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25th Annual Conference on Recent Advances in Flame Retardancy of Polymeric Materials

Conference Program

Monday, May 19, 2014

8:00 a.m. – Introduction to the meeting

Charles Wilkie

Chairperson: Kelvin Shen

Session 1: Approaches to Fire Retardancy

8:15 – 8:45

Flame Retardants: What Do We Have - What Do We Need 1

Martin Klatt, BASF SE, 67056 Ludwigshafen, Germany; martin.klatt@basf.com

Plastic materials are a constant company of our daily life. From foams for insulation over engineering plastics and epoxy resins for electrical/electronic parts to polyolefins for films and cables, plastics often have applications which require flame resistance.

While most high volume plastics are combustible on its own there are a lot of choices for flame retardants to impart flame retardancy. However, most flame retardants used have also negative impact on the properties of the plastic material. As such the use and benefit of a flame retardant is always a compromise between meeting the required flame retardance and the best performance of the plastic compound.

An overview of mode of action of flame retardants will be given and typical flame retardant families for major plastic materials including engineering plastics, polyolefins, epoxy and polyurethanes will be presented.

From halogenated substances over red phosphorus to nitrogen based flame retardants there are many different solutions possible for the various plastic materials. For each system the deficiencies will be discussed and the needs for better performance will be illustrated. As such a wish list for an improved flame retardant system will be given from the perspective of a producer of flame retarded plastics.

8:45 – 9:15

The History and Future Trends of Non-Halogenated Flame Retarded Polymers 19

James Mitchell; Solvay Engineering Plastics; James.mitchell@solvay.com

Non-halogenated flame retardants have emerged as the dominant additive system used in engineering plastics. This is mainly due to new environmental regulations but also due to their ability to meet the end customer requirements without compromising safety. Key fire tests like the UL94 and the glow wire can be passed to the highest safety levels using these additives. Further, unlike traditional halogenated systems they provide a low fume toxicity and density allowing their use in railway and other public transportation systems where ease of escape is a key requirement.

High grow potential is expected in various Asian countries with special attention on China and India. In Europe applications are moving east into countries like Poland and Bulgaria, while Russia appears to offer future opportunities. North America has re-emerged as a power in engineering plastics due to the revolution in cheap energy coming from shale gas fracking. This new possibility of cheap energy could change the face of the industry over the coming years and will depend highly on political decisions coming from individual states.

While standard electrical protection applications will continue to provide growth it is with new applications that the major growth is expected. LED lighting, photovoltaic parts and both electrical and structural parts in the automotive industry are of particular interest.

Non-halogenated flame retardant use shows little sign of slowing down and will continue as the additive of choice for the considerable future.

9:15 – 9:45

US EPA Alternatives Assessments for Flame Retardants 31

Emma T Lavoie; U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics (US EPA OPPT), 1200 Pennsylvania Avenue NW, Washington DC, 20460; Lavoie.emma@epa.gov

The exposures and hazards associated with polybrominated diphenyl ethers (PBDEs) in particular have driven a focus on flame retardants that will require choices in policy to balance the risk-risk trade-off between fire safety and environmental safety that is debated by interest groups. While the challenge to find the right approach may continue for years, green chemistry principles argue the need to identify the least hazardous chemicals for uses in the mean time. Because exposure to flame retardant chemicals is inevitable at one or more parts of a product life cycle, selecting the least hazardous chemicals that perform the needed functional use is an important approach to reducing chemical risks. The US EPA Design for the Environment Program has provided information in several projects over the last ten years by assessing more than 50 flame retardants in four projects covering alternatives for pentaBDE, decaBDE, TBBPA, and HBCD used in furniture foam, textiles, electronics and polystyrene building insulation. These projects are voluntary and stakeholder informed. The alternatives assessments have not only identified relevant chemicals and provided environmental hazard profiles but also presented a forum for all stakeholder voices, assessed many chemicals at one time and importantly have shared data not previously available to EPA or the public. The evidence shows that 1) flame retardants have inherent persistence 2) there is a spectrum of inherent hazards across the broad class of chemicals but 3) some flame retardants do have lower hazards (e.g., some metal oxides and some very large polymers). Providing data about flame retardant availability, uses, inherent hazards, and associated tradeoffs gives stakeholders the information needed to make informed decisions about chemicals they use, research and development priorities, policy approaches, and life-cycle impacts while flammability standards shift and scientific evidence is gathered.

9:45 – 10:15

Influence of Flame Properties on the Effectiveness of Gas-phase Fire Retardants ..... N/A

Gregory Linteris; National Institute of Science and Technology, Engineering Laboratory, 100 Bureau Drive MS-8665, Gaithersburg, MD

20899-8665, USA, linteris @nist.gov; 301-975-2283; linteris@nist.gov

For fire retardants which act in the gas phase, the mechanisms typically are either temperature reduction (for inert compounds) or radical reduction (for chemically active moieties), with the latter occurring through radical trapping or catalytic recombination reactions. Hence, these mechanisms are very similar to those of gas-phase fire suppressants which are added to flames. Nonetheless, for fire suppressants, it has been found that the effectiveness of the agent is highly dependent upon the characteristics of the flame to which the agent is being added, and this flame dependency varies with the particular chemical being added. The effectiveness of some gas-phase flame inhibitors in different flame types is discussed, as are the flame characteristics which control their behavior.

10:15 – 10:30 Coffee Break

Chairperson: Walid Awad

Session 2: Equipment

10:30 – 11:00

Flaming Combustion Calorimetry: A New Tool for Flammability Assessment using mg-sized Samples 48

Stanislav I. Stoliarov, Fernando Raffan, Xi Ding, Roland Krämer; University of Maryland, stolia@umd.edu

Microscale Combustion Calorimetry (MCC) was developed to address the need for rapid and reproducible screening of new flame retardant additives and flame resistant polymer chemistries. While this technique proved to be excellent in providing information regarding the heat release rates, total heats of combustion and solid degradation kinetics, it does not directly account for the effects of gas-phase flame inhibition, which can be observed in many bench-scale flammability tests. To overcome this limitation, we have developed a new technique, Flaming Combustion Calorimetry (or FCC). FCC is based on the same key principles as MCC. In both cases, the material sample is small (about 30 mg, in the case of FCC). Solid pyrolysis is conducted under linear heating conditions and is completely uncoupled from the gas phase combustion. In both cases, the oxygen consumption principle is utilized to measure heat release. However, unlike in the case of MCC, gaseous pyrolysis products generated in FCC are not forced to be completely oxidized; instead, they are combusted in a laminar diffusion flame similar in structure to that observed in LOI and cone calorimetry tests. FCC provides a capability for a full control of gaseous atmosphere surrounding the flame. The design of the instrument can be extended to accommodate additional flame characterization including measurement of soot and carbon monoxide yields or flame temperature.

11:00 – 11:30

Flaming Combustion Calorimetry: Application to Flame Retarded Polymers ..... N/A

Roland H. Krämer, Fernando Raffan, Xi Ding, Stanislav I. Stoliarov; BASF SE, Advanced Materials & Systems Research, B001, 67056 Ludwigshafen, Germany; roland.kraemer@basf.com

The Flaming Combustion Calorimeter (FCC) is a new characterization method that allows one to measure the effect of a flame retardant on the heat release rate and on the soot yield of a small diffusion flame fed solely by the pyrolysis gases of a polymeric compound. The residual mass left after pyrolysis is determined gravimetrically. The FCC offers the opportunity to measure the most important parameters determining the mode of action of a flame retardant, using the actual fuel. In a first series of experiments, the new tool was used to analyze the effect of a benchmark halogen-free flame retardant, aluminium diethlyphosphinate, on the flaming combustion of poly(butylene terephthalate). A comparison between the new technique and Microscale Combustion Calorimetry and Cone Calorimetry was performed.

11:30 – 12:00

Survey of Ignition Sources for Electrical and Electronic Materials 65

Marcelo M. Hirschler; GBH International; 2 Friars Lane, Mill Valley, CA, 94941, US gbhint@aol.com

This survey describes a series of ignition sources potentially applicable to assessing fire-test-response characteristics resulting from the ignition of electrical and electronic insulation materials or of electrical or electronic products containing such materials. This survey describes both flaming and non-flaming ignition sources, since the outcome of a non-flaming ignition can be the eventual flaming ignition of these materials or products.

Non-flaming ignition sources include smoldering cigarettes, glow wires, hot wires and radiant heat sources. Radiant heat sources are often accompanied by a supplementary igniter, which can be a pilot flame. Flaming ignition sources include both premixed flames and diffusion flames.

The overall characteristics of ignition sources being discussed include:

1. The intensity of the ignition source. This is a measure of the thermal insult onto the test specimen resulting from the combined conduction, convection and radiation effects caused by the ignition source.
2. The location of the impingement of the ignition source on the test specimen.
3. The duration of exposure of the test specimen and whether it is continuous or intermittent.
4. The orientation of the test specimen in relation to the ignition source.
5. The ventilation conditions in the vicinity of the ignition source and exposed surface of the test specimen.

A variety of standard test methods, specifications and regulations have been issued (by organizations including ASTM, NFPA, ISO, IEC, IEEE, UL and FAA) that contain ignition sources used for electrical and electronic insulation materials and the products in which they are used. This survey describes such ignition sources and includes information on the standard method in which they were first described.

12:00 – 12:30

Quantitatively Measuring the Gas Phase and Condensed Phase Flame Retardant Efficiency 93

Jinfeng Zhuge, Xin Chen, Wilson Cheung; SABIC Innovative Plastics, 475 Creamery Way, Exton, PA 19341 USA; Jinfenge.zhuge@sabic-ip.com

Microscale combustion calorimetry (MCC) can be run with nitrogen environment and nitrogen/oxygen mixture environment. In both of the environments, the decomposed species will be completely oxidized. Therefore, no gas phase FR activity will be revealed. However, in the condensed phase, when the test is conducted under the nitrogen environment, which simulates the real fire scenario that solid polymer would undergo anaerobic decomposition, it should preserve any char that a sample can generate. Nevertheless, when the test is conducted in nitrogen/oxygen mixture environment, since there is enough oxygen supply and the temperature of the pyrolysis chamber continuously increases, even the char will be decomposed, i.e. energy that had been preserved in char is released in this case. Therefore, the difference in total heat release (THR) measured in the two environments should provide an indication of condensed phase flame retardant efficiency. Similarly, since materials in both Cone calorimetry and MCC (nitrogen) undergo similar anaerobic decomposition condition, the difference between the two test methods is in the combustion process (incomplete, if any, in Cone and complete oxidation in MCC), therefore, the gas phase FR efficiency can be estimated.

12:30 – 1:00

Green Construction: The Implications for Fire Safety and Flame Retardants 102

Tim Earl, GBH International; tearl@gbhinternational.com

Green construction is a major part of the global movement towards sustainability and environmental stewardship. A number of voluntary labels and guidelines have been developed, and continue to be developed and revised, to designate certain types of construction as more or less desirable from a "green" point of view.

Many of these guidelines have the desirable effects of minimizing energy waste and increasing efficiencies. Unfortunately, such guidelines do not generally take into account fire safety, and some of them may unintentionally increase fire hazard and fire risk.

In particular, some of the recommendations being made focus on material composition. A common focus of this type of recommendations is to advocate for the elimination of the use of flame retardants, often based on prejudicial information regarding their effects.

Often, the organizations advocating for green construction do not have the expertise to fully appreciate how the changes to methods of building construction can impact fire safety.

