

# **23rd Annual Conference on Recent Advances in Flame Retardancy of Polymeric Materials 2012**

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## 23<sup>rd</sup> ANNUAL BCC CONFERENCE ON FR

MONDAY, MAY 21, 2012

8:00 – 8:15

Opening Remarks

Charles A. Wilkie

Monday, May 21, 2012

### Session 1: Foams, Fabrics and Textiles

Chairperson: Martin Klatt

8:15 – 8:45

#### **Layer-by-Layer Assembly of Antiflammable Nanocoatings for Foam and Fabric Using ""4 Renewable and/or Environmentally-Benign Materials**

Jaime C. Grunlan, Department of Mechanical Engineering, Department of Chemical Engineering & Materials Science and Engineering Program, Texas A&M University

This research involves making multifunctional thin films, using layer-by-layer (LbL) assembly, within the Polymer NanoComposites (PNC) Laboratory (<http://nanocomposites.tamu.edu/>). LbL deposition involves exposing a substrate (e.g., plastic film, fabric, foam, etc.) to solutions of oppositely charged ingredients. Each anionic (e.g., clay) and cationic (e.g., polyethylenimine) layer is 1 – 100 nm thick depending on a variety of deposition conditions. In an effort to create an environmentally-friendly flame retardant system for foam and fabric, LbL thin films were assembled using “green” materials obtained from completely renewable sources. Ten bilayers of pH 3 chitosan (CH), as the cationic layer, and pH 10 montmorillonite (MMT) as the anionic layer, were deposited on cotton fabric and foam. In the case of open-celled polyurethane foam, only the outermost surface was charred after being exposed to the direct flame from a propane torch for 10 seconds. When cut open, white flexible foam was revealed under a black char layer. These results demonstrate the first fully “renewable” LbL flame retardant for foam. With just 4 wt% addition to the polyurethane foam, 10 BL of CH-MMT cut the peak heat release rate in half. In related work, cotton fabric was treated with intumescent nanocoatings, composed of poly(ally amine) and poly (sodium phosphate). The fabric structure and integrity is highly preserved following vertical flame testing and in some cases, no ignition occurs (i.e., the fabric did not burn when exposed to direct flame). Postburn analysis of coated fabric shows a cellular (foamed) layer and significant bubble formation on fibers with SEM imaging. Cone calorimetry shows that peak heat release rate and total heat release has 30 % and 65 % reduction, respectively, compared to the uncoated fabric, with only 4 wt% added to the original fabric weight. This study marks the first intumescent flame retardant nanocoating.

8:45 – 9:15

#### **Halogen Free Flame Retardants for Polystyrene Foams ""5**

Manfred Doering, Michael Ciesielski, Jochen Wagner, Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany, manfred.doering@kit.edu

Phosphorus flame retardants are mostly phosphorus oxygen compounds and can provide condensed-phase or gas-phase activities. Replacing oxygen against sulfur in the phosphorus flame retardants the gas-phase efficiency will be increased in epoxy resins (1). Moreover, synergistic mixtures of phosphorus and sulfur compounds show a strong gas-phase efficiency in epoxy resins.

Recently, phosphorus compounds together with elemental sulfur were described as non-halogenated flame retardants for polystyrene (2). We will introduce phosphorus sulfur compounds, which are particularly

generated by a direct reaction of phosphorus compounds with sulfur and discuss also their flame-retardant effect in polystyrene. Mixtures of phosphorus and sulphur compounds with a distinguishing structural feature are predestined as non-halogenated flame retardants for polystyrene foams.

#### References

- (1) Ciesielski, M., Schaefer, A., Doering, M., *Polym Adv Technol* 2008, 19, 507
- (2) Shankar, R.B., Kruper, W.J., Wilson, D.R., Hudack, M.L., King, B.A., Murray, D.J., Wang, C., Stobby, W.G., Morgan, T.A., Beach, M.W., Beulich, I., PCT Patent Application WO 2009/035881

9:15 – 9:45

### **DECA ALTERNATIVES FOR TEXTILE/COMPOSITE APPLICATIONS ""39**

Jeffrey Stowell, Ella Rapaport, Itzhak Shalev, ICL-IP America Inc.

Flame retardants play an important role in safeguarding life and property by reducing the overall fire risk associated with using highly combustible raw materials in new consumer products (e.g., textiles, composites, etc.). Flame retardants are carefully formulated and used to help prevent fires from starting and/or dramatically slow the combustion process. As such, flame retardants may contribute to longer escape times and reduce the associated risks for people in fire situations. Over recent years there has been an ever-growing public demand for new flame retardant product options; a request that has not gone unrecognized by the companies responsible for developing and introducing these new products. For example, the rapid and voluntary phase-out in the US of decabromodiphenyl ether (decaBDE) from the textile and composite finishing industries has created a need for deca alternatives that perform well, have a favorable ecological profile, are durable, and cost effective. A new product approach combining an efficient source of bromine as well as low-melt characteristics, has recently obtained considerable attention in the market as the next generation of flame retardants developed to provide a sustainable fire safety solution. Products based on this technology enable significant reduction in the add-on weight percent of bromine required and a substantial reduction in the amount of antimony trioxide synergist needed to pass stringent flammability tests. Durability is enhanced and binder demand is lowered due to the intimate incorporation of the FR product melt onto the treated substrate.

Data will be presented for several case studies of these flame retardants on a variety of textile substrates. Add-on and performance data of traditional and the new brominated flame retardants will be compared.

9:45 – 10:15

### **A Novel Halogen-Free Flame-Retardant Flexible Polyurethane Foam: Thermal, Flame-""4: Retardant and Mechanical Properties**

Ming-Jun Chen, Li Chen, Yu-Zhong Wang\*, Center for Degradable and Flame-Retardant Polymeric Materials (SC Key Laboratory), National Engineering Laboratory for Eco-Friendly Polymeric Materials (Sichuan), College of Chemistry, Sichuan University, Chengdu 610064, China. E-mail: [yzwang@scu.edu.cn](mailto:yzwang@scu.edu.cn) Tel.& Fax: +86-28-85410259

A novel nitrogen-phosphorus-containing flame retardant CMA was synthesized and used to prepare flame retardant flexible polyurethane foams (FPUF). The effect of CMA on the thermal, flame-retardant and mechanical properties of FPUF was investigated using TGA, LOI, flame propagation test (Cal T.B. 117A-Part I standard), cone calorimeter and tensile test, respectively. The cell morphology of FPUF was characterized by SEM. The results show that the onset temperature of the foam decreases, and the char yields increase due to the addition of CMA. When an appropriate amount of CMA is added, the foam can pass Cal T.B. 117A-Part I standard, and the structure and mechanical properties of the flame-retardant FPUF can almost keep accordance with those of FPUF without CMA.

10:15 – 10:30 Coffee Break

Chairperson: A. Morgan

10:30 – 11:00

## **Characterization of Flame Retardant Military Fabrics and Industrial Textile Fibers by Simultaneous DSC-TGA, and Pyrolysis GC-MS**

Pearl Yip, US Army – Natick Soldier System Command Center, Pearl.yip@us.army.mil

In this paper, a group of flame retardant (FR) fabrics, woven with different types of polymeric fibers to achieve fire protection as well as various other military requirements, are examined with simultaneous DSC-TGA (Differential Scanning Calorimetry-Thermal Gravimetric Analysis), and pyrolysis GC-MS (Gas Chromatography and Mass Spectrometry). Simultaneous DSC-TGA enables us to study the thermal behaviors of these textiles/fibers beyond their decomposition temperature. Pyrolysis provides a means to break up the polymers into smaller, volatile fragments, which can be analyzed by the GC-MS subsequently. Individual industrial textile fibers which constitute the woven fabrics are also examined separately as well as the woven textiles. Relevant testing parameters are necessary to relate experimental measurements to real-world military situations for protective clothing and fabric shelters. Results from these combined thermal and chemical analyses will be discussed for several FR fiber/fabric systems. The ultimate goal of this work is to develop additional characterization methods to study flammability and thermal stability of FR polymeric fibers and textiles to support the transition of new FR polymers under development for clothing and individual equipment.

