MAY 23 - 25, 2016 • SHERATON STAMFORD HOTEL, STAMFORD CT USA

FLAME
2016

27th Annual

Conference on Recent Advances in Flame Retardancy of Polymeric Materials

FEATURING PRESENTATIONS
from outstanding scientists from around the world on topics covering the entire spectrum of flame retardancy. Topics include:

- Commercial Products
- Foams and Fabrics
- Nanocomposites
- Phosphorus
- New Flame Retardants and Specific Polymers
- Instrumentation

CHAIRMAN

CHARLES WILKIE
Marquette University

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27th Annual

CONFERENCE ON RECENT ADVANCES IN FLAME RETARDANCY OF POLYMERIC MATERIALS

May 23-25, 2016

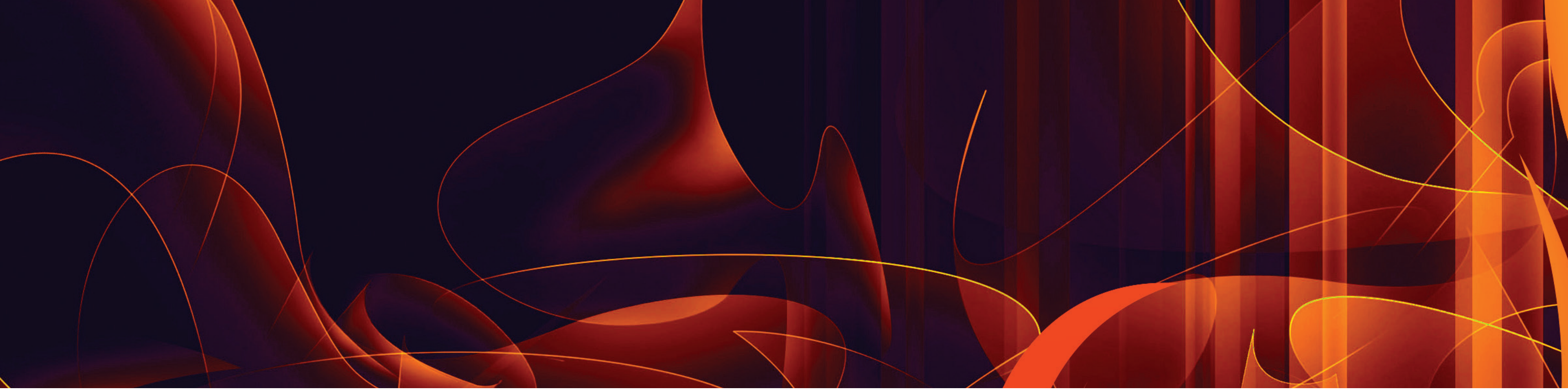
The complete technical and commercial development meeting on flame retardancy

PRESENTATIONS AT THE CONFERENCE WILL:

- Create a forum for introducing new technological achievements and developments in the field of flame retardancy (FR)
- Offer an overview of the current state of science and technology in FR
- Review the applications and markets for FR products
- Present recent developments in local and global standardization in testing technology
- Discuss toxicity and environmental issues
- Provide a unique opportunity for newcomers to become acquainted with the FR field in all its aspects
- Discuss nanoparticles effects on flammability
- Address regulatory issues for flame retardancy

CONFERENCE BENEFITS

- Network with colleagues including expert speakers in Flame Retardancy
- Discover the latest technological advances
- Learn about leading commercial applications
- Hear the latest regulatory, environmental, and testing findings



Intensive Short Course

SELECTION, EVALUATION AND COMMERCIAL APPLICATIONS OF FLAME RETARDANT POLYMERS

May 22, 2016

Designed for technical specialists new to this industry, this comprehensive one-day course will serve as a primer prior to attending at the main conference. The course consists of three interactive lectures by prominent industrial scientists.