This paper will discuss the impact which these guidelines are likely to have on fire safety, and in particular the use of fire retardants.

1:00 – 2:00 Lunch

Chairperson: Serge Bourbigot

2:00 – 2:30 Fred Schall

Science based testing for Regulation – the new European Requirements for Railways 116

Fredrick P Schall, Govmark Ltd., McHenry, IL. fpschall@comcast.net; Janet Murrell, Exova Warringtonfire, Warrington, UK

In the same manner as the European Union developed a single harmonised package of test methods and classifications for construction products so there was a need to undertake the same harmonisation for railways so that trains can move easily between the 32 countries in the European Economic Area. The development of EN 45545 has paved the way for improved fire safety and interoperability across the European railway system ensuring that the same levels of safety apply in all countries. Although a European project, the research behind its development could potentially form the basis of a framework for a global change in transport systems. Methodology developed is already feeding into the International Maritime Organisation to further develop the test methods they currently use. The seven part standard provides a complete fire safety approach; covering reaction to fire, fire resistance, fire detection, etc.

The work began with the Regulators and Train Operating Companies defining, based on statistical incidents, typical train fire scenarios which were then recreated in the real scale. The data derived allowed qualification and quantification of the fire parameters required to be controlled and determined the tests which would be conducted, the output from which should be science based to allow the use of fire safety engineering to determine evacuation potential which would also feed into criteria for the test methods.

The reaction to fire behaviour of materials is covered by part 2 of EN 45545, which was published in February 2013. We expect that in three years time, all materials used on European rolling stock will comply with EN 45545-2 and the current national standards will be withdrawn. During this three year period of coexistence, the reaction to fire behaviour of materials must be assessed against whichever standard (EN 45545-2, BS 6853, NF F 16-101, etc.) is specified in the train build fire safety plan.

This paper will discuss the development of the testing regime for materials use on European railways and in addition how the test methods selected have been developed and improved to enhance the determination of fire safety. Examples will be given of the future development of fire test methods, for example, the assessment of toxic fume emission for which the European Commission part funded a project, TRANSFEU, which further developed a small scale toxicity test used in IMO in which the ISO 5659 smoke chamber was coupled with Fourier Transform InfraRed (FT-IR) analysis.

Session 3: Textiles, Foams, Fabrics and Wood

2:30 – 3:00

Flame Retardancy of Cotton Fabrics with Self-Curing Coating Treated by Dipping and Spray 132

Jun-Chi Yang, Jian-Qian Huang, Yu-Zhong Wang; Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China; E-mail: yzwang@scu.edu.cn*

A water-based coating composition which is self-curing at room temperature, has been deposited on cotton fabrics through dipping and spray in order to enhance their flame retardancy. To this aim, different content of coatings were deposited on cotton fabrics, and the difference between two deposition procedures, dipping and spray, has been considered and compared. In particular, the self-curing coating composition of ammonium polyphosphate (APP) and branched polyethyleneimine (BPEI) is easy to control and synthesize. The synthesis mechanism of self-curing coating, which is the reaction between APP and BPEI, was discussed. The morphologies of the self-curing coating have been discussed by scanning electron microscopy (SEM) in detail. The thermal stability of the cotton fabrics with different content of self-curing coating was investigated by thermogravimetric analysis (TGA). Vertical flame testing has been used to evaluate the flame retardancy of the cotton fabrics. The char residues, collected after the vertical flame testing, were examined with SEM. Furthermore, cone calorimeter has been used to evaluate the flammability. This work was expected to present a new approach for the flame retardancy of cotton fabrics, and this approach is easy to operate.

3:00 – 3:30

Water-Based, Flame Retardant Nanocoatings for Foam, Textiles and Other Polymeric Substrates: New Environmentally-Benign Opportunities 134

Jaime C. Grunlan; Department of Mechanical Engineering; Department of Chemical Engineering & Materials Science and Engineering Program; Texas A&M University; jgrunlan@tamu.edu

This presentation will highlight new flame retardant (FR) nanocoating systems, prepared from aqueous polyelectrolyte solutions, developed within the Polymer NanoComposites (PNC) Laboratory (http://nanocomposites.tamu.edu/). In an effort to create an environmentally-friendly flame retardant system for foam and fabric, thin films were assembled layer-by-layer (LbL) using "green" materials obtained from completely renewable sources. Ten bilayers of pH 6 chitosan (CH), as the cationic layer, and pH 10 montmorillonite (MMT) as the anionic layer, were deposited on flexible polyurethane foam (30 nm thick and added 4 wt%). When cut open after direct flame from a propane torch for 10 seconds, white undamaged foam was revealed under a thin black char layer. In related work on foam, vermiculite (VMT) clay was layered with CH, followed by layers of an intumescent system comprised of CH and APP (or polysodium phosphare [PSP]). This 'stacked' FR system (i.e., intumescent layers on top of clay layers) reduced the foam's peak heat release rate by 66%. Just two clay layers provide enough support to the foam during heating to allow intumescence to occur prior to collapse, creating our best result to-date. Another recipe, involving layers of poly(vinylsulfonic acid sodium salt) and CH, completely extinguishes the flame from a butane torch on this same foam. This exciting result is due to a 'gas blanket' effect in which the coating releases small amounts of NH3, SO2 and H2O that prevent oxygen from reaching the foam surface. On cotton fabric, we will show how a single aqueous polyelectrolyte suspension, made with polyethylenimine and PSP. Weight gain on the fabric is controlled by the time in solution and the treated fabric is able to pass standard vertical flame testing. This has been dubbed the "OnePot" system, which was inspired by LbL nanocoating, but is more efficient due the need for only a single layer.

3:30 – 4:00

Modified Bench Scale Test and Reference Polyurethane Foams for Assessing Smoldering in Upholstered Furniture 150

Mauro Zammarano1,2, Szabolcs Matko1,William M. Pitts1, Douglas M. Fox2, Rick D. Davis1

1Flammability Reduction Group, Engineering Laboratory, National Institute of Standards and Technology, USA; Mauro.zammarano@nist.gov; 2Dept. Chemistry, American University, Washington DC.

Smoldering poses a severe fire hazard due to the potentially lethal amount of toxic carbon monoxide released, and the possible transition from smoldering to flaming (eventually leading to rapid fire growth and flashover) with ignition sources otherwise too weak to directly induce flaming. Smoldering in residential-furniture upholstery materials can be assessed at a bench-scale by using reference materials with consistent smoldering behavior. However, the preparation of a reference foam has proven to be a challenging task, and the bench-scale tests currently in use may underestimate smoldering in the actual furniture.

The aim of this work is to provide guidance for the selection/development of: (i) a reference flexible polyurethane foam with reproducible and well-characterized smoldering, and; (ii) the development of a bench-scale smoldering test capable of identifying the upholstery materials (e.g., fabric, filling/padding, barrier, welt cord) that most likely prevent smoldering ignition in the actual furniture.

4:00 – 4:15 Coffee Break

Chairperson: Chandrasiri Jayakody

4:15 – 4:45

Investigation of the Heat Release Property and Flammability of Cotton Blends Used for Protective Clothing ..... N/A

Charles Q. Yang and Qin Chen; Department of Textiles, Merchandising and Interiors

The University of Georgia, Athens, Georgia 20602; cyang@uga.edu

Cotton blends containing a synthetic fiber are commonly used in the production of productive clothing. The adding of a synthetic fiber, such as nylon and polyester, to the cotton fabrics used for protective clothing significantly increases the strength and abrasion resistance and reduces absorbency, thus making the final garments more durable and fast-drying. Many of those fabrics used for protective clothing requires flame retardant (FR) treatment. Since many of FR agents used on synthetic fibers are melting enhancers, the FR treatment of the cotton blends could become a challenge because of the so-called "scuffling effects". In this research, we studies the decomposition, heat release properties and the flammability of the cotton blends without FR treatment and those treated with a reactive and self crosslinkable organophosphorus system. Microscale calorimetry, thermal analysis techniques such as TG and DSC, LOI and the standard fabric burning testing were used in the investigation. Three cotton blend fabrics studied included 50/50 cotton/nylon blends, cotton/polyester blends with different ratios and 35/65 cotton/nomex blends. We discovered that the two fibers in a blend interacted with each other in their decomposition and combustion and consequently the flammability of the blends is lower than that of the individual fibers. When the crosslinkable organophorus FR system was applied to the cotton/nylon and cotton/polyester blends, it can be bound to the blend fabrics and is effective in decreasing the peak heat release property of both fibers in the fabrics and reducing LOI and flammability of the treated blend fabrics.

4:45 – 5:15

Studying Fire Behaviour of Furniture Foam with a Cone Calorimeter 166

W.K. Chow and S.S. Han, Research Centre for Fire Engineering, Department of Building Services Engineering, The Hong Kong Polytechnic University, Hong Kong, China, wan-ki.chow@polyu.edu.hk

Consequent to a big building fire started with burning furniture foam, safety requirements of furniture materials are established. Foam should be treated with fire retardant additives, and their ignitability should also be tested under a small flame. However, it has not been proved that those requirements are workable by in-depth investigations.

The fire behavior of materials should be assessed under flashover fires. In this presentation, samples of furniture foam, including those with and without fire retardants, were tested in a cone calorimeter under heat fluxes up to 70 kWm-2. Both the thermal and smoke aspects were studied.

It was observed that foam treated with fire retardant was not ignited under an incident heat flux of 10 kWm-2. However, when burning under heat fluxes of higher than 20 kWm-2, they did not show much improvement in the thermal aspect compared with untreated foam. Even more smoke and toxic gases, such as carbon monoxide, were emitted.

Therefore, it appears that foam treated with fire retardant would only show greater resistance under small fires. In order to have a better understanding of commercial products, chemical constituents were analyzed.

5:15 – 5:45

Fire retarded wood products and their application in timber constructions in Europe ..... N/A

Barbora Deppe, Dirk Kruse, Helmut Wiehn, Pieter Daeseleire; Ecochem; nv barbora.deppe@t-online.de (http://www.ecochem.be/contact_us.php); info@ecochem.be; kruse@kd-brandschutz.de

Wood is easily workable and has a high load-bearing capacity in relation to its weight. Furthermore it is a sustainable and renewable resource. Therefore it is particularly suited as a construction material. Apart of these advantages wood is a combustible material and its use is restricted in Germany (and Europe) by safety regulations and requirements concerned with its ignitability and fire spreading characteristics.

Wood burns primarily because the cellulose and hemicellulose decompose to a mixture of volatiles, tarry compositions and highly reactive carbonaceous char. Gas-phase oxidation of the combustible volatiles and tarry products leads to flaming combustion. Solid-phase oxidation of the remaining char produces glowing or smouldering combustion typical for wood fiber insulation materials.

Fire retardant treatments of solid wood as well as wood-based materials (veneer, chipped wood, wood fiber and composite materials) can firstly delay the ignition for a meaningful time and secondly lower the heat release rate after ignition. Both of these effects together do strongly affect the potential for spreading fire beyond the location of its original ignition. Pressure impregnation, mass incorporation and after treatment through intumescent coatings are the available technologies.

Generally, a tailor-made method and individual chemical structure of fire retardants as well the respective amount of the components in fire retardant mixtures are necessary to achieve the targeted fire retardancy level depending on safety requirements. Fire retardant activity is provided by phosphorus-nitrogen and nitrogen-sulfur compounds (i.e. phoshate, phosphonate, sulphate, sulphamate). Most commercial fire retardants for wood and wood-based materials operate by reducing the amount of flammable gases and increasing the amount of carbonaceous char formed. The higher char yield is caused by an acid-catalyzed hydrolysis of the cellulose and hemicellulose influencing also the condensation and cross-linking reactions of the carbon skeleton. The char will thermally and physically insulate the remaining wood.