11:00 – 11:30

## **Fiber Reinforcement and Fire Retardancy in Polypropylene**

K. Bocz, H. Erdélyi, P. Anna Gy Marosi, Budapest University of Technology and Economics, Organic Chemistry and Technology Department, [gmarosi@mail.bme.hu](mailto:gmarosi@mail.bme.hu)

Combined application of reinforcement and fire retardancy is a challenge in transportation and construction industries. Various structures have been prepared comparing their performance. The potential use of recycled polymers and renewable components has been evaluated as well improving their fire resistance and mechanical characteristics. Key factors of the performance are the degree of orientation, the interfacial structure and interaction. The use of advanced analytical methods, such as micro-Raman and LP-FTIR, contributed to the better understanding of the relationship between the phase-structure and performance.

### Session 2: Regulations

11:30 – 12:00

## **A Sustainable Landscape For Flame Retardants**

Susan D. Landry, Raymond B. Dawson, Albemarle Corporation, 451 Florida Street., Baton Rouge, LA 70801 [susan\\_landry@albemarle.com](mailto:susan_landry@albemarle.com)

Since its discovery centuries ago, fire quickly became both an integral part of our lives and a hazard to our very existence. The need for flame retardancy was subsequently recognized. The use of flame retardants has had a positive impact on the overall safety of homes, hotels, hospitals, nursing homes, offices, automobiles, and public transportation. Lives are saved by the use of flame retardants. Flame retardants are used to delay the spread of fires or delay the time of flashover to enable people time to escape. Many of the items we use on a daily basis, including electrical equipment, automobiles, and aircraft, are undergoing intense examination and scrutiny. The implications of the worldwide swing of regulatory programs impacts a broad range of materials, including flame retardants. Emerging chemical regulations are focusing on the need for characterizing all chemical substances in use in terms of their environmental and human health impacts.

Industry is responding to the market driven and regulatory challenges to ensure that flame retardants are safe, effective, sustainable, and meet evolving marketplace demands. In order to insure that the products will be available for continued use in the future, regulatory decisions need to be based on sound science. If society is to operate effectively and efficiently, then acceptance of good regulatory programs is of the utmost importance. The importance of end-of-life and recyclability requirements, as well as life-cycle implications, are crucial aspects of sustainability that often get overlooked.

Programs are in place to drive all members of the supply chain to identify the products in their formulations, reduce or eliminate chemical emissions to the environment, understand human health and environmental characteristics, and make transitions to more environmentally preferred products. This paper will address the

current global regulatory status, criteria for desired products, and current developments on the next generation of flame retardants.

12:00 – 12:30

### **Mattresses vs. Upholstered Furniture: A Case Study in the Development of Fire Test Requirements**

Timothy T. Earl, GBH International

In 2006, the US Consumer Products Safety Commission issued 16 CFR Part 1633, *Standard for the Flammability (Open Flame) of Mattress Sets*. The effort to establish a federal regulation for the fire performance of mattresses sold in the US for residential use was surprisingly quick, bypassing the code process and going straight into federal regulation. This paper will describe the entire chain of events leading up to the issuance of this standard and compare it to stalled efforts to establish a flammability standard or requirement for upholstered furniture.

12:30 – 1:00

### **A New Fire Test for School Bus Seating :**

Marcelo M. Hirschler, GBH International

The only mandatory US requirements for fire safety of school bus seating is the infamous FMVSS 302 flame spread test, in place since the late 1960s. ASTM has been working on the development of a new, more reliable, fire test. The test requires that a school bus seat assembly (3 seats) be exposed to flames from two gas burners. One gas burner (like the one used for room-corner tests) exposes the assembly from underneath the seats and another one (like the one for seats in CA TB 133) exposes the seats from above. The test assesses whether the seats burn up and whether the flame spreads from the exposed seat assembly to others in the school bus. It is similar to the “paper bag” test used by many US and Canadian school bus authorities for such assessments.

1:00 – 2:00 lunch

## **Session 3 : Modeling Chairperson: M. Hirschler**

2:00 – 2:30

### **Uncertainty and Calibration in polymers pyrolysis modeling**

Nicolas BAL and Guillermo REIN, University of Edinburgh / BRE Centre for fire Safety Engineering, King’s Buildings / John Muir Buildings, EH9 3JL EDINBURGH (Scotland)

Polymer pyrolysis is a key phenomena in solid ignition, flame spread and fire growth, and it is therefore essential to understand fire behaviour. A range of pyrolysis models have been developed in the past several decades with the main objective to predict solid ignition. Their complexity has increased mainly with the larger computational resources available, and also with the better understanding of the phenomena. The first models were simple analytical expression for the ignition time based on heat conduction. The most recent ones are numerical and multi-physics models of the heat and kinetic transient response of the polymer. However, the main drawback of this ever increasing complexity is that the number of parameters required as input is also increasing. Since the uncertainties from these inputs accumulate in the output, it can lead to significant modeling errors. Calibration routines comparing to experiments have been developed to reduce the modeling error in a local range of the parameter space (sample size, heat flux level, chemical formulation). But the error grows again when the model is applied away from its calibration range. These errors rapidly become higher than the errors caused by the physical and mathematical approximations into the model. It is desired to find a compromise between complexity, error and uncertainty. But the question of how to determine the most beneficial level of model complexity escapes simplistic approaches. The issue grows rapidly with the number of

possible heat and kinetic mechanisms that can be added. In this paper, the importance of the level of complexity and the calibration range for the particular pyrolysis problem of polymer ignition is investigated for clear PMMA using state-of-the-art experimental data and modeling tools.

2:30 – 3:00

### **Probabilistic Analysis of Fire Test Results''''''''''337**

R.E. Lyon (FAA) and N. Safronava (TAMI)

Several material fire properties were evaluated as sole explanatory variables for two pass/fail flammability tests using two different probabilistic models. The fire behavior and properties investigated span the range of commercial polymers and flame retardant plastics. The flammability tests were a fire test used by the Federal Aviation Administration for regulatory purposes and a flame test used by Underwriters Laboratories, both with categorical outcomes. The probabilistic analysis involved nonlinear least squares regression of these dichotomous pass/fail data coded as a binary outcome on each of the continuous explanatory variables using the logistic response function and a new (phlogistic) response function. The chi square test showed that both probability models were appropriate for describing the fire and flame test results using the heat release capacity, heat of combustion, volatile fuel fraction and heat release parameter as the sole explanatory variable, but neither model was appropriate for thermal decomposition temperature as an explanatory variable. The overall efficacy of the thermal and combustion properties for predicting flammability test results based on the correlation coefficient and mean deviation of the grouped data from the fitted functions is: heat release capacity = heat of combustion > heat release parameter > volatile fuel fraction > thermal decomposition temperature. Both of the probabilistic models are suitable for the analysis of binary flammability test results using the thermal and combustion properties investigated, but the phlogistic model provides a better fit of the data when the probability of passing the test approaches unity.

## **Session 4: Phosphorus-based and other Flame Retardants**

3:00 – 3:30

### **Novel polymeric, non-halogenated flame retardants with broad applicability in multiple''''''353 industries**

Jan-Pleun Lens, Lawino Kagumba, and Marc A. Lebel, FRX POLYMERS, Chelmsford, MA

FRX POLYMERS<sup>®</sup> is the first company to have developed a polymeric form of phosphorus that is being used as a non-migrating flame retardant (FR) additive. The polymeric nature is a huge advantage over the traditional small molecule FR additives that can migrate out of applications in which they are used and thereby expose humans to these (often) toxic chemicals. Also, by migrating out of these applications, small FR additives lose their efficacy and can cause parts to fail.

The polyphosphonates are produced through a solvent free melt polymerization process where a high purity phosphonate monomer is reacted with aromatic dihydroxy compounds. The by-product of the polymerization reaction is captured and reused to produce one or more of the starting materials, so little or no waste is generated. The novel monomer and polymer chemistry allows production of polymers with phosphorus content greater than 10%. This unique polymer has a Limited Oxygen Index (LOI) value of 65%, which is the highest number measured for a thermoplastic material. Additionally, the polymerization process can be modified to produce phosphorus-containing analogs of polycarbonate with inherent FR properties.

