alexander Kulichenko, Europiren

outlined flame retardant application of brucite, a natural magnesium hydroxide mineral. Performance and chemical composition are improved by sorting of the mined mineral using X-ray technology (stone by stone) according to content of other elements (calcium, magnesium, iron, silicon), precision milling to maintain specific surface area and surface treatment (with stearic acids, silanes). Coating can prevent problems of temperature resistance and ageing resulting from impurities in the brucite. A new coating with alkyl silane is now available, this enables application in polypropylene for cables, for example in the automotive cable market or for roofing, where companies are looking for non-halogenated solutions.