After treatment by intumescent fire-retardant coatings represent an efficient way for fire retardancy of wood and wood-based materials. Intumescent coatings are filled with active ingredients including an acid source, a polyhydric carbon rich source and a blowing agent. They expand by flame exposure and form in a temperature-controlled complex process a thick porous charred layer. The latter insulates the substrate against an excessive increase of temperature and oxygen access. The choice of intumescent components has an essential effect on the formation rate of charred layer and its structure.

Fire retarded wood products comply with the most stringent regulations, thus extending the market use of this most natural of building materials. Moreover fire retarded wood products are used even in applications restricted for the use of wood.

This article will discuss the restriction for the use of wood in high rise building applications and in buildings of special type and use (e.g. industrial buildings). It will be shown by best practice examples that new approaches in the protection of wood products by fire retardancy can overcome these restrictions.

5:45 – 6:45

Foam Core Particleboards with Intumescent FRT Veneer: Cone Calorimeter Testing With Varying Adhesives, Surface Layer Thicknesses, and Processing Conditions 194

Mark A. Dietenberger[1], Ali Shalbafan[2], and Johannes Welling[3]*

[1] *USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726-2398, USA,*

[2] *Department of Wood Science, University of Hamburg, 21031 Hamburg, Germany,*

[3] *Thuenen-Institute (TI), Institute of Wood Technology and Wood Biology, 2103 Hamburg, Germany.*

The intumescent FRT Veneer as adhered on novel foam core particleboard surfaces to provide adequate fire protection were evaluated by means of cone calorimeter tests (ASTM E1354). Foam core particleboards were prepared with variations of surface layer treatment, adhesives, surface layer thicknesses, and processing conditions to provide the test specimen. Ignitability, heat release rate profile, peak of heat release rate, total heat released, effective heat of combustion, mass loss rate, gaseous emissions and specific extinction area were measured using the cone irradiance, 50 kW m-2, as appropriate for panel products. The unprotected foam core panels generally had much higher heat release rates, somewhat higher heat of combustion and much higher smoke production due to the polymeric foam component of tested panels, whereas time to ignition and total heat release were not pronounced from the veneer treated boards. Adding commercial fire retardant (EnviroGraph's Intumescent cloth with veneer) to the face particleboard provided a dramatic improvement to the measured flammability properties, with the best FRT performance associated with thicker face layer (5mm), lower press temperature (130C), and adhered with acrylic thixotropic adhesive named Intumescent Adhesive. Such protected foam core particleboard is likely to receive a high flame spread rating that is typical of commercial FRT plywood for both SBI and Steiner Tunnel Tests.

Poster Session and Reception

Chairperson: Chuck Wilkie

7:00

Fabrication of Graphene/Inorganic Compound Hybrids for Reducing Fire Hazards of Polymers ..... N/A

Ningning Hong[a], Lei Song[a], Yuan Hu[a,b]

[a] *State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China yuanhu@ustc.edu.cn*

[b] *Suzhou Key Laboratory of Urban Public Safety, Suzhou Institute of University of Science and Technology of China, Suzhou, P.R. China*

Recent reports have demonstrated the possibility of graphene used as flame retardant additive due to its layered structure and high aspect ratio. However, there are at least two important issues hindering the fire safety application of graphene in polymers: one is the severe trend to agglomerate or restack due to the strong van der Waals force between the graphene sheets; the other is the low flame retardant efficiency similar to its carbon analogue. This work presents a promising approach to prepare graphene/inorganic compound hybrids to improve the flame retardancy of polymer by combining their individual advantages. Several graphene hybrids, including graphene/cobalt oxide (Gs-Co_3O_4), graphene/nickel oxide (Gs-NiO), graphene/Ni–Ce mixed oxide (Gs-NiCexOy) and graphene/Ni-Al layered double hydroxide (Gs–LDH), were successfully fabricated and characterized by XRD, Raman, XPS, TEM, etc. The inorganic nanoparticles with uniform diameters were assembled on the surface of graphene, which efficiently prevented the aggolemeration of graphene sheets. Incorporating graphene hybrids played an important function on the fire safety of polymer composites. The thermal stability of the composites was enhanced upon the incorporation of graphene hybrids. In addition, the addition of graphene hybrids noticeably improved the fire safety of the composites, as evidenced by reduction of PHRR, THR, SPR and COPR. The flame retardant mechanism was attributed to the combined effect of the physical barrier of graphene nanosheets and the catalytic activity of inorganic compounds. This work could allow to open the door to a future potent graphene based nanomaterial in the domain of risk.

Effects of a Lewis Acid Catalyst on the Thermal Properties and Flame Retardancy of HDPE/BPS/GNPs Composites ..... N/A

Shiya Ran^{1,2}*, Zhenghong Guo*^{2}*, Zhengping Fang*^{1,2} *;* ^{1}*MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Institute of Polymer Composites, Zhejiang University, Hangzhou, 310027, China.* ^{2}*Laboratory of Polymer Materials and Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China zpfang@zju.edu.cn*

A Lewis acid catalyst, aluminum chloride (AlCl$_3$), was adopted to initiate the electrostatic attraction bttween polymer chains and graphene nanoplatelets (GNPs). This kind of adhesive force improved the dispersive state of GNPs in brominated polystyrene (BPS) flame-retarded high-density polyethylene (HDPE) composites. The thermogravimetric (TG) analysis and microscale combustion calorimeter (MCC) were used to study the effect of catalyst content on the thermal properties and flame retardancy of composites. The maximum decomposition temperatures (T_{max}) increased and the peak heat release rate (PHRR), total heat release (THR) decreased with increasing catalyst content because the improved dispersion of GNPs was crucial for forming continuous and compact char layer. However, gel permeation chromatography (GPC) verified the degradation with scission reactions for HDPE at high catalyst concentration, and then thermal oxidation stability and flame retardancy worsen. At 0.8 wt% AlCl^3 loading content, an optimized composition was reached, which possessed the highest T_{max} and lowest PHRR. The variety of thermal behaviors and flammability of the composites was the results of the competition between improving dispersion at low catalyst content and degradation of composites at high catalyst content.

A Novel Flame Retardant Copolyester Modified with 1,3,5-Tris(2-Hydroxyethyl) Cyanuric Acid 203

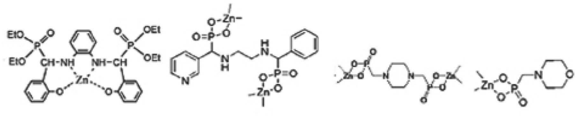
De-Ming Guo, Teng Fu, Xiu-Li Wang, Li Chen, Yu-Zhong Wang*; Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China'yzwang@scu.edu.cn*

Poly(ethylene terephthalate) (PET) has been widely applied in various fields such as fibers, films, bottles and engineering plastics for automobiles and electronics. Its flame retardant modification has made great progress in the past decades. Some phosphorus-containing monomers are usually used to improve its flame retardance, which could be achieved mostly through dripping, removing the fire from flaming part. Thus, the flame-retardant and anti-dripping of phosphorus-containing PET during combustion are incompatible. Nitrogen-containing compounds could also be introduced to the backbone of PET to get a good balance between flame retardance and anti-dripping properties. In this study, a series of novel copolyesters (TPETs) were synthesized by melt polycondensation from 1,3,5-tris(2-hydroxyethyl) cyanuric acid (Theic), which contains 16 wt% of nitrogen and three active function groups(-OH), terephthalic acid (TPA) and ethylene glycol (EG). Their chemical structures were proved by 13C NMR. DSC measurement was carried out to investigate the melt crystallization behaviors of the copolyesters. With the increasing molar ratio of Theic content increased (more than 1%), the glass-transition temperature (Tg), melting temperature (Tm), crystallization temperature (Tc) and cooling crystallization temperature (Tcc) of copolyesters were decreased. In the cone calorimeter test, the PHRR values of TPETs were much lower than that of PET, which showed certain flame retardance. Furthermore, TPETs presented obvious expanded char in combustion, which suggested that Theic could also enhance the char-forming of the copolyesters during combustion.

A Series of Metal Complexes Containing both Phosphorus and Nitrogen for Improving the Flame Retardancy of Polyethylene ..... N/A

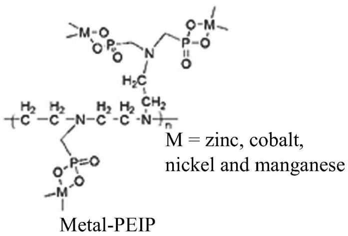
Yan Zhang, Zhenhu Cao, Zhengping Fang; Lab of Polymer Materials and Engineering, Ningbo Institute of Technology, Zhejiang University; Ningbo 315100, China zpfang@zju.edu.cn

Various flame retardant additives have been developed worldwide. Halogen-containing compounds had been under regulatory scrutiny due to their environmental persistence, and in some cases, bio-accumulation and toxicity. Intumescent flame retardant (IFR) additives containing phosphorus and nitrogen have been developed as alternative additives for imparting flame retardancy to polymeric materials, which also have some disadvantages, such as high loading fractions and the apparent decrease of the mechanical properties of the flame retardant polymers. Therefore, great attention has been focused on exploring more effective halogen-free flame retardant systems. Divalent or multivalent metallic compounds such as metal oxide, metal chloride, metal sulfate and metal phosphate have been reported to be able to catalyze the char forming reaction of the IFR systems and make IFR more effective in polymer. However, such catalyzed IFR systems are always studied through physical blending of the metal compound and IFR, which may result in the problems of dispersion and compatibility. To solve the problems mentioned above, our group has designed and synthesized some novel metal complexes, which combines the two intumescent flame retardant elements, phosphorus and nitrogen, with the metal elements through chelate bonds in one molecular. Such metal complex can be fabricated from various ligands with different chemical structures and different metal elements, thus can meet different demands for the flame retardancy of different polymers. Figure 1 and Figure 2 showed a series of metal complexes synthesized by our group. The chemical structures of these metal complexes were characterized by IR, 1H-NMR, 13C-NMR and 31P-NMR. The results of thermal analysis showed that they had excellent char-forming ability and the thermal stability match well the processing temperature of polyethylene. Incorporation of the metal complexes in polyethylene not only resulted in the improved LOI values, but markedly reduced the heat release rate.



Zn-TEPAPM Zn-EIBPA Zn-PPMPA Zn-MMPA

Figure 1 the chemical structures of metal complex with low molecular weight (Mn<10000)



Metal-PEIP

Figure 2 the chemical structures of metal complex with long chains (M_n >10000)

Peculiar Flame Retardant Behaviour Of Nanocellulose And Nanocellulose-Clay Materials ..... N/A

F. Carosio,[1] A Bergfelt,[1] J. Kochumalayil,[1] G. Camino,[2] L. Berglund[1]*

[1]Department of Fiber and Polymer Technology, Royal Institute of Technology, SE-10044 Stockholm, Sweden Wallenberg Wood Science Center, Royal Institute of Technology (KTH), SE-10044 Stockholm, Sweden

[2]Politecnico di Torino, Alessandria site, Viale Teresa Michel 5, 15121 Alessandria, Italy. federico.carosio@polito.it

Nanofibrillated cellulose (NFC) combine the important properties of cellulose such as hydrophilicity, broad chemical modification capacity, and the formation of versatile semicrystalline fiber morphologies with the specific features of nanoscale materials. This particular class of materials has created great interest in the scientific community due to the wide spectrum of its applications and its bio-based characteristic. In recent years, the NFC has been adopted as building block for new nanocomposites by direct addition in several polymer matrices or used as nanofibrous matrix to clay nanoplatelets. These latter have shown interesting and promising mechanical properties, high thermal resistance, oxygen barrier properties and transparency.[1]

In the present work we have addressed the complete flame retardant characterization of pure NFC and its nanocomposite with sodium montmorillonite.