The polymers can be used as standalone, melt processable, inherent FR material but are also compatible with and deliver FR performance plus a number of unique properties to polycarbonate (blends), polyesters, polyurethanes, epoxies, and polyureas. Being polymeric, the polyphosphonates will hardly deteriorate the physical properties of these systems. Eliminating bromine in the FR package further allows greater recovery and recycle of plastics after their intended use.

A number of examples will be presented that show favorable results in industrial carpeting, textiles, electrical connectors and switches, building and construction, and electronic housings.

3:30 – 4:00

### **Chitosan as a Base for the Development of Green Phosphorus Flame Retardants ""354**

Bob A. Howell, Adina Dumitrascu and Mahmoud Al-Omari, Science of Advanced Materials Program, Center for Applications in Polymer Science, Department of Chemistry, Central Michigan University, Mt. Pleasant, MI 48859-0001

Chitin, a poly(saccharide) obtained from the shells of crustaceans, is the second most abundant naturally occurring biopolymer after cellulose. It is a copolymer of N-acetylglucosamine and N-glucosamine. Chitosan is derived from chitin by deacetylation. It, therefore, is a natural renewable resource and has many outstanding properties such as biocompatibility, biodegradability and nontoxicity. These properties make it an almost ideal base from which green phosphorus flame retardants may be developed. Treatment of chitosan with either 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide in carbon tetrachloride or diethyl chlorophosphite generates a phosphorus-containing polymer which displays a much reduced peak heat release rate upon combustion compared to that of unmodified chitosan. This material should function well as a flame-retarding additive for a number of polymers.

4:00 – 4:15 Coffee Break

Chairperson M. Doering

4:15 – 4:45

### **Strategies for Greener Innovation in Flame Retardants ""364**

Marshall Moore, Director of Technology and Advocacy, Great Lakes Solutions, a Chemtura business, West Lafayette, Indiana U.S.A.

Flame retardant additives for polymeric materials play an essential role in the design of safe and economical consumer and industrial products. They are required to achieve compliance to fire safety standards with most polymer systems used in electrical and electronics, building and construction and transportation applications where an ignition hazard exists. Conversely, flame retardants enable the use of low-cost, readily available polymer systems, such as polyolefins, styrenic polymers or polyurethane which would otherwise be too flammable to meet fire safety standards for many applications. In recent years research and innovation in the field of flame retardants has been greatly influenced by a demand for new products offering a reduced potential for environmental release and improved overall hazard classifications when compared to certain widely-used classes of flame retardants which have been found in the environment. However, while designing products with an improved environmental profile, performance criteria including flammability, physical properties, durability, and manufacturability must be maintained or improved. Following a strategy of Greener Innovation, Great Lakes Solutions has launched the Emerald™ line of flame retardants to provide solutions to these market needs. This paper will provide insights into approaches and challenges in designing more sustainable, high-performing, commercial flame retardants.

4:45 – 5:15

### **Review of Recent Advances on the use of Boron-Based Flame Retardants – Boron/Carbon ""365 Interaction in Fire Retardancy**

Kelvin K. Shen (consultant), Rio Tinto Minerals, Denver, CO 80111, USA

Recently reported new boron-based flame retardants as well as new applications of existing boron-based flame retardants will be presented. In addition, synergistic interaction between “boron and carbon”, “boron and metal oxide”, “boron and nitrogen”, and “boron and phosphorus” will be discussed. Special emphasis will be on the “boron and carbon” interaction.

5:15 – 5:45



## **Synergies of Metal Molybdates and Metal Hydroxides in Fire Retardant "377 Polyolefin Compounds**

Alex Isarov, David Temples, Mark Herndon, Tong Chen, J. M. Huber Corporation  
Fairmount, GA 30139

In the past several years, demand for low-smoke/zero-halogen polymer compounds has increased, and this trend is expected to continue. Need for such compounds is driving the advancement of related material technologies including fire retardants.

Fire retardant polyolefin compounds are typically flame retarded with metal hydroxides (ATH or MDH) where loading levels greater than 50% are common. However, high metal hydroxide loading levels have negative effects on the processability and physical properties of final compounds. The use of co-additives to enhance FR efficacy of metal hydroxides in polyolefin compounds and therefore achieve desired fire performance at lower total FR loading levels continues to be an active area of research.

Metal molybdates have been recognized for years as effective char formers in PVC systems. It was also recently demonstrated that zinc molybdate can promote char formation in certain EVA compound systems. In this work we further examine the contribution of molybdates to char formation in ATH- and MDH-filled polyolefin compounds such as polyethylene, polypropylene, and EVA.

5:45 – 6:15

## **NEW HIGH-PERFORMANCE ORGANOPHOSPHORUS FLAME RETARDANT "378**

Kimberly M. White, Vijay Kotian, Douglas Luther, Albemarle Corporation, 451 Florida Street, Baton Rouge, Louisiana 70801 [Kimberly.white@albemarle.com](mailto:Kimberly.white@albemarle.com)

A new organophosphorus flame retardant has been developed at Albemarle Corporation. This non-reactive phosphorus-based material satisfies fire safety needs for high-performance applications utilizing a broad range of resins including epoxy, polyolefin, polyamide and polyester. The combination of superior flame retardant efficiency, high thermal stability and excellent electrical properties is unique to this organophosphorus flame retardant and makes it a breakthrough technology for fast growing wireless and wired infrastructures. Resin performance data, including formulations with synergists, will be presented.

Tuesday, May 22, 2012

### **Session 5: Composites and Nanocomposites**

Chairperson: Kelvin Shen

8:15 – 8:45

## **Progress with nanocomposites as a flame retardant concept "37:**

Günter Beyer, Kabelwerk EUPEN AG, Malmedyerstrasse 9, B - 4700 EUPEN, Belgium  
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It has been demonstrated that the tubular filler Halloysite shows FR properties as indicated by UL 94 enhancements; this filler can also act as a char strengthener resulting in improved cone calorimeter data. We investigated the processing of Halloysite, Halloysite/ATH and Halloysite/MDH compounds by a BUSS compounding extruder and will report about the dispersions by SEM and the flame retardant properties by cone calorimeter.

A new filler, thermal pre-treated but not organically modified Illit, will be introduced as an alternative to organically modified montmorillonites with improved FR properties. Dispersions are at a nanometer level and the FR properties are quite similar to modified montmorillonites. These FR

properties are also demonstrated by a cable passing the B2 class described in the new European Construction Product Directive (CPD) for cable fire tests.

We will report also about the enhancements of viscosities of ATH-based EVA compounds by peroxide crosslinking or by nano-dispersion of modified montmorillonite. The increases of viscosities have a positive effect on flame propagations and dripping of burning polymers.

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8:45 – 9:15

### **Flame Retardancy of Thermoplastic Composites – Methodology and case studies 163**

Sophie Duquesne, Fabienne Samyn, Serge Bourbigot, 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

Thermoplastic composites are composed of a thermoplastic matrix including polyamides, polyesters or also polyolefins which is reinforced with glass, carbon and other fibres. The advantages compared to thermoset-matrix composites are for example faster production rate and recycling. Thus, those materials should find more and more applications in the next future. Among them, building and transportation could be cited. In those applications, a high level of flame retardant properties is required and thermoplastic composites are flammable. Dealing with the flame retardancy of composites, several points have to be taken into account. First, it has to be noted that thermoplastic matrixes behave differently in presence or not of the fibres. Second, the fibres used in such composites could be natural, such as for example, flax fibres and in that case, due to its organic nature could thus contribute to the development of the fire.

The objective of this talk is to present and discuss, using different examples from recent works carried out in the laboratory, the effect of the fibres in the flame retardant behaviour of thermoplastic composites.