To this aim, the reaction of NFC and NFC/Clay nanocomposites to a direct flame application (i.e. through flammability tests) and to an irradiative heat flux (by using cone calorimetry tests) have been assessed. When exposed to a direct flame, pure NFC was capable of stopping combustion within few seconds after ignition leaving a coherent charred residue; on the other hand, the NFC/Clay nanocomposite showed no ignition even after multiple flame applications. A similar trend has been assessed by cone calorimetry test, performed under 35 kW/ m^2, where pure NFC ignited upon exposure to the cone calorimeter heat flux while NFC/Clay nanocomposite showed no ignition.

Finally, the insulating properties of NFC and NFC/Clay have been tested by assessing their resistance to a propane/butane flame torch penetration (T≈1300°C) while monitoring the temperature on the unexposed side of the sample. Collected results clearly demonstrate the excellent performance of the NFC/Clay nanocomposite. Indeed, when subjected to a flame torch penetration, the NFC/clay nanocomposite was capable of maintaining its structure thus successfully insulating the unexposed side of the sample that yielded temperature readings below 100°C during 90 s of flame torch application. Such results have been achieved with a specimen thickness of only 1 mm.

[1] A. Liu, A. Walther, O. Ikkala, L. Belova, L A. Berglund, Biomacromolecules, 2011, 12 (3), 633–641.

Tuesday, May 20, 2014

Chairperson: Anteneh Worku

Session 4: Approaches to Fire Retardancy

8:00 – 8:30

Surface Approach to Polymer Fire Retardance: Engineering and Nanostructuration 205

A. Fina, F. Carosio, J. Alongi, A. Frache, G. Malucelli, G. Camino; Politecnico di Torino, Alessandria site, Viale Teresa Michel 5, 15121 Alessandria, Italy; alberto.fina@polito.it

Despite fire retardancy of polymer materials is typically obtained by the bulk addition of fire retardant additives, engineering of the material surface currently appears as a fascinating method to deliver the fire retardancy action right where it is needed.

One of the most valuable fire retardant strategy is indeed based on the production or accumulation of a thermally stable surface layer able to act as a barrier to mass and/or heat exchange. Such a layer can be built during the earlier stage of combustion as a consequence of polymer surface layer decomposition, in the presence of different kinds of fire retardants, including inorganic nanoparticles. However, the time required for buildup of the surface barrier is straightforwardly connected to the development of the fire in the early stage, consequently affecting the subsequent growth of the fire.

On the other hand, modification of the material surface to readily obtain a surface barrier layer is possible via different methods, including intumescent coatings, Layer by Layer assembly, sol-gel or dual-cure depositions, biomacromolecules deposition as well as plasma treatments.

In this paper, recent achievements on fire retardancy based on surface modification will be discusses through selected case studies on different substrates, including textiles, films and bulk polymers.

8:30 – 9:00

The Practical Side of Developing Flame Retardant Formulations 208

Donald M. Demko, Polymer Products Company, Inc., 100 Station Avenue, Stockertown, PA 18083 ddemko@pmc-group.com

Flame-retardant polymer formulations play an important role in the manufacture and safe use of a variety of everyday products. Office equipment, appliances, wire and cable, building products, fabrics, film, and transportation are some of the key areas where these materials are found. Many of the scientists responsible for the development of these formulations would probably agree that one of the more challenging aspects of their work is not in creating a product but in working effectively with the customers, suppliers, and sales staff to thoroughly define the necessary parameters for the product. The speaker will discuss some of the practical issues and needs related to the development and evaluation of flame retardant compounds and masterbatches from the perspective of a product development scientist.

Session 5: Composites and Nanocomposites

9:00 – 9:30

Composites: Finding the Right Balance Between the Fire Performances and Mechanical Properties 220

F. Samyn[1]*, S. Duquesne[1], P. Ouagne[2], E. Kandare[3] and S. Bourbigot[1]

*[1] Unité Matériaux et Transformation, Equipe Ingénierie des Systèmes Polymères (UMET-ISP) – UMR-CNRS 8207, Ecole Nationale Supérieure de Chimie de Lille (ENSCL), BP 90108, 59652 Villeneuve d'Ascq Cedex, France *fabienne.samyn@ensc-lille.fr*

[2] Polytech'Orléans (Site Léonard de Vinci) Laboratoire PRISME (EA 4229)/ Equipe Mécanique Milieux Hétérogènes, 8 rue Léonard de Vinci, 45072 Orléans Cedex 2, France

[3] Composite Materials Group, School of Aerospace, Mechanical and Manufacturing Engineering, RMIT University, Bundoora East Campus, Bundoora, Melbourne, Victoria 3083, Australia

Thermoplastic and thermoset fiber reinforced composites are very attractive materials as they exhibit high mechanical properties with the advantage of a tremendous weight reduction compared to the classical materials they tend to replace. However their flammability is a major drawback even if the incorporation of flame retardants (FRs) permits to overcome this drawbacks. The loading of FRs lies indeed between 15 and 40 wt% and low flammability of the composites is achieved at the expense of their outstanding mechanical properties. In this work, three new routes toward fire proof composites have been investigated to find the right balance between the fire performances and the mechanical properties. The first approach is based on applying on the surface of an unmodified composite a glass veil coated with intumescent formulations that will bring the fire performances. The second approach is based on a partial modification of the matrix of the composite using FRs. FR Flax fiber/poly(lactic acid) (PLA) laminates have been prepared by replacing progressively the neat PLA films by flame retarded ones beginning from the outside layers of the composites. The last approach consists in the treatment of the flax fabric by pad finishing using different FR formulations before applying films of neat polymer. The impact of these treatments on the fire behaviour and on the mechanical properties has been evaluated and will be presented in the talk.

9:30 – 10:00

Multi-Component Flame Retardants: Combining Anionic and Cationic Clays as Trojan Horses for Molecular Flame Retardants 236

Bashar Diar-Bakerly[1], Josef Hausner[1], Hussein Kalo[1], Andreas Edenharter[1], Mazen Ziadeh[1], Günter Beyer[2], Josef Breu[1], [1]Lehrstuhl für Anorganische Chemie I, Universität Bayreuth, 95440 Bayreuth, Germany, [2]Kabelwerk Eupen AG, 4700 Eupen, Belgium*

*Correspondence to Josef Breu (josef.breu@uni-bayreuth.de;
Fax: (+49) 921-552788; Telephone: (+49) 921-552531)*

A multi-component flame retardant (FR) was established by combining two synthetic clays; high aspect ratio hectorite (cationic-type) and layered double hydroxides (LDHs, anionic-type) in polystyrene nanocomposites. Both LDH and hectorite were organophilized with thermally stable molecular FR such as phenyl phosphate and melaminium, respectively.

PS nanocomposites were prepared via solution blending utilizing a three-roll mill. A large portion of the aggregates were destroyed upon mechanical agitation as indicated by recording the particle size distributions. The obtained PS nanocomposites showed enhanced thermal stability and flame retardancy. Cone calorimetry proved a synergism between these two nano-additives where a reduction of peak of heat release of 51 % at low loadings of 5 wt% was recorded. For this combination of nano-additives the reduction of the peak of heat release is some 10% higher as compared to the average reduction by a singular nano-additive. Furthermore, an intumescent effect was observed for PS nanocomposite with this multi-component FR.

10:00 – 10:30

Synthesis of Flame Retardant Polypropylene/LDH-Borate Nanocomposites 245

Qiang Wang[1], Jean-Charles Buffet[2], Charles A. Wilkie[3] and Dermot O'Hare[2]*

[1] College of Environmental Science and Engineering, Beijing Forestry University, 35 Qinghua East Road, Haidian District, Beijing 100083, China

[2] Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford OX1 3TA, UK, dermot.ohare@chem.ox.ac.uk

[3] Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201, USA

New nanocomposites have been prepared using unmodified polypropylene (PP) and a new type of highly dispersed $[Zn_2Al(OH_6)][B_4O_5(OH)_4]_{0.5}$ (Zn^2Al-borate) and $[Mg_3Al(OH)_8][B_4O_5(OH)_4]_{0.5}$ (Mg_3Al-borate) layered double hydroxides (LDHs). PP/LDHs nanocomposites with LDH loadings of 1, 3, 6, 9, 15 and 30 wt% have been prepared by a novel solvent mixing method. Cone calorimetry analysis indicates that PP/Zn_2Al-borate nanocomposites exhibited superior performance than the equivalent PP/Mg_3Al-borate nanocomposites; a 15 wt% of the highly dispersed Zn_2Al-borate LDH in PP was found to be the optimal loading. The 15% Zn_2Al-borate LDH in pristine (unmodified) PP resulted in reduction of the PHRR (Rdctn) by 63.7%. In these examples we find that the solvent mixing is superior to the melt mixing method. With a 6 wt% LDH loading, the reduction in PHRR is 23.8% for the melt mixing sample, which is worse than that observed for the solvent mixing sample (29.9%). We attribute this behavior to the severe aggregation and poor dispersion of LDH particles.

10:30 – 10:45 Coffee Break

Chairperson: Sergei Levchik

10:45 – 11:15

Functionalized Graphene Oxide for Fire Safety Applications of Polymers ..... N/A

Keqing Zhou[a], Lei Song[a], Yuan Hu [a,b]

[a] State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China yuanhu@ustc.edu.cn;

[b] Suzhou Key Laboratory of Urban Public Safety, Suzhou Institute of University of Science and Technology of China, Suzhou, P.R. China

Polymer nanocomposites, especially polymer/layered inorganic compounds have been demonstrated as one of most promising halogen-free flame retardants method. Just like its counterpart montmorillonite or layered double hydroxides, the rising graphene was also expected to impart flame retardancy with polymers owing to the lamellar structure and high aspect ratio. In order to obtain homogeneous dispersion and strong interface in matrix, graphene oxide (GO) was functionalized with phosphorus containing agents and reactive compounds, and then incorporated into polymer matrix to obtain nanocomposites via in situ polymerization. Compared with pristine GO, the functionalized graphene oxide (FGO) was soluble and stable in certain solvents. The electronic microscopy results showed that the FGO can achieve better dispersion due to the covalent bonding with the matrix. The incorporation of FGO led to a noticeable improvement in both thermal stability and flame retardancy of polymer/FGO nanocomposites. Furthermore, the mechanical properties of the nanocomposites were considerably enhanced at a low FGO loading due to the strong interfacial adhesion and effective stress transfer. The synergism between phosphorus and GO layer structures of FGO promoted the formation of continious and insulating char layer, preventing the underlying matrix from further burning. This study represents an effective approach to prepare FGO to not only improve the flame retardancy of polymer, but also to enhance the mechanical properties, which paves a way for the development of novel graphene-based flame retardants with potential applications.