9:15 – 9:45

### **Novel flame retardancy effects of DOPO-POSS on epoxy resins 172**

Wenchao Zhang, Rongjie Yang, National Laboratory of Flame Retardant Materials, School of Materials, Beijing Institute of Technology, Beijing 100081

A series of flame retarded epoxy resins (EP) are prepared with a novel polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS). The DOPO-POSS can be dissolved in diglycidyl ether of biphenol A (DGEBA) at 140 °C to form a homogeneous and transparent mixture at molecular level. The flame retardancy of these EPs are tested by the LOI and UL-94, indicating that DOPO-POSS has meaningful effects on the flame retardancy of EP composites. 2.5 wt. % DOPO-POSS incorporation into epoxy resin (EP-2.5) results in a LOI value 30.2 and UL-94 V-1 ( $t_1 = 8$  s and  $t_2 = 3$  s) rating. However, flame retardancy of the epoxy resins weaken while DOPO-POSS content increases from 5 wt. % to 10 wt. %. A very important result is in that the blowing-out self-extinguishing effect through the pyrolytic gases spurt is observed in UL-94 test for the EP-2.5. The pyrolytic gaseous products of the epoxy resins with and without DOPO-POSS are detected by TGA-FTIR under air atmosphere. Releases of gaseous species are found to be similar between the pure EP and EP-2.5. The details of fire behaviors, such as TTI, HRR, p-HRR, TSR, SEA, COPR, CO<sub>2</sub>PR, and TML, are tested by cone calorimeter. It is exciting that 2.5 wt. % DOPO-POSS in the EP makes the COPR and CO<sub>2</sub>PR reach maximum, which can explain the blowing-out extinguishing effect, a novel flame retarding mechanism.

9:45 – 10:15

### **Carbon nanotubes: New approach for innovative flame retardant solutions 182**

M. CLAES, C. DEWAGHE, Nanocyl SA, rue de l'essor, 4, 5060 Sambreville, BELGIUM

Since their first observation in 1991 by Iijima, carbon nanotubes (CNT) attracted both academics and industries, owing to their exceptional properties. Indeed, they have shown amazing intrinsic behaviour such as mechanical (1TPa), electrical ( $10^2$ - $10^5$  S/m), and thermal properties (3000 W/m.K). This is the reason why this allotropic variety of carbon has been tested as advanced multifunctional filler in polymer-based nanocomposites. In particular, their fire retardant effect have been investigated and highlighted in literature.

For the past few years fire retardant polymers market is changing following two major drivers: harmonisation of regulation and standards in European Community and Health-Safety and Environmental (HSE) concerns. Those actions cause increase of fire tests severity and banishment of most hazardous substances.

As a consequence plastic industry is requested to develop new Fire Retardant (FR) polymer solutions to foresee those modifications of regulations. In this frame, although some early results were not very convincing regarding the ability of CNTs to prevent fire, new approaches have been developed to use the best of the CNTs actions. Benefits of carbon nanotubes on flame retardant properties of polymer are now under strong investigation as a new solution for a more demanding market.

Among the universities, companies and research centres involved in this search, Nanocyl has built a great know-how. Working on this topic from the early beginning, its collaboration with universities, companies, fire test centres has led rapidly, for instance, to interesting results for Ethylene Vinyl Acetate (EVA) and Polypropylene (PP) solutions. Cone calorimeter and UL94 results showed an improved and strengthened charring effect, a drastic reduction of dripping and flame spread rate as well as an additional synergist effect with phosphorus based flame retardant.

It has led to solutions for fire resistant thermoplastics. In particular we have developed a Halogen Free Flame Retardant (HFFR) PP which passes UL 94 V0 @ < 2 mm.

Nowadays, an even deeper work is ongoing in order to develop new HFFR solutions in Thermoplastic PolyUrethane (TPU) and PolyEthylene (PE). These products should comply with UL94 V0 and more severe standards. These studies investigate how CNT can increase fire performances of plastics in order to reach new fire class rank and how CNT can be used to achieve a high level of fire properties as well as improve global functionality of polymer solution (better mechanical properties, processability, ...). To achieve the best performances, we developed news solutions and processes, such as CNTs with particular properties and characteristics (surface chemistry, length, diameter, hydrophobicity, ...) dedicated to fire resistant coating for example.

10:15 – 10:30 COFFEE BREAK

Chairperson: S. Landry

10:30 – 11:00

### **Carbon Black, Multiwall Nanotubes and Graphene – Promising Approach to Flame Retarded Nanocomposites? 183**

Bettina Dittrich,<sup>1</sup> B. Schartel,<sup>1,\*</sup> D. Hofmann,<sup>2</sup> K.-A. Wartig,<sup>2</sup> R. Mülhaupt<sup>2</sup>

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Carbon black (CB), multiwall carbon nanotubes (MWNT), expanded graphite and graphene were used and compared in nanocomposites as adjuvants and flame retardants with respect to fire properties. Their potential is discussed considering different fire scenarios. The fire behavior of the nanocomposites was changed significantly by incorporation of these carbon nanomaterials. During the anaerobe pyrolysis feeding the flame, the investigated carbon additives acted as inert fillers. They formed fire residual protective layers on top of the burning specimen reducing the peak heat release rate in particular. The efficiency of the protection layer was dependent on the dispersion within the nanocomposite. However, also other nanocomposite properties influence the complex fire behavior crucially such as viscosity and heat absorption. Structure-property relationships are described as basis to deduce guidelines for future flame retarded carbon particle nanocomposites.

11:00 – 11:30

### **Fire Retardant Evaluation and Thermal Degradation Modeling of Carbon Nanopaper-Coated Polymer Matrix Composites 192**

Jinfeng Zhuge, Jihua Gou, Ruey-Hung Chen, Composite Materials and Structures Laboratory, Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL 32816

Three types of hybrid carbon nanofiber based nanopapers were developed and their flame retardant efficiency was compared with thermogravimetric analysis and cone calorimeter test with 50 kW/m<sup>2</sup> of heat flux. The fire response of glass fiber reinforced polyester composites with and without the nanopaper coating was thoroughly examined with cone calorimeter test using varied heat fluxes. It was found that at a higher heat flux, the flame retardant efficiency of the nanopaper was better revealed. When the samples were exposed to 100 kW/m<sup>2</sup> of heat flux, the 1<sup>st</sup> and 2<sup>nd</sup> PHRR of the nanopaper coated sample were more than 32% and 47% lower than the PHRR of the control sample, respectively. In order to gain a deep insight into the pyrolysis process and flame retardation mechanism, the middle and back temperature profiles of the samples subjected to the above heat fluxes were recorded. At 100 kW/m<sup>2</sup> of heat flux, the final temperature within the nanopaper coated sample was roughly 280°C lower than that the control sample. The degradation rates in flexural moduli of the samples with a coupon shape were determined using three-point bending. When a sample was exposed to 25 kW/m<sup>2</sup> heat flux for 240 seconds, the flexural modulus of the control sample almost completely disappears, whereas the nanopaper coated sample still retains half of its flexural modulus. Based on the above analysis, a flame retardation mechanism was proposed for the nanopaper coated composites. Furthermore, a simple 1D finite element model was developed to predict the temperature evolution and thermal mechanical degradation of the composites subjected to constant heat flux. A temperature-dependent post-fire mechanical property model was proposed and implemented. The calculated temperature and residual mechanical modulus showed a good agreement with the experimental data.

11:30 – 12:00

### **Engineering Flame Retardant Biodegradable Nanocomposites** **217**

Kai Yang, Shan He, Seongchan Pack\*<sup>1</sup>, Neil Muir<sup>3</sup>, Rachel Davis, Caroline Juang, Menahem Lewin, Sufal Swaraj<sup>4</sup>, Harald Ade<sup>4</sup>, Chad Korach Takashi Kashiwagi<sup>5</sup>, and Miriam H. Rafailovich<sup>1</sup>

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<sup>4</sup> Department of Physics, North Carolina State University, Raleigh, North Carolina 27695,

<sup>5</sup> Fire Research Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8665

Starch-based polymer blends can potentially be a promising class of biodegradable nanocomposites. Despite their benefits, starch-based nanocomposites with thermoplastic polymers can be very brittle, when sufficient amounts are added to obtain flame retardant properties. Furthermore, melt-blending starch with other biodegradable polymers is also difficult since very few polymers are compatible with starches. We have recently developed a new class of nanoparticles where resorcinol diphenyl phosphates (RDP) is used to modify the surface energy, allowing the particles to be easily dispersed within polymer matrices using melt blending. When multiple types of particles share the same coating, they can be melt blended simultaneously and synergies can be achieved, imparting properties to the nanocomposite, which can not be achieved by any single additive. Here we show that RDP modified starch, and RDP modified clays, RDP especially RDP-Halloysite Clay tubes, can be extruded together with the biodegradable polymers, Ecoflex and polylactic acid (PLA), to produce flame retardant nanocomposites which can pass the UL-94-V0 test. Since the total amount of added particles is less than 10%, impact testing indicates that the embrittlement is minimized. TEM and Scanning transmission X-ray microscopy (STXM) images of the blend, show that the RDP-coated starch particles were well dispersed within the polymer matrix providing the flame retardant properties, while the RDP clays are localized at the polymer interfaces, reducing the interfacial tension and contributing to the compatibilization. Nanomechanical measurements of the chars remaining after cone calorimetric measurements indicate that maintaining flexibility of the chars may be an additional factor in achieving good flame retardant properties. In this case the higher energy of the RDP coating inhibits surface migration of the clays, which otherwise results in embrittlement.

12:00 – 12:30

### **Halloysite: Natural, Reinforcing and Fire Resistant** **218**

Andre Zeitoun and Christopher DeArmitt, Applied Minerals Inc.

This paper presents Halloysite, a natural, reinforcing mineral, which imparts fire-resistance to a range of polymeric materials. Halloysite releases structurally bound water when heated, similar to ATH or MDH but because the release temperature begins above 400°C, Halloysite can be used in a wide range of polymers from PE to PEEK. Due to its high surface area and thermal stability, it is an effective char former and the high aspect ratio makes for effective reinforcement of the plastic, hence improved mechanical properties.

Fire retardance has been demonstrated in a range of materials from LLDPE, PP, PA6, PA12 and PET to elastomers like EPDM, EVA and thermosetting epoxies. Furthermore, Halloysite can be used as a char forming synergist or as a stand-alone reinforcing FR solution. Some novel formulations with interesting synergistic effects will be presented.

12:30 – 1:30 Lunch

Chairperson: S. Bourbigot

1:30 – 2:00

**Fire retardancy of polypropylene nanocomposites based on halloysite nanotubes: 219 synergistic effects with intumescent flame retardant.**

**B. Lecouvet<sup>1</sup>, M. Sclavons<sup>1</sup>, S. Bourbigot<sup>2</sup> and C. Bailly<sup>1</sup>,** <sup>1</sup>Bio- and Soft Matter (BSMA), Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain (UCL), Croix du Sud 1 bte 4, 1348 Louvain-La-Neuve. Belgium, [benoit.lecouvet@uclouvain.be](mailto:benoit.lecouvet@uclouvain.be)  
<sup>2</sup>Ecole Nationale Supérieure de Chimie de Lille (ENSCL), Unité Matériaux et Transformations, Villeneuve d'Ascq, 59652, France.

Naturally occurring halloysite nanotubes (HNTs) with hollow tubular structure were used in this work to prepare PP/HNTs nanocomposites using a novel “one step” water-assisted extrusion process with and without the use of a maleic anhydride grafted PP compatibilizer (PP-g-MA).

Scanning electron microscopy and transmission electron microscopy were employed to analyze the morphology of the composites and to compare it to the rheological behaviour studied by dynamic shear measurements. The flame retardancy was studied using cone calorimeter and UL-94 tests.

A uniform dispersion of HNTs in PP is only achieved when compatibilizer **and** water injection are combined together. Consequently, these nanocomposites exhibit the lowest flammability due to the formation of a homogeneous, rigid and stable inorganic residue at the surface of the condensed phase that acts as a potential barrier to heat and mass transport.

Synergistic effects of halloysite nanotubes with intumescent flame retardant (IFR) were also investigated. Results of UL-94 and cone tests revealed that a synergy between HNTs and IFR only exists for an appropriate amount of halloysite, resulting in enhanced flame retardancy of IFR-PP systems.

The char residue observed by SEM revealed that synergistic effects between HNTs and IFR are associated to the formation of a mechanically reinforced and more compact char barrier at the surface of the condensed phase.

In view of these results, PP/HNTs nanocomposites prepared using this novel processing route are promising candidates for flame retardant applications.

2:00 - 2:30

**Combustion Behavior of Nanoclay Reinforced Glass-Fiber/PBT Composites Containing 226 Aluminum Hypophosphite\***

Wei Yang, Yuan Hu, State Key Lab of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, P R China

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\* The work described in this paper was financially supported by National Basic Research Program of China (973 Program) (2012CB719700), National Natural Science Foundation of China (No.51036007), and Specialized Research Fund for the Doctoral Program of Higher Education (20103402110006).

Glass-fiber reinforced polymer composites have become attractive engineering materials widely used in automotive, military and civil infrastructure applications. As one of most commonly used engineering thermoplastic materials, poly(1,4-butylene terephthalate) (PBT) is often reinforced by glass fiber to fabricate various composites with high performance. However, the development and application of glass-fiber reinforced PBT (GRPBT) are greatly limited due to its high flammability when subjected to elevated temperature or combustion. The objective of this study is to develop halogen-free fire retardant GRPBT composites with enhanced fire retarded performance using nanoclay and aluminum hypophosphite (AHP). The morphology of the nanocomposites was studied by transmission electron microscopy and X-ray diffraction. Exfoliated clay nanocomposites of flame retarded/GRPBT were formed during melt blending process. Combustion behaviors were investigated by microscale combustion calorimeter, limiting oxygen index (LOI) and Underwriters Laboratories 94 (UL 94). For the GRPBT/clay nanocomposite in combination with AHP, the heat release capacity which is an indicator of a material fire hazard reduced by 51%. Moreover, significant improvements were obtained in LOI along with maintained UL 94 ratings. Thermogravimetric analysis and residue characterization revealed the flame retardancy mechanism in which the well dispersed layered silicates in polymer matrix probably play an important role of “microreactor” during the combustion.

2:30 – 3:00

### High Aspect Ratio, Synthetic Clay as Flame Retardant in Polyolefin Nanocomposites 227

Bashar Diar-Bakerly, Michael R. Schütz, Hussein Kalo, Andre H. Gröschel, Axel H.E. Müller, Josef Breu, Department of Chemistry, University of Bayreuth, Germany ([www.ac1.uni-bayreuth.de](http://www.ac1.uni-bayreuth.de)); Charles A. Wilkie, Department of Chemistry and Fire Retardant Research Facility, Marquette University, USA. [Josef.breu@uni-bayreuth.de](mailto:Josef.breu@uni-bayreuth.de)

While the flame-retardant-mechanism of clays is still under debate, we have shown that high aspect ratios of clay nano-fillers are beneficial and yield a significantly reduced peak of heat release as compared to commercial montmorillonite fillers [1, 2]. Such huge aspect ratios (> 1000) are easily obtained by melt synthesis of clays [3]. However, the flame retardant potential of any filler may generally be masked by the quality of its dispersion in the matrix. Therefore, not surprisingly, we found that solvent casted nanocomposites of such synthetic hectorites outperformed melt compounded nanocomposites of the same filler. Aside from the method of dispersion, the quality of dispersion may be crucially improved by optimizing the surface modification of the filler. In that line, a synthetic Mg-hectorite was exfoliated in a stirred media mill. Next, the Mg-hectorite was turned into a heterogenous, metallocene-based polymerization catalyst (Fig. 1) that can be dispersed homogenously in organic solvents. Heterogeneous slurry polymerization then yields a polyolefin/Mg-hectorite masterbatch (30%wt; clay content) which was used to fabricate nanocomposites tested as flame retardants.