11:15 – 11:45

The Influence of Metal Oxide/Layered Compound and Metal Oxide/Carbon Nanotube Composite Powders on Thermal Properties of Polymeric Materials 251

Hongdian Lu*, Xiaofang Tan[a], Juan Wang[a], Hongyan Xie[a], Jin Liu[a], Qing Ye[a]

*Department of Chemical and Materials Engineering, Hefei University, Hefei, Anhui, 230601, P. R. China; *Corresponding author hdlu@ustc.edu.cn*

Composite powders of layered compounds mainly montmorillonite (MMT) and α-type zirconium phosphate (α-ZrP) supported with Fe2O3, and multi-walled carbon nanotubes (MWNTs) coated with metal oxides, such as titanium oxide (TiO2) and zinc oxide (ZnO), were prepared and characterized by X-ray diffraction (XRD), scanning electron microscopy, Fourier transform infrared spectra (FTIR), and N2 adsorption-desorption. Polymeric composites including polystyrene (PS) and polypropylene (PP) containing these composite powders were prepared by melt blending, and the influence of these powders on thermal stability of the materials were investigated. The results from thermogravimetric analyses (TGA) demonstrated that these polymeric materials exhibited improved thermal stability when compared with their corresponding pure polymer matrixes. A possible mechanism of the improvement is discussed.

11:45 – 12:15

Effects of Fullerene on the Thermal Stability and Flame Retardancy of Polyolefins ..... N/A

Liping Zhao[1,2], Zhenghong Guo[2], Zhengping Fang[1,2]; [1]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China. [2]Laboratory of Polymer Materials and Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China zpfang@zju.edu.cn

Fullerene (C_{60}) in many reactions behaves as an electron-deficient compound and it is known as a radical sponge. Despite the complexity of the combustion process, the degradation of most polymers during combustion is though a free radical chain scission process; the presence of C60 may reduce the flammability of polymers. The thermal stability and flame retardancy of polypropylene/fullerene (PP/C_{60}) nanocomposites were investigated by thermogravimetric analysis (TGA) and cone calorimeter. In air, the onset decomposition temperature (T_{onset}) and the temperature at maximum rate of mass loss (T_{max}) values of PP/2.0 wt% C_{60} were 21 and 61 ºC higher than the corresponding temperatures of pure PP, indicating that C_{60} could considerably delay the thermal oxidative degradation of PP. The presence of C_{60} in the PP matrix not only prolonged the t_{ign} (time to ignition) but also considerably reduced the PHRR (peak heat release rate). PP/2.0 wt% C_{60} showed a t_{ign} of 36s, which was much longer than that pure PP; this implied that C_{60} could delay the start of combustion. Furthermore, the PHRR of PP/C_{60} nanocomposites was around 55% (2.0 wt% C_{60}) of pure PP, demonstrating that the addition of C_{60} to the PP matrix improved the flame retardancy of PP. C_{60} reduced the flammability of PP by trapping free radicals in the gas phase and in situ forming a gelled-ball crosslink network to improve the flame retardancy of PP in the condensed phase. The presence of C_{60} also could remarkably enhance the thermal stability of high-density polyethylene (HDPE)/ethylene vinyl-acetate copolymer (EVA) and cone calorimeter measurements indicated that the incorporation C_{60} could result in a significant reduction in the peak heat release rate and a much longer time to ignition of HDPE/EVA. Furthermore, the larger the C_{60} loading level, the better thermal stability and flame retardancy of HDPE/EVA/C_{60} nanocomposites.

While the thermal degradation and combustion mechanisms of some polymers are free radical chain reaction, such as PP; the others are non-radical chain reaction, such as polycarbonate (PC). It is interesting to investigate the influence of C_{60} on the radical and non-radical chain reaction and study the sensibility of C_{60} to the structure of the polymer chain during degradation. High density polyethylene (HDPE), polypropylene (PP) and polymethyl methacrylate (PMMA) were chosen as polymers for the free radical chain degradation with different chain structures and polycarbonate (PC) were chosen as an example for non-radical chain degradation. The TGA results showed that the influences of C_{60} on the resistance to the thermal degradation of different polymers were dependent on their thermal degradation mechanism. The resistance to the thermal degradation of HDPE, PP and PMMA were improved with the addition of C_{60}, especially for HDPE matrix, which indicated that the radical trapping played a dominant role. PP and PMMA released more gaseous products at high temperature by the random scission of C-C backbone; owing to the lower bond dissociation energy of C-C in the backbone for the existence of side chains. Meanwhile, the steric hindrance of side chains also made the radicals hard to recombine with each other and accelerated the random scission, leading to the less effect on the resistance to the thermal degradation of PP and PMMA. However, few changes of resistance to the thermal degradation were found in PC matrix with the addition of C_{60} for its non-radical degradation mechanism.

As the thermal stability of HDPE was greatly improved with the addition of C_{60}, the thermal and thermo-oxidative degradation behaviors of HDPE/C_{60} contents in the range from 0.05 to 2.5 wt% were studied in detail. Under different atmosphere, the influences of C_{60} on the thermal stability of HDPE were different. Thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TG-FTIR) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) demonstrated that in N_2 the addition of C_{60} increased T_{onset} by about 10 ºC with more heavy compounds (more than 34 carbons). Also the thermal stability of HDPE in air was remarkably improved with the addition of C_{60}. When the content of C_{60} was 2.5 wt%, T_{onset} increased by about 91 ºC, compared with pure HDPE. The results of viscoelastic behavior and gel content revealed that C_{60} could trap the alkyl radicals and alkyl peroxide radicals to inhibit hydrogen abstraction to suppress the chain scission and preserve the long chain structure. However, in the absence of C_{60} or with low C_{60} concentration, hydrogen abstraction occurred, resulting in the formation of a series of alkyl radicals and alkyl peroxide radicals, which accelerated the chain scission and plays a leading role in the thermal oxidative degradation.

As is known that most flame retardants work at higher temperature, C_{60} can be used a synergistic flame retardant at the early stage of degradation to improve the thermal stability of polymer which experiences radical chain degradation.

12:15 – 12:45

Combustion and Thermal Decomposition of Polystyrene / Sulfides Nanocomposites ..... N/A

Zhengzhou Wang[a], Jianwei Yang[a], C.A. Wilkie[b];

- [a] *School of Materials Science and Engineering, Tongji University, Shanghai 200092, P.R. China ; zwang@tongji.edu.cn*
- [b] *Department of Chemistry and Fire Retardant Research Facility, Marquette University, Milwaukee, WI 53201, USA*

It is known that halogen-free flame retardation of polystylene (PS) is still a challenge. Recently sulfur-containing compounds as flame retardants in polymers have aroused great attention. Metal sulfide nanoparticles have attracted considerable interest because of their unique semiconducting, electronic and thermal properties. In the present work, two kinds of cadmium sulfide nano particles, i.e. hollow spheres (CdS-HS) and rods (CdS-NR), were synthesized by ultrasonic and solvothermal processes, respectively, and ZnS nano particle synthesized by ultrasonic method. CdS and ZnS nano particles were characterized by XRD and SEM. PS/CdS and PS/ZnS nanocomposites were melt compounded using a Brabender mixer at 180 ˚C for 30 min at a screw speed of 60 rpm. Combustion characteristics were investigated using the cone calorimeter (Cone) and microscale combustion calorimeter (MCC). The incorporation of small amount of CdS nano particles (1 wt%, 3 wt%, 5 wt%) leads to a reduction in the peak heat release rate (PHRR) compared to pristine PS; CdS-NR is more efficient in reducing the PHRR. In comparison with CdS nano particle, ZnS nano particle is less efficient in reducing the PHRR of PS. Thermal decomposition of PS/CdS and PS/ZnS nanocomposites was studied by TGA. The TGA results show that the addition of the nano particles mainly increases thermal stability of PS at high temperatures.

12:45 – 2:00 Lunch Break

Chairperson: Larry Timberlake

2:00 – 2:30

New Discovery of Fire Retarding Polymer (Nano)Composites . N/A

DE-YI WANG; Madrid Institute for Advanced Studies of Materials (IMDEA-Materials), C/ Eric Kandel, 2, Getafe (Madrid) 28906, Spain; deyi.wang@imdea.org

Polymeric materials are widely used in different house hold appliances, packaging, automotives, engineering applications, aerospace, interior decoration, etc. Due to their high flammability, in many of these applications there exists severe risk of fire related causalities and loss of valuable properties. Therefore, it is often needed to make these products more fire retardant by using suitable fire retardants in the original materials. In last decades, it had been recognized that the formation of nanocomposites can improve the fire retardant performance at relatively low filler loadings. [1-3]

In this talk, some new discovery of fire retardant polymer (nano) composites developed in my laboratory will be delivered. Some new functional nano-fire retardant and new fire retardants designed and developed in my group would be reported. Different polymeric materials, such as PP, Epoxy, are chosen as polymer matrix. **In this talk, it is noted that the functional nanomaterials at low loading provides a possibility as an independent fire retardant for polymers to pass UL-94 V-0 rating**. Moreover, the fire retarding polymer nanocomposites also shows low heat release rate, low total heat release rate, etc, in the reinforced fire test. Furthermore, the smoke release production of the fire retarding polymer nanocomposites has been influenced greatly by introducing different functional nanomaterials; CO production during the combustion is also affected.

2:30 – 3:00

The Effect of APP, APP/MMT Nanocomposite on the Thermal Degradation and Flammability of ABS Resin ..... N/A

Yinping Deng, Zhiyuan Zhang, Xiangmei Li, Yongjie Yang; Beijing institute of technology materials institute, National professional flame retardant materials research laboratory, Engineering research center of fire-safe materials and technology, ministry of education, National Engineering Research Center of Flame Retardant Materials, Beijing 100081, China; bjlglxm@126.com

The thermal degradation of ABS added APP (ammonia polyphosphate), APP/MMT montmorillonite) nanocomposite was studied. The whole degradation progress of ABS could be regarded as the combination of the thermal degradation of PS and PB, and PB influenced the formation of char while PS influenced the maximum weight loss rate and its decomposition temperature. A series of ABS/APP/MMT composites were prepared. APP and APP/ MMT nanocomposite decreased the maximum weight loss rate and promoted the formation of char at the same time, a SiO2 network was formed on the surface of the ABS-APP/MMT composite which could improve the strength of the surface and flame retardancy. It was found that when physical mixture of APP and MMT or APP/MMT nanocomposite are added to ABS, NH3 (the gas product of APP) was buried in the residue and released until full degradation of ABS.

The synergistic of micro-capsulated red phosphorus (MRP) with APP/MMT nanocomposite was studied. Thermal gravimetric analysis (TGA) results show that both APP/MMT and APP/MMT/MRP can decrease the initial decomposition temperature of ABS, while giving much more char residue at 700ºC. The fire retardancy was investigated by limiting oxygen index (LOI) and UL-94 vertical burning test, which indicates that APP/MMT and APP/MMT/MRP could reduce the flammability of ABS. With 5wt.% MRP and 15-22.5wt.% APP/MMT, the composite could pass the UL-94 V-0 (1.6mm) rating easily, accompanied by a relative low LOI value of 24.7-29.6%. Fire behavior was tested by cone calorimeter, and it's notable that APP/MMT and MRP could significantly inhibit the heat release and smoke generation. Thermal oxidation test and water resistance test were accelerated at 70ºC for 30 days and 7 days, respectively. ABS/APP/MMT/MRP composites show a high resistance to thermal oxidation aging, but a low resistance to water. With 15-22.5wt.% APP/MMT and 5wt.% MRP, samples can still pass the V-0 rating (1.6mm) in UL-94 vertical burning test after thermal oxidation treatment, but all ABS/APP/MMT/MRP composites can only pass the V-1 rating (3.2mm) after the hot water treatment.