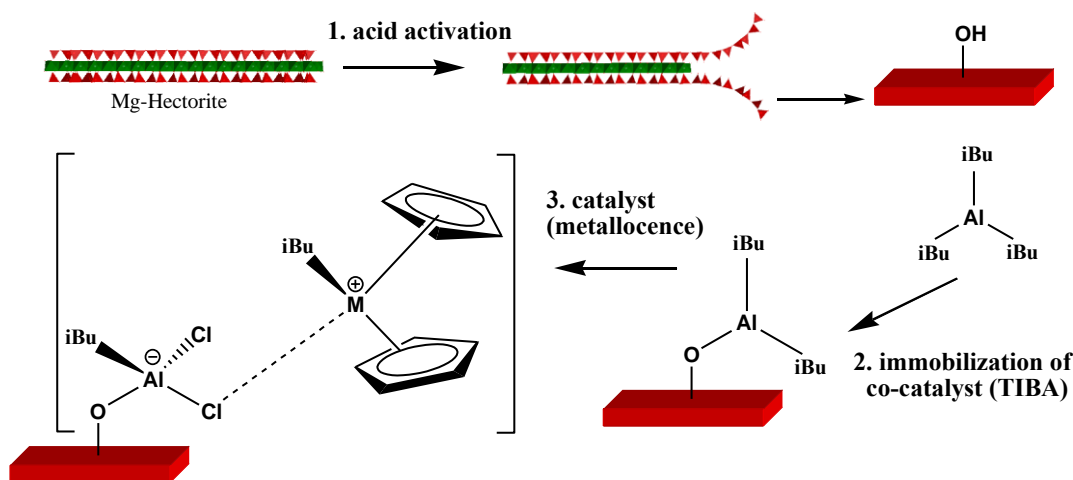


Fig. 1. Schematic presentation of the activation steps of Mg-hectorite to obtain a heterogeneous metallocene-based catalyst.

[1] Schütz et al., J. Polymer, 2011; (52) 3288 – 3294.

[2] Schütz et al., J. Mater. Chem., 2011; (21) 12110 - 12116.

[3] Kalo et al., Appl. Clay. Sci., 2010; (48) 39 – 45.

3:00 – 3:30

### **Ignition Mechanisms in Polymer Nanocomposites; Experimental Evidences and Interpretation 228**

A. Fina, F. Cuttica, G. Camino, Politecnico di Torino, Alessandria site, Viale Teresa Michel 5, 15121 Alessandria, Italy

The investigation of ignition of nanocomposites evidenced different trends in the time to ignition: a reduction of TTI compared to neat polymers is often observed, but the opposite effect is also reported in some cases.

In this work, nanocomposites and microcomposites based on different polymers (PET, PP, PA6) containing nanoparticles (montmorillonite, hydrotalcite, organofunctionalized or not) were addressed, showing variable trends in the time to ignition, as compared with the reference polymers.

Temperatures on the surface layer of specimens irradiated in the cone calorimeter were measured during the test, to investigate the surface temperature at ignition and correlate with the ignition time. Additionally, physical and chemical characterization of the condensed phase at different time, either before or after ignition, were carried out to investigate the evolution of the material during the combustion process.

The results of this work and relevant interpretation will be reported in this talk.

3:30 – 3:45 COFFEE BREAK

Chairperson: R. Lyon

3:45 – 4:15

### **Influence of thermophysical properties of materials on the heating rate and time to ignition of filled polymer composites 234**

L. Ferry, R. Sonnier, J.M. Lopez Cuesta, Ecole des Mines d'Alès, Centre CMGD, 6 avenue de Clavières, F-30319 ALES CEDEX

Numerous works have investigated the use of submicronic or nanometric fillers to improve the fire behaviour of polymers. Beneficial effects such as decrease of pHRR, limitation of dripping, improvement of self-extinguishability have been highlighted in the presence of those small size fillers. On the opposite, the reduction of time to ignition is often the detrimental counterbalance generated by those additives. Several mechanisms have been invoked to explain this phenomenon: (i) the early decomposition of particle surfactant, (ii) the early decomposition of polymer catalyzed by nanofillers, (iii) the rapid increase of polymer surface temperature due to lower convective heat exchange when viscosity increases. In this study, we have investigated the role of filler thermophysical parameters upon the heating rate and the time to ignition.

Different virgin polymers (PE, PP, PMMA, PET...) and filled polymers (fillers: aluminum particles, boehmite, carbon nanotube...) have been exposed to the controlled radiant flux of an epi-radiator. The temperatures of the upper and lower surface of the sample have been recorded using an infrared pyrometer up to the ignition. The results have been analyzed according to the intrinsic thermal properties (absorptivity, reflectivity) of the materials but also considering the morphology of the fillers (size and aspect ratio). It appears that the heat distribution in the material, and thus the polymer decomposition, is significantly affected by the thermophysical properties of the components.

4:15 – 4:45

### **Organoclays as Drip Suppressants 235**

Doug Hunter Southern Clay Products, Gonzales, Texas

Historically organoclays in flame retarded polymer formulations have been shown to reduce the peak heat release rate, increase char formation and strength, reduce smoke and extend the time to dripping in different resins. It is noted that flame tests required for product specifications cannot be passed unless a synergistic flame retardant is included in the formulation. Recent experiments using organoclays as drip suppressants will be discussed.

4:45 – 5:15

## **Design of New Multifunctional TPU/Attapulgite Nanocomposites via Synergistic Flame Retardant Approach 240**

Feng Yang and Gordon L. Nelson, College of Science, Florida Institute of Technology, Melbourne, FL

A new thermoplastic polyurethane / attapulgite nanocomposites was designed by the synergistic flame retardant approach. It was found that the combined use of a phosphorus flame retardant with smoke suppression agents or silicone in flexible polyurethane foams can significantly reduce the flammability of PUR foams in our past research. Cone results of the obtained flexible foams strongly support “synergism”. With 15 pbw of phosphorus FR, Antiblaze<sup>®</sup> 230, in the PUR formulation, the peak heat release rate was reduced by 23%, while 5 pbw of smoke suppression agent, zinc stannate, only reduced the PHRR by 14%. However, the combined use of Antiblaze<sup>®</sup> 230 with zinc stannate reduced the PHRR of the resulting PUR foams by over 40%. Considering the similarity of burning behaviors between PUR foams and TPU, the synergistic flame retardant approach by using phosphorus containing compounds as the surface treatment for attapulgite clay, which lead to the strong interaction between P-containing compounds and nanosized attapulgite. The fire performance of the flame retardant TPU nanocomposites was evaluated by Cone Calorimetry, Oxygen Index and UL 94, to illustrate the efficacy of such a combination approach.

During this conference, we will present some of the latest developments in the field and an overview of the potential applications for carbon nanotubes in the fight against fire.

### **Session 6: Cone and MCC**

5:15 – 5:45

## **Study of Commercial Flame Retardants for Polyurethanes via Pyrolysis Combustion Flow Calorimetry 254**

Alexander B. Morgan, University of Dayton Research Institute, 300 College Park, Dayton, OH 45469-0160

In this paper we seek to understand the relationship between chemical structure and flame retardancy in polyurethanes for a series of commercial flame retardants. The flame retardants studied cover both halogenated and non-halogenated chemistries, as well as reactive and non-reactive flame retardant additives. We studied the relationship between chemical structure and flame retardancy of the flame retardants themselves via pyrolysis combustion flow calorimetry (PCFC), and again when the flame retardants were put into flexible or rigid foams. Finally, the flame retardant foams were studied by cone calorimetry. Data from all three measurements (PCFC of the additives, PCFC of the additive + PU foams, cone calorimeter of the additive + PU foams) was then compared and contrasted. The results suggest that for flexible foams, the results between cone calorimeter and PCFC are similar, but for rigid foams, the results are very different. We present in this paper what we hypothesize is the reason for these similarities and differences, and provide guidance on how one can and cannot use the PCFC for flame retardant development in light of the data collected.