3:00 – 3:30

Graphene Polypropylene Nanocomposites: Optimizing Mechanical, Thermal, and Flame Retardant Properties ..... N/A

Kai Yang[1], Joseph Cappadona[2], Ivy Ren[3] , Joseph Jacob[6], Ning Sun[1], Thomas Butcher[4] ,Gerald Alessio[5], Dilip Gersappe[1], Miriam Rafailovich[1];[1]Materials Science and Engineering, SUNY-Stony Brook, Stony Brook, New York; [2]Lynbrook Senior High School, Lynbrook, New York; [3]Thomas Jefferson High School for Science and Technology, Alexandria, VA; [4]Energy Division, Brookhaven National Laboratory, Upton, New York. [5]ICL-Industrial Products, Ardsley, New York; [6]The Wheatley School, Old Westbury, New York; Miriam.rafailovich@stonybrook.edu

The recent trend towards replacing traditional fossil fuels with biofuels in applications ranging from transportation to power generation and home heating has also introduced new materials challenges. All these applications require materials with high strength, which could withstand large shear or compression stresses, combined with either thermal or electric conductivityand ductility for ease of processing. Traditionally metals, which could also withstand high processing or operating , temperatures have been better suited for most of these applications. In contrast to fossil fuels, biofuels also tend to have much higher acidity and higher combustion temperatures, making them very corrosive and difficult to store or operate in metal containers. Here we study a polymer nanocomposites system that is being developed as a viable alternative. Polypropylene is easily processed, stable at high temperatures, ductile, and most important highly resistant to corrosion. But before it can be developed as a functional substitute for metals, its flame retardant and thermal conductivity properties must be improved, while maintaining adequate mechanical properties for ease of processing. Here we show the results for rapheme/ propylene nanocomposites where we measured the thermal conductivity, impact toughness, and cone calorimetric behavior as a function of the type of rapheme and its concentration. We find that the thermal conductivity coefficients could be increased by more than an order of magnitude, with a concentration of rapheme which also renders the composite flame retardant (according to the UL-94-V0 criteria). Theoretical modeling indicates that the shape of the rapheme platelets and their interfacial properties with the polymer matrix plays a critical role in explaining these phenomena.

3:30 – 4:00 Andre Zeitoun
4:00 – 4:15 Coffee Break

Chairperson: Martin Klatt

4:15 – 4:45

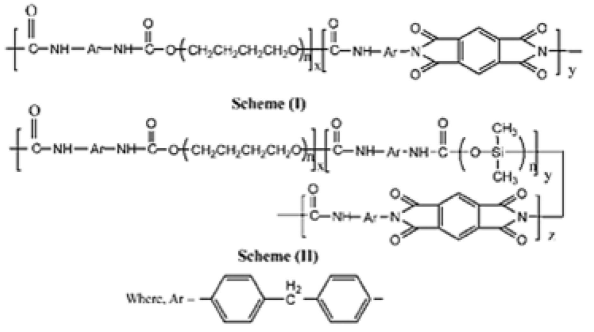
Carbon nanotubes for innovative eco-friendly flame retardant solutions 266

D. Bonduel, M. Claes; Nanocyl SA; rue de l'essor, 4; 5060 Sambreville, BELGIUM; Daniel.bonduel@nanocyl.com
Michael.claes@nanocyl.com

Literature has reported many time the effect of Carbon nanotube as fire retardant. For example, cone calorimeter and UL94 results showed an improved and strengthened charring effect, a drastic reduction of dripping and flame spread rate as well as synergist effect with conventional flame retardant.

On the other hand, harmonization of regulation and standards in European Community and Health-Safety and Environmental (HSE) concerns led to a modification of the fire retardant market. As a consequence plastic industry is requested to develop new Fire Retardant (FR) polymer solutions to foresee those modifications of regulations.

In collaboration with different partners, Nanocyl has built a great know-how leading to solutions for fire resistant thermoplastics. In his last development, novel approach has been undertaken to satisfy on multifunctional performances for market oriented solution. Some of the latest developments in the field and an overview of the potential applications for carbon nanotubes in the fight against fire will be present.



Flame Retardant Chemicals: Technologies and Global Markets (CHM014L)

This BCC Research report by Anna Welch Crull presents an overview of the worldwide market size, growth and trends for Flame Retardant Chemicals. Global consumption of flame retardant chemicals for 2012 was 3.9 billion pounds. In 2013 consumption is expected to have increased to more than 4 billion pounds, and is projected to increase to about 5.2 billion pounds by 2018. This represents a compound annual growth rate (CAGR) of 5% for the next five years.

The report provides:

- An overview of the global market for flame-retardant chemicals, with coverage of plastics, textiles, wood/paper, coatings/paper, coatings/construction, and coatings/decorations market applications.
- Analyses of global market trends, with data from 2008 and 2012, estimates for 2013, and projections of compound annual growth rates (CAGRs) through 2018.
- Reviews of government regulations and their impact on the market, as they obligate manufacturers to add flame-retardant chemicals to a wide range of products used every day.

Anna Welch Crull, a chemist and experienced private consultant, is qualified in flame retardant chemistry, polymers, membrane materials and protective advanced materials. Ms. Crull has worked with BCC for 30 years and has authored more than 113 technical/marketing reports, helped establish 10 technical newsletters and assisted in numerous special consulting studies and conferences for more than 35 corporations and intelligence analysis for U.S. government entities. She has worked for the U.S. Army Materials Command on rocket technology, propellants and explosives. Ms. Crull is a graduate of the School of Engineering, University of Mississippi and holds a Masters Degree in Chemistry from the University of Missouri.

Session 6: Some Specific Polymers

4:45 – 5:15

Flame Retarding Polyesters and Copolyesters – Properties, Applications and Challenges 286

Robert Young, Eastman Chemical Company, Polymers Technology – Transformational Technology Research Lab, ryoung@eastman.com

Polyesters and Copolyesters present some unique advantages in processing, impact properties, clarity and fabrication. Applications include fibers, clear sheet, packaging and shrink films, medical devices and building and construction. Flame retarding Polyesters and Copolyesters has traditionally been challenging due to their sensitivity to degradation from certain types of flame retardants, loss of physical properties and increased cost. Eastman has recently developed a flame-retardant concentrate for use with its Polyester and Copolyester products. This paper will discuss the unique properties of Copolyesters, some end uses requiring flame-retardancy and their associated tests and continuing challenges in flame retarding copolyesters.

5:15 – 5:45

Development of a New Sustainable Inorganic Flame Retardant Additive System for Polyamide 6,6 with Improved Performance 303

Imane Belyamani and Joshua U. Otaigbe, School of Polymer and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS; Joshua.otaigbe@usm.edu

William Fielding, Chemtura Corporation, West Lafayette, IN

This project is aimed at developing new sustainable inorganic flame retardant additive system based on inorganic phosphate glass (P-glass) for polyamide6,6 (PA6,6) with improved flame retardancy. Three phosphorous based glasses(P-glass) differing in chemical composition and glass transition temperature (Tg) were prepared and their thermal properties were tested. The low Tg P-glass (ILT-1) was found to be a promising flame retardant for PA6,6 at a concentration of up to 15% by weight. This P-glass composition decreased the peak heat release rate(PHRR) and the total heat amount released from the PA6,6/ILT-1 hybrids, resulting in an efficient formation of a glassy char layer.

5:45 – 6:15

Design, Synthesis and Characterization of Novel Ferrocene-Containing Polyurethane Copolymers ..... N/A

Feng Yang, Brian Silver, Gordon L. Nelson; Florida Institute of Technology, 150 W. University Blvd, Melbourne, FL 32901; fyang@fit.edu*

Surface charge dissipative polyurethane coatings are typically used in microelectronic devices and space applications because they are thermally stable, chemically resistant, and have good mechanical and dielectric properties. It was previously observed that a copolymer of a diol-terminated ferrocene oligomer (FcOH) and a 4,4'- methyldiphenyl diisocyanate - based polyurethane (MDI-PU) exhibited FcOH blocks which preferentially localized toward the copolymer surface. This surface sequestration of the FcOH was essential for improved charge dissipation performance of the synthesized copolymers compared to unmodified MDI-PU and MDI-PU containing ferrocene as an additive. However, copolymers of FcOH and a polyimide based on 3,3',4,4'-biphenyltetracarboxylic dianhydride /3,3'-oxydianiline (BO-PI) did not exhibit surface localization of FcOH.

In this work, novel copolymers of diol-terminated ferrocene oligomers (FcOH) with designed phosphorus flame retardant functional group in their backbone are synthesized, to enhance both the flame resistance and the surface charge dissipative properties of the resulting polyurethane copolymers. Surface levels of ferrocene components in newly synthesized polymers are evaluated using Energy Dispersive X-ray Microanalysis (EDX) and attenuated total reflectance infrared spectroscopy (ATR-IR). Films were also evaluated using thermogravimetric analysis (TGA). The flame resistance of the newly designed ferrocene containing polyurethane copolymers are tested by Oxygen Index and UL 94, and compared with previous work.

6:15 – 6:45

Novel Cost-effective Alternative to Conventional Flame Retardant Styrenic Alloy Formulations 318

Brett Wallet and Kumar Kumar, Albemarle Corporation, Gulf States Road, Baton Rouge, LA 70805, Phone: 225-359-2155,
brett.wallet@albemarle.com

Historically, electronic enclosures have been manufactured from high-impact polystyrene (HIPS) or acrylonitrile-butadiene-styrene (ABS) resins mainly due to their inherent properties allowing for lower cost-in-use while maintaining a necessary performance level. However, advancements in display technology have driven to more demanding resin requirements. A growing trend in this market is to alloy HIPS and ABS with more thermally stable and mechanically robust resins such as polyphenylene oxide (PPO) and polycarbonate (PC), respectively, to provide a compounded final product with enhanced thermal-mechanical and flammability properties than that of solely HIPS or ABS. Current PPO/HIPS and PC/ABS solutions use phosphate esters as flame retardants due to the difference in cost-in-use between phosphorous flame retardant (PFR) vs. brominated flame retardant (BFR) alloys, caused by escalating antimony trioxide (ATO) pricing increasing the BFR solution cost. A major disadvantage of the PFR solution for styrenic alloys is the limitation it imposes on the styrenic loading of these alloys, due to their plasticizing nature and lower FR efficiency compared to BFRs. Use of BFRs could potentially increase the use of HIPS or ABS, thereby reducing the overall cost of the base resin alloy, with the likelihood of also minimizing or eliminating the use of ATO. The present invention provides flame retardancy to PPO/HIPS and PC/ABS styrenic alloys through incorporation of a polymeric BFR with and without the use of ATO and polytetrafluoroethylene (PTFE). Key points of understanding were developed for the relationships between the chosen independent variables to gain knowledge regarding optimal additive loadings.

Wednesday, May 21, 2014

Chairperson: Marcello Hirschler

8:00 – 8:30

Easier Said Than Done: Halogen-Free Multi-Component Flame Retardants for SEBS-Copolymers 333

A. Wilke, B. Schartel, K. Langfeld, B. Ulmer, M. Bastian; BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin; SKZ-KFE gGmbH, Friedrich-Bergius-Ring 22, 97076 Würzburg, Germany; bernhard.schartel@bam.de

Halogen-free flame retardancy of styrene-ethylene-butylene-styrene-copolymers (SEBS)-copolymers is a most challenging task. The high effective heat of combustion of the volatiles and the char yield close to zero demand considerable action that is extremely hard to achieve with acceptable filling levels. Further SEBS-components pyrolysing show hardly any tendency to interact with flame retardant in the condensed phase. Halogen-free multi-component flame retardant approaches are presented including different phosphorus flame retardants, mineral fillers and the combination with different adjuvants. OI, UL-94 and cone calorimetry are used to analyze the fire behavior. A few promising approaches are worked out.