5:45 – 6:15

## **Monitoring the combustion efficiency in Pyrolysis Combustion Flow Calorimeter (PCFC) – Correlation with Cone Calorimeter 267**

R. Sonnier, B. Otazaghine, L. Ferry, J.M. Lopez-Cuesta, *CMGD Material Center, Ecole des Mines d'Alès, Alès (France)*

PCFC standard tests are performed using a high furnace temperature (900°C) leading to the complete combustion of gases released from the polymer degradation. Therefore, the efficiency of some flame retardants (such as halogenated compounds) is underestimated at PCFC test while their main mechanism of action is flame inhibition.



Nevertheless, decreasing the furnace temperature allows monitoring the combustion efficiency. The combustion efficiency at different furnace temperatures (calculated as Total Heat Release at a given furnace temperature divided by the Total Heat Release at 900°C) varies according to the nature of the material. In particular, halogenated compounds need higher furnace temperature to ensure complete combustion (Figure 1).

In this work, we have plotted the curves of combustion efficiency versus temperature at PCFC for 3 series of materials: pure polymers, 5 polystyrenes with different chemical groups grafted onto the aromatic ring and acrylonitrile butadiene styrene (ABS) copolymers containing various flame retardant additives. Released gases were identified using pyrolysis coupling gas chromatography and mass spectrometry (Py-GC/MS) at 600°C in order to correlate combustion efficiency and gases (Figure 2). Combustion efficiency in cone calorimeter was also measured and a correlation with the corresponding curves obtained using PCFC was performed.

It can be concluded that it is possible to estimate 'flame inhibition' effects observed at cone calorimeter which are conferred by specific additives by means of PCFC experiments.

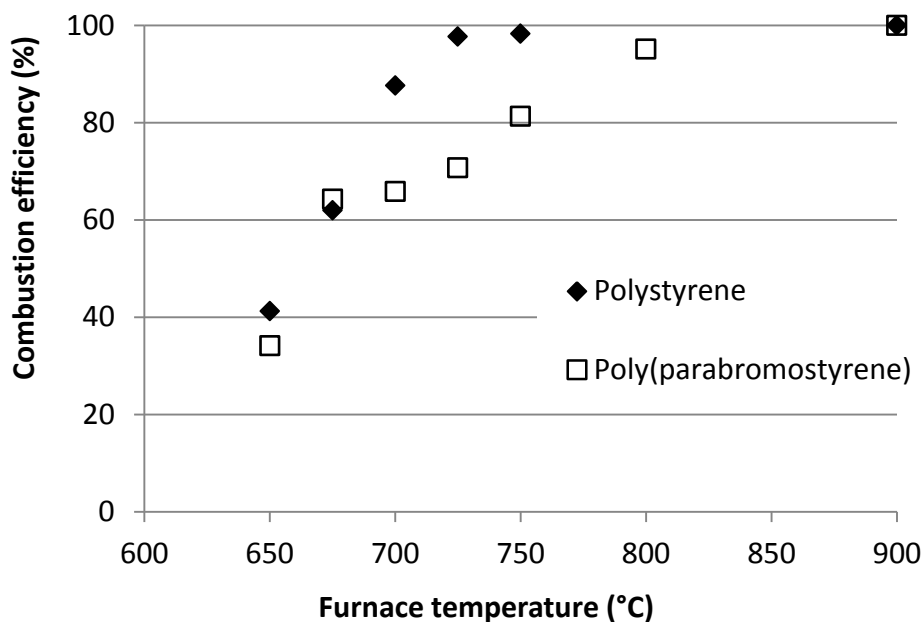


Fig 1 – Combustion efficiency versus furnace temperature in PCFC

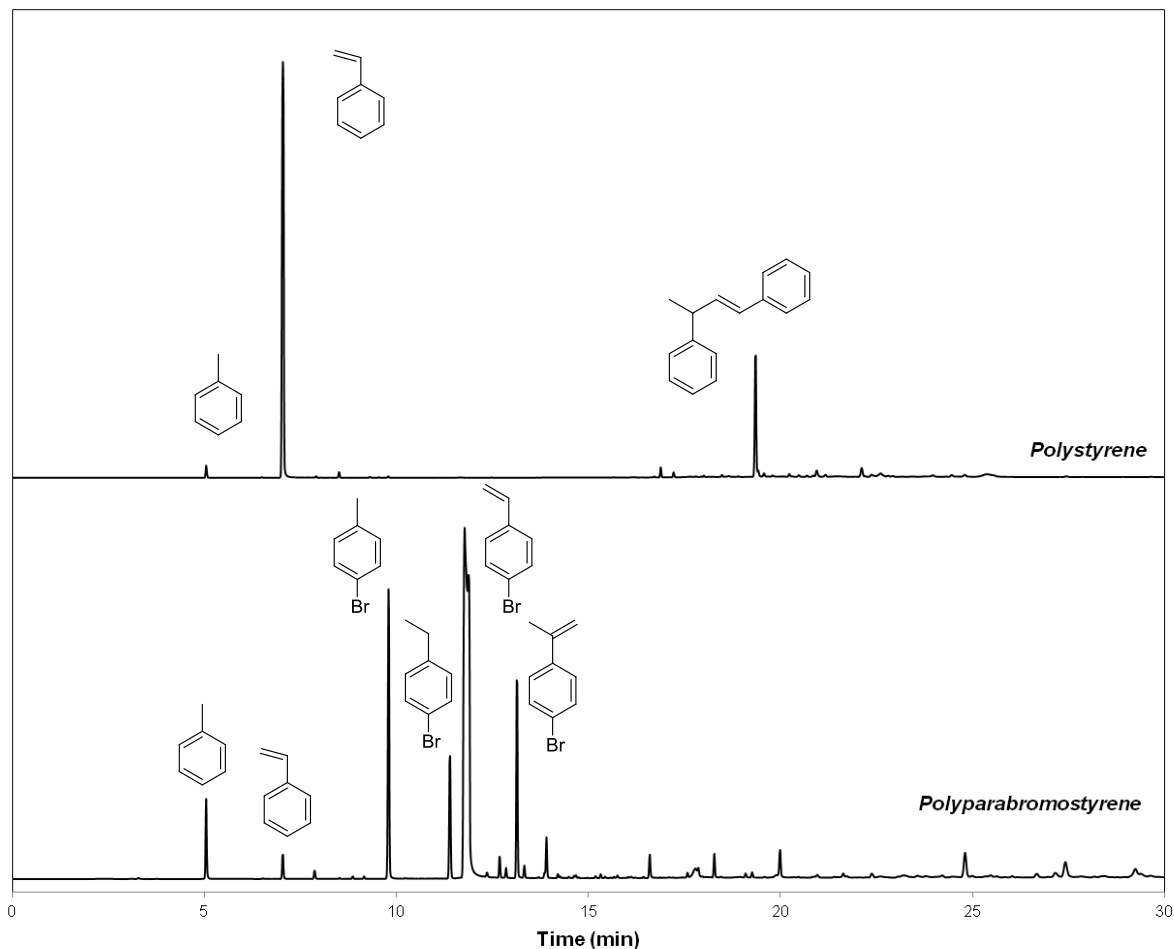


Fig 2 – Py-GC/MS analysis of polystyrene and poly(parabromostyrene)

Wednesday, May 23, 2012

**SESSION 7. FLAME RETARDANTS FOR SPECIFIC POLYMERS**

Chairperson: S. Levchik

8:15 -8:45

**Synthesis of Bisphenol Triazole (BPT)-Based Polymers and Cured Resins 270**

Todd Emrick, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA

This presentation will describe novel bisphenol-1,2,3-triazole (BPT) based polymers, including a background discussion on BPT-polyesters, followed by a description of BPT-containing epoxy and cyanate ester structures that are amenable to curing chemistry in the absence of added reagents or catalysts. These novel BPT-containing adhesives were characterized during the curing process, as well as post-curing, and compared to conventional epoxies and cyanate esters for curing and thermal properties. The curing process and products were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), pyrolysis combustion flow calorimetry (PCFC) for measuring heat release capacity, and small scale flame tests. Notably, these novel BPT-

based resins cure in the absence of added catalysts, and exhibit exceptionally low heat release values and high levels of char residue. Despite the absence of anti-flammable additives (neither halogenated or inorganic compounds were blended into the resins), the cured BPT-cyanate esters were found to be non-ignitable, have extremely high char residue (67%), and give extraordinarily low heat release capacity values (HRC of  $\sim 10$  J/(g K)).