8:30 – 9:00

Thermal Stability and Flame Retardance of Novel Thermoplastic Poly(Imide-Urethane) 351

Qiheng Tang, Jiyu He, Rongjie Yang; School of Materials Science and Engineering, Beijing Institute of Technology, National Fire-retardant Materials Engineering Technology Research Center, 5 South Zhongguancun Street, Haidian District, Beijing 100081, China; yrj@bit.edu.cn

A kind of novel thermoplastic poly(imide-urethane) (TPIU) was synthesized through combining pyromellitic dianhydride (PMDA) into normal polyurethane. Further, hydroxyl terminated polydimethylsiloxane (PDMS) was inserted into the TPIU chain to form thermoplastic TPIU-PDMS. The chemical structures of TPIU and TPIU-PDMS are shown in Schemes (I) and (II).

In thermal stability, TPIU of the imide group has higher thermal decomposition temperature than commercial thermoplastic polyurethane (TPU) according to the TGA analysis. The total heat released (THR) and peak heat release rate (p-HRR) of TPIU were lower than those of the TPU by 14.62 % and 64.02 %, respectively, based on cone calorimeter testing. Limited oxygen index (LOI) values of TPIU increased with the PMDA content in the chain. In UL 94 vertical burning test based, the TPIU burnt without any dripping. TPIU-PDMS showed good thermal stability by TGA, and its LOI value increased with the content of PDMS. The cone calorimeter testing showed that TPIU-PDMS could reduce THR and p-HRR values compared with the TPIU with the only imide group, meaning the improved flame retardancy because of coexistence of the imide and dimethylsiloxane groups in the chain.

9:00 – 9:30

Antimony Trioxide Free and Low Antimony Trioxide Systems for Flame Retarded Engineering Thermoplastics 356

S. Levchik[a], R. Shtekler[b] ,Y. Hirschsohn[b], E. Eden[b] and M. Leifer[b]; [a]ICL-IP America, 430 Saw Mill River Rd., Ardsley, NY, 10502. sergei.levchik@icl-ipa.com; [b]ICL-IP, P. O. Box 180, Beer Sheva 84101, Israel

Availability of antimony trioxide, the common synergist for halogenated flame retardants, is said to decrease significantly due to depletion of explored mineral deposits.

Moreover, Antimony Trioxide replacement has in recent years become a priority due to environmental concerns and cost-efficiency issues.

This paper reports data on glass-fibers reinforced Polyamide and PBT formulations of brominated flame retardants with significant reduction of antimony trioxide loading or with no antimony trioxide at all. It was found that the efficiency of brominated flame retardants, in terms of minimum Br level and Br to antimony trioxide ratio required to achieve high UL-94 @V-0 fire safety ratings, depends on the chemical structure of the flame retardant.

9:30 – 10:00

World Premiere: Flame Retardant Plastic BMC 0204 Sets New Standards 362

Peter Ooms, Fa.Lorenz Kunststofftechnik GmbH, Hansastrasse 75 D-49134 Wallenhorst, Germany. Peter.ooms@lomix.com

The huge breadth of synthetic material types available on the market is not only due to the extremely wide range of plastic applications they serve but is also necessary to ensure that components comply with all relevant standards and regulations. Many of these materials possess a single outstanding characteristic but display deficiencies in their other characteristics. As a consequence, several plastics are frequently combined in a single component. But now, Lorenz Kunststoff GmbH is about to launch a new duroplast, BMC 0204, worldwide, which will allow a considerable reduction in the diversity of plastic types used in this way. This unique new material is not only extremely flame retardant but also displays a great number of other very useful mechanical properties, thus opening up whole new possibilities for synthetic material applications.

Session 7: Phosphorus-Based Fire Retardants, Including Intumescence

10:00 – 10:30

Latest Developments in Resistance to Fire: Protection of Steel and Composite by Intumescent Coatings 373

Serge Bourbigot, Bastien Gardelle, Pierre Bachelet and Sophie Duquesne

Unité Matériaux et Transformations (UMET) - UMR-CNRS 8207, Equipe Ingénierie des Systèmes Polymères, Ecole Nationale Supérieure de Chimie de Lille (ENSCL), BP 90108, 59652 Villeneuve d'Ascq Cedex – France serge.bourbigot@ensc-lille.fr

Fire protection of substrates such as steel or composite can be achieved with reactive insulation coatings which react when exposed to fire increasing their thermal insulation properties, thereby protecting the underlying substrate. It happens with intumescent coatings which expand and form an insulative layer at the surface of the substrate upon heating. The intumescence process results from a combination of charring and foaming at the surface of the substrate. The charred layer acts as a physical barrier which slows down heat and mass transfer between gas and condensed phase. The formation of an intumescent char is a complicated process involving several critical aspects: rheology (expansion phase, viscoelasticity of char), chemistry (charring) and thermophysics (limitation of heat and mass transfer). This approach will be examined in the talk considering classical intumescent paints and new silicon-based coatings.

The resistance to fire of intumescent coating protecting steel or composite is typically measured by a curve 'temperature as a function of time' and usually requires large scale equipment. Those tests are very expensive and time consuming. It is the reason we have developed reliable, repeatable and fast small scale tests. Examples for protecting steel (building applications) using small furnace delivering ISO 834 and UL-1709 temperature/time curves will be presented. Composites used for roofing and for aircraft applications will be also covered in the talk. The associated fire scenarios are flame spread evaluated by a mini Steiner tunnel (roofing) and jet fuel fire mimicked by a propane burner (10kW propane burner) delivering a heat flux of 200 kW/m^2 on the material. The fire behaviour of the materials according to the different fire scenarios will be presented and discussed.

10:30 – 10:45 Coffee Break

Chairperson: Tim Reilly

10:45 – 11:15

Phosphorus Flame Retardants with Different Chemical Environment. Thermal Stability and Flame-Retardant Efficiency 387

Manfred Döring, Bettina Burk, Michael Ciesielski; Fraunhofer-Institute for Structural Durability and System Reliability LBF, Division Plastics, Schlossgartenstr. 6, 64289 Darmstadt, Germany; manfred.doering@lbf.fraunhofer.de

Engineering plastics (PA, PBT) have their own high processing temperatures (250-350°C and even higher). To realize fire-resistant polymers it is necessary to compound polymers and flame retardants at these temperatures without a serious change in the characteristics of the polymer. Furthermore, a synergistic interaction of condensed phase and gas phase effects often guarantees in particular for fiber reinforced engineering plastics a maximum of the flame retardant efficiency.

The chemical environment of phosphorous compounds (P-O, P-N, P-C) is responsible for the specific flame retardant behavior (1). Due their less plasticizing effect and the marginal tendency of migration bridged rod-like, star-shape, and particularly polymeric compounds are preferred.

Here we describe the synthesis and structure of different phosphorus compounds including selected polymers, their thermal stability, and flame retardant efficiency in relation to their chemical environment.

11:15 – 11:45

Condensed Phase Mechanism of Phosphorus Flame Retardancy in Polymers 400

Richard Lyon, FAA Technical Center, Atlantic City, NJ Richard.e.lyon@faa.gov

A condensed phase mechanism by which phosphorus imparts flame retardancy to polymers is proposed. The mechanism is modeled as a chemical kinetic process in which organic phosphorus compounds RPOx hydrolyze to phosphoric acid, which catalyzes the dehydration of hydroxyl-containing compounds to form char, water, and fuel gases. The relative rates of P-catalyzed and non-P-catalyzed (homogeneous) charring are obtained from a single-parameter fit of the kinetic solution to experimental data for char yield versus phosphorus concentration. The results show that the molar charring efficiency of phosphorus increases as the number of P-O bonds in the starting compound, i.e., P < PO < PO2 < PO3 < PO4. The observed gas phase activity for RPOx for x < 2 and condensed phase activity (charring) for x > 2 may simply be a consequence of the solid state kinetics.

11:45 – 12:15

Designed Flame Retardancy with Phosphorus Polymers 410

D. Pospiech[1], O. Fischer[1,2], A. Korwitz[1], T. Hoffmann[1], M. Ciesielski[3], M. Döring[3], T. Köppl[4], V. Altstädt[4], S. Brehme[5], D. Vollmerhausen[5], B. Schartel[5];*

[1] Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany, pospiech@ipfdd.de

[2] Technische Universität Dresden, Organic Chemistry of Polymers, 01062 Dresden, Germany

[3] Fraunhofer Institute for Structural Durability and System Reliability LBF, Schloßgartenstr. 6, 64289 Darmstadt, Germany;

[4] University of Bayreuth, Polymer Engineering, Universitätsstr. 30, 95447 Bayreuth, Germany;

[5] BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

Polymers with phosphorus-containing structural elements can form the base for REACH-conform, alternative and halogen-free flame retardants (FR's). The past years have seen an increasing variety of polymeric structures that were designed to meet the requirements of new regulations for FR's whose FR potential was reported using degradation, combustion, flame, fire and burning behavior. However, usually the consequences of chemical modifications for the more general property profile and the influence of addition of such FR's on the overall property profile of the respective polymer matrix is not discussed.

Here, we will present two examples in which specially designed phosphorus polymers will be used to introduce flame retardancy in plastic materials.

Example 1 concerns FR in high performance epoxy resins. Here, phosphorus-containing poly(aryl ether)s were developed for use as combined toughness modifiers/FR's. The influence of structural variations on the decomposition and combustion including degradation pathways will be shown and the FR performance in cured epoxy formulations will be discussed concluding that polysulfones with DOPO-substituents mixed with standard PSU provided optimum results.

Example 2 will show two series of phosphorus-containing polyesters designed to enhance flame retardancy in poly(butylene terephthalate) (PBT). Again, the influence of variations in the chemical structure on solid state structure, decomposition and combustion will be discussed. In all structures, the phosphorus is incorporated in the substituent which results in each case in the loss of crystallinity and thus, reduction of toughness of the materials. However, the FR efficiency is demonstrated to be high, which could be maintained also in PBT using the P-polymers as additives. In these blends, roughly the level of the commercial benchmark was achieved.

Finally, the additional use of nanocomposite formation of the polyesters with organophilically modified clays or multiwalled carbon nanotubes, respectively, to further enhance the flame retardancy of polyester materials will be discussed. While addition of only nanomaterials did not yield a dramatic positive effect, combination of both nanomaterial and phosphorus polyester additive provided an additional reduction effect on total heat evolved and effective heat of combustion.

It can be summarized that work with polymeric FR's seems to be very promising, although much effort to optimize the systems and get the maximum effects will be necessary in future.

12:15 – 12:45

Benefits of Radical Generators in Flame Retarded Polymers: Review and New Developments 431

Rudolf Pfaendner, Fraunhofer Institute for Structural Durability and System Reliability, Division Plastics, Darmstadt, Germany; Rudolf.pfaender@lbf-fraunhofer.de

Radical generators as synergists in flame retarded polymers have been used in combination with brominated flame retardants for decades. However, due to the low thermal stability of radical generators under the usual polymer processing conditions the use was limited to selected applications e.g. in polystyrene foams.

The need to find efficient halogen free flame retardants resulted inter alia in the discovery and commercialization of hindered amine light stabilizers based on alkoxyamines (NOR-HALS). NOR-HALS provide flame retardancy of polypropylene and polyolefin fibers, non-wovens and films. The performance of the NOR molecules depends on their structure i.e. the capability to degrade into nitroxyl plus alkyl or aminyl plus alkoxy radicals. Through formation of radicals a fast degradation of the polymer chain is induced and flame retardancy is achieved by removing the substrate from the flame. On the other hand, the formed radicals are involved in the free radical chemical reactions during the combustion process. Furthermore, alkoxy amines can interact with brominated flame retardants and facilitate the release of bromine, consequently increasing the overall FR performance. Therefore, it is possible with NORs to design flame retardant polyolefin molding compositions with lower levels of halogenated flame retardants and, in addition, to eliminate antimony trioxide. Moreover the hindered amine (HALS) structure provides light and long-term thermal stability of flame retarded formulations.

Following the success of NOR based flame retardants a number of alternative radical generator molecules have been identified namely azo compounds, triazenes, hydrazones and azines. Especially combinations of Azo and NOR structures in one molecule show increased performance at loadings as low as 0.5 % in polypropylene films, including light and long-term thermal stability, and act synergistically with halogen, phosphorus and inorganic flame retardants.

Although the performance of alkoxyamines in thin sections such as films is well documented and the UL 94 V-2 classification is often obtained in moldings, formulations usually fail in achieving the UL 94 V-0 classification as burning drips cannot be avoided despite short burning times. For the first time a new class of nitrogen based radical generators can be presented whereas in combination with selected phosphorus derivatives flame retarded polypropylene with UL 94 V-0 classification is accessible. Thermal stability and degradation of the new class into radicals is correlated to the molecular structure and can be adjusted in line with the degradation of the polymer and the synergist. Moreover the necessary loadings to achieve UL 94 V-0 are below 10 %.

12:45 – 2:00 Lunch Break

Chairperson: Qiang Yao

2:00 – 2:30

SAFIRE®: A New Class of Halogen-Free N/P Based Flame Retardant for Plastics 443

J. Louisy, X. Delva[1], J. Dumoulin[1], Y. Bourgeois[1]; [1]Floridienne Chimie S.A., 12 Quai des Usines, BE-7800 Ath, Belgium; jlouisy@floridiennechemis.com

Halogen-free flame retardants attract attention since new regulations aimed at restricting old classes of brominated/chlorinated flame retardants (RoHS, WEEE, REACH) will soon enter into force[1]. Nowadays, industrial partners may deal with a number of known halogen-free compounds endowed with excellent fireproofing performances. A new range of halogen-free flame retardants, commercialized under the tradename SAFIRE®, has been launched on the market by the Belgium company Floridienne Chimie, a subsidiary of Floridienne Group. SAFIREs can be considered as melamine polyphosphate (MPP)-type substances wherein melamine is partly substituted by metallic cations such as aluminium, zinc or magnesium. They have been proved to substantially enhance the flame retardant properties of various thermoplastics and thermoset resins. This paper is giving an overview of SAFIRE's FR performances in Polyamide 6.6 (PA6.6), PolyButylene Terephthalate (PBT) and Epoxy resins. Many of the materials' properties, including fire performances, smoke production, arc-tracking resistance, corrosivity could be improved by combining SAFIRE products with phosphinate based substances. Accordingly some of the most stringent requirements could be fulfilled, especially in the transportation sector.

The paper will at first focus on evaluating the performances of the new flame retardant system SAFIRE / aluminium diethylphosphinate in glass fiber reinforced PA6.6. The so-called FR system provides outstanding fire properties together with improved arc-tracking resistance to the reinforced polyamide as compared to traditional halogenated and non-halogenated flame retardants. The use of zinc borate as co-additive with the SAFIRE based FR blend is afterwards discussed since it was proved to enhance further the thermal stability as well as the fire and smoke properties of reinforced PA6.6. Zinc Borate has proven to be particularly beneficial to reduce the smoke toxicity and smoke opacity of the plastic material when evaluated through standard smoke testing methods. This allowed achieving the highest ranking (HL3) according to the R22 and R23 requirements of the new railways standard EN 45545-2. The flame retardant blend SAFIRE / aluminium diethylphosphinate was also studied in glass fiber reinforced PBT and Epoxy resins. Emphasis will be put on advantages of using SAFIREs in PBT to improve fire performances and arc-tracking resistance and in Epoxy coatings to achieve low smoke production with sought CFE (Critical Flux at Extinguishment) value in the radiant panel test.

Finally a novel flame retardant system that intends to be a relevant alternative to traditional flame retardant systems will be presented. This novel system, which consists in a mixture of SAFIREs with a DOPO based derivative, exhibits among other assets a low propensity to corrode processing equipments (i.e. extruder barrel). This shall be considered as very positive feature especially for processing of high temperature polymers (i.e. PA6.6, PA6/6T,…).

2:30 – 3:00

Intumescing Flame Retardants Derived from Natural Materials 470

Douglas Fox and Mauro Zammarano – Chemistry Department, American University, Washington DC and Fire Research Division, National Institute of Standards and Technology, Gaithersburg, MD dfox@american.edu

Novel flame retardants have been developed by the chemical modification of natural materials, such as clays, proteins, and cellulose. The modification procedures and component ratios in flame retardant mixtures were optimized by visually observing evidence of intumescence and conducting microcombustion calorimetry experiments. The mixtures were used to form either a flame retarding coating for foams or a char producing network in melt-blended polystyrene composites. Thermal behavior and flammability of the treated polymers were examined. Factors contributing to the durability, efficacy, and intumescence of the treated polymers will be discussed.

3:00 – 3:30

New Non-halogenated Flame Retardants for Thin-walled Applications 485

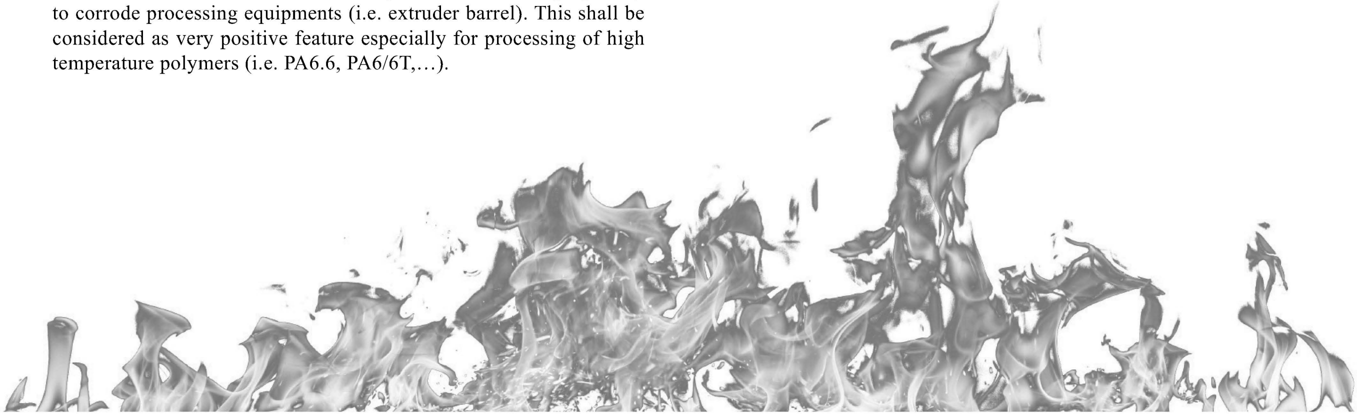
Volker Butz, Jerôme DeBoysère, Kyle Mitchell, Thor Specialities; Kyle Mitchell , kmitchell@thorsp.com , Tel:(219) 548 1805 & Cell: (847) 602 2625; Jérôme De Boysère, jdb@thor.com, Cell: +49 160 908 51 935

Building on more than 30 years expertise in phosphorus chemistry and flame retardants (FRs) for textiles, Thor (www.thor.com) has recently developed an extensive range of non-halogenated FRs dedicated to plastics applications. Cornerstones of the portfolio are two new substances, AFLAMMIT® PCO 700 and PCO® 800 that have been registered under REACH and TSCA, and another proprietary high-performance FR, AFLAMMIT® PCO 900

While they can be used in various polymers, thicknesses and applications, these new substances are expected to find commercial use primarily in polyolefin based thin-films, tapes or foams, where they fill the gap between traditional formulations (based on organic bromine or chlorine based FRs and antimony trioxide) and the available halogen-free additives, which are essentially limited in performance.

The paper will introduce the new AFLAMMIT® products and their synergistic combinations in a benchmark approach and will demonstrate their unique FR effectiveness. These new additives not only represent the first halogen-free alternatives to the widely used halogenated compounds in the targeted applications, but have also demonstrated to be successful in particular applications without halogen-free requirements, where performance based criteria are most important (i.e. highly flame-retarded films with preserved transparency or light-weight FR polyolefin foams).

3:30 – 3:45 Coffee Break



Chairperson: Kumar Kumar

3:45 – 4:15

New DOPO Chemistries and FR Applications 503

Timea Stelzig, Matthias Neisius, Aleksandra Buczko, Lea Bommer, Shuyu Liang, Henri Mispreuve, Sabyasachi Gaan; Chemistry Group, Advanced Fibers, Empa Swiss Federal Laboratories for Materials Science and Technology; *Foampartner, Fritz Nauer AG, Switzerland; Sabyasachi.Gaan@empa.ch*

In this work we will report development of bridged derivatives of DOPO (BDD) as flame retardant additives for application in engineering plastic, fibers and polyurethane foams. The BDD are characterized by their good thermal stability and depending on their chemical structure, good compatibility with polymeric substrates. Such BDD have P-C, P-N and P-O bonds and can be synthesized in high yields and usually obtained as diastereomeric mixture. This work provides a good account of structure –flame retardant property relationships of BDD in PU foams. These BDD have comparable or better fire performance as compared to commercially available FRs for certain application. Depending on the chemistry of BDD one can achieve highest UL 94 ratings in PA6 plastics and PU foams.

4:15 – 4:45

From Starch and Castor Oil to Phosphorous Flame Retardants 514

Bob A. Howell and Yoseph Daniel; Center for Applications in Polymer Science; Department of Chemistry; Central Michigan University; Mount Pleasant, MI 48859-0001; Bob.a.howell@cmich.edu

Starch may be derived from any of a number of seed plants (primarily corn in the US). Hydrolysis of starch provides glucose (this will come from cellulose in the future). Hydrogenation followed by double dehydration converts glucose to isosorbide, a diether diol. Castor oil is obtained from the castor bean and is available in large quantities. It is a non-edible oil and its use in a chemical process does not impact the world food supply. Pyrolysis of castor oil or a major constituent generates 10-undecanoic (undecylenic) acid. The ester derived from isosorbide and undecanoic acid contains two terminal unsaturations. This compound undergoes smooth thiol-ene reaction with 2-hydroxyethanethiol to afford a diol. Treatment of the diol with a variety of phosphorous reagents generates phosphorous esters. These compounds display good thermal stability. Thermal decomposition begins at approximately 230 °C and reflects elimination of a phosphorous acid. This process may be conveniently monitored using infrared spectroscopy. These compounds are, in the main, good char formers.

4:45

Conference Wrap-up

Chairperson: Charles Wilkie