8:45 – 9:15

### **New Trends in Flame Retardancy of Engineering Plastics 271**

**SERGE BOURBIGOT AND SOPHIE DUQUESNE**

ISP/UMET – UMR/CNRS 8207, Ecole Nationale Supérieure de Chimie de Lille (ENSCL),  
Avenue Dimitri Mendeleïev – Bât. C7a, BP 90108, 59652 Villeneuve d'Ascq Cedex, France

Engineering thermoplastics covers a broad range of thermoplastics (with or without fillers or reinforcements) and they include polyamides (PA), polycarbonates (PC), polyesters (PET, PBT ...), polysulfones, polyimides and poly-amide-imides and also blends of them (e.g. orgalloy® which is a blend of PP and PA). An engineering plastic is chosen for its range of enhanced physical properties which are high heat resistance, mechanical strength, rigidity and chemical stability. The applications are numerous and many of them require flame retardant properties and thus the plastics must be flame retarded. As an example, the use of those plastics in electrotechnical applications is often and materials have to comply with technical fire-safety standards such as UL-94, glow wire test, LOI ... It is the goal of this talk to survey the methods (intumescence, heat sink, surface treatment ...) to make flame retarded engineering plastics. Flame retardants used in the formulations will be discussed and the synergistic aspects will be covered in the presentation. Examples in PA, PET, PBT, PC and orgalloy® will be given based on recent work of our laboratory and on literature.

9:15 – 9:45

### **How to enhance flame retardancy of intumescent polyurethane? A combination of chemical and physical effects governing synergy 280**

Muller, Maryska<sup>a</sup>; Bourbigot, Serge<sup>a</sup>; Duquesne, Sophie<sup>a</sup> Lindsay, Chris<sup>b</sup>; Klein, Rene<sup>b</sup>; Giannini, Giacomo<sup>b</sup>,

<sup>a</sup> (ISP) - UMET - ENSCL, Bât. C7 Cité Scientifique 59652 Villeneuve d'Ascq, <sup>b</sup> Huntsman PU, Everslaan 45, B-3078 Everberg, Belgium

Polyurethanes are unique polymeric materials with a wide range of physical and chemical properties. With well-designed combinations of monomeric materials, polyurethane can be tailored to meet diversified demands of various applications such as coatings, adhesives, fibers, thermoplastic elastomers, and foams.

Ammonium polyphosphate has been added to a polyurethane coating model leading to a very efficient intumescent system. Intumescence describes the ability of a material to swell when exposed to a temperature increase leading to the formation of an expanded insulating layer. The addition of synergists considerably enhanced the fire performance of the intumescent polyurethane by a combination of chemical and physical effects.

The purpose of the talk is to present the systematic approach to draw general rules associated to well defined governing parameters for designing polyurethanes with enhanced flame retardancy.

9:45 – 10:15

### **Flame retardancy of biobased polymers 291**

**GAËLLE FONTAINE, CARMEN HOFFENDAHL AND SERGE BOURBIGOT**

ISP/UMET – UMR/CNRS 8207, Ecole Nationale Supérieure de Chimie de Lille (ENSCL),  
Avenue Dimitri Mendeleïev – Bât. C7a, BP 90108, 59652 Villeneuve d'Ascq Cedex, France

Bio-based plastics (PLA, polyether-block-amide polymer (PEBAX), PBS, PA-11 (Rilsan)...) may offer an alternative to the dependence on fossil fuels and the environmental impacts. Moreover, the developments in the past years in emerging bio-based plastics are spectacular from a technological point of view. Nevertheless one of the main drawbacks of polymers and bio-based polymers is their high flammability. The talk will investigate the flame retardancy of bio-based polymers by the incorporation of conventional flame retardant and/or nanofillers. Intumescence is a method to provide flame retardancy to polymers and it will be also examined for bioplastics. Flammability has been evaluated through fire tests including cone calorimetry and Limiting Oxygen Index showing huge improvement of the fire performance. Thermal degradation and the analysis of the fire retardant mechanism will be also discussed in this talk.

10:15 – 10:30 **Coffee BREAK**

**Chairperson: G. Marosi**

10:30 – 11:00

**Flammability and Thermal Stability Studies of Cyclotriphosphazene Derivative Containing <sup>14</sup>C; ; Silicon in Halogen-Free Flame Retardant Polypropylene**

Lanlan He, Dinghua Li, Rongjie Yang, National Laboratory of Flame Retardant Materials, School of Materials, Beijing Institute of Technology, Beijing 100081

As a novel flame retardant containing silicon, phosphorus and nitrogen, the cyclotriphosphazene derivative with organosilicon group,  $N_3P_3[NH(CH_2)_3Si(OCH_2CH_3)_3]_6$  (ACTP) was synthesized from hexachlorocyclotriphosphazatriene and 3-aminopropyl(triethoxy)silane and used in preparing flame retardant Polypropylene (PP) based on ammonium polyphosphate (APP). The properties of the obtained PP composites were investigated after incorporating different loading of ACTP in the flame retardant PP respectively. The results have indicated that the addition of ACTP influences both physical-mechanical properties and fire performance significantly. The possible mechanisms are also discussed. The thermogravimetric analysis (TGA) has demonstrated the synergistic effect of ACTP and APP on the thermal stability of PP composites with the improvement of residues weight. The fire behavior was studied through cone calorimeter analysis and limited oxygen index (LOI) test. LOI value increases to 26.5% with the 8 wt% loading of ACTP in APP/PP composites. The results from the cone calorimeter are in agreement with those of LOI and TGA; the ACTP-filled composites show a considerable decrease of heat release rate (HRR) with respect to the composites without ACTP. Furthermore, the morphology investigations revealed that the presence of ACTP causes a better dispersion and more homogeneous distribution of APP particles in the PP composites. In particular, SEM profiles of the residual chars showed that the charring has been enhanced with the addition of ACTP, which plays an important role in the process of flame retardancy.

11:00 – 11:30

**Flame retardants for copper clad laminates and printed circuit boards <sup>522</sup>**

Frank Osterod, Clariant Produkte (Deutschland) GmbH, Tim Reilly, Clariant Corporation, USA

A large number of flame retardants is nowadays available, but for a specific polymer and end application the choice is generally limited because many other important parameters beside the fire properties have to be considered. Especially materials for the electronic industry have to fulfill several technical requirements in addition to the UL 94 test. The lecture explains the challenging parameters for flame retardants in epoxy laminates for the printed circuit board industry and gives an overview about possible flame retardant solutions. The difference between reactive and additive type of flame retardants will be explained in more detail. Especially the two new reactive, phosphorus based flame retardants from Clariant which were developed for this application will be described in more detail and compared with already existing products.

11:30 – 12:00

**Polyurea – an antiblast but quite flammable material – what can we do? <sup>527</sup>**

Charles A. Wilkie, Department of Chemistry and Fire Retardant Research Facility, Marquette University, PO Box 1881, Milwaukee, WI 53201

Polyurea is a well-known anti-blast material which is in commercial usage to protect structures and it does this very effectively. Unfortunately, polyureas burn quite easily with high heat release rates, for instance the peak heat release rate is more than  $2000 \text{ kW/m}^2$  when irradiated at  $50 \text{ kW/m}^2$ . There are two distinctly different threats against which protection is required: the possibility that someone may detonate a device in close proximity to your structure and the possibility of an accidental fire. The possibility of an accidental fire is real and must be protected against. For the past few years, we have studied the fire retardancy of polyureas and this will be reported in this paper.

12:00 Closing Remarks Charles A. Wilkie

Lunch