COURSE DIRECTOR

CHARLES WILKIE
Marquette University

COURSE INSTRUCTORS

MATTHEW BLAIS, Ph.D

Fire Technology Department, Southwest Texas Research Institute (SwRI)

Fire Testing of Fire Retardant Polymers

SERGEI LEVCHIK, Ph.D

Product Development Manager, ICL-IP America

Modes of
Fire Retardant Action

KELVIN SHEN, Ph.D

Consultant, Rio Tinto Minerals

Review of
Flame Retardants in Commercial Use and Development

CONFERENCE PROGRAM

HOSTED BY bccResearch

SUNDAY
MAY 22nd, 2016

2:00-6:30
Pre-Registration

6:00–7:30
Opening Reception

MONDAY
MAY 23rd, 2016

7:00-8:00
Breakfast

8:00
Introduction to the Meeting
CHUCK WILKIE

SESSION 1: SUSTAINABILITY

Presiding: **RICH LYON**

8:15
New Generation of Flame-Retarded High Temperature Plastics Tailored for Sustainability

James Mitchell, Adam Marcinkowski, *Solvay Engineering Plastics, Lyon, France, adam.marcinkowski@solvay.com*

Product miniaturization together with increasing functionality is a permanent challenge in the E&E industry. Many automotive and electronics parts are now required to have high temperature behaviour, which is further increased when the wall thickness is severely reduced. As the limits are pushed these types of requirements cannot always be met with mainstream Engineering Plastic products. Thus, many "high temperature" polyamides have been developed. These polymers differ in many ways, such as melting point, viscosity behaviour, dimensional stability and moisture uptake, resistance to ageing and mechanical performance. Thus, it is crucial to understand the interaction between polymer matrix, flame retardant and other additives, processing conditions and processing equipment.

Reducing tool corrosion from high temperature Engineering Plastics is still perceived as a major challenge for both formulators and processors when dealing with some specific halogen-free solutions. Use of the wrong tooling or the wrong material can severally shorten the tool life which can lead to major problems in terms of cost and quality management. This particular problematic aspect was the driving force towards the creation of the new family of high temperature Flame retarded PA range from Solvay which are now entering their second generation in terms of performance.

This paper will introduce the major requirements and concerns of High Temperature Flame retarded Polyamides, with particular attention to the new family of low corrosive, high performing materials. It will also introduce a new concept on product sustainability.

8:45
Flame Retardant Properties of Phosphorus Esters of Isosorbide

Bob A. Howell and Yoseph G. Daniel, *Science of Advanced Materials, Center for Applications in Polymer Science, Department of Chemistry and Biochemistry, Central Michigan University, Mt. Pleasant, MI 48859-001, howel1ba@cmich.edu*

Flame retardants derived from renewable biomaterials are particularly attractive. They are independent of the supply/cost of petroleum, are often nontoxic or biodegradable and display a small carbon footprint. Starch from seed plants is currently a source of a variety of bio-derived building blocks. One of these, isosorbide, is a dihydroxy ether which may be converted to phosphorus esters. A series of such esters has been prepared, characterized and evaluated for flame retardant potential in DGEBA epoxy. A 1% phosphorus loading is generally sufficient to provide polymer with LOI > 25 and UL 94 V1.

9:15
How Important Is Synergy?

Charles A. Wilkie, *Department of Chemistry and Fire Retardant Research Facility, Marquette University, Milwaukee, WI 53201; Charles.wilkie@marquette.edu*

I have contended in the past that synergy was a badly misused term. Now I wish to take this additional step and inquire if synergy is important. We regularly find in the literature claims of synergistic behavior, often this is simply an assertion with no mathematical proof that the effect is more than additive. In this talk, I will explore the question of synergy and I expect that I will assert that synergy is an overrated notion.

SESSION 2: COMPOSITES AND NANOCOMPOSITES

9:45

Flame Retardancy and Thermal Stability of Polyamide 6 Filled with Melamine Cyanurite-Modified Montmorillonite Nanocompound

Deqi Yi, Min Zhao, Rongjie Yang*, *National Engineering Technology Research Center of Flame Retardant Materials, School of Materials, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, 100081 Beijing, P. R. China, yrj@bit.edu.cn*

Polyamide 6 (PA6) was filled with melamine cyanurate (MCA), organically-modified montmorillonite (OMMT), and melamine cyanurate modified montmorillonite nanocompound (MCA-MMT), respectively, to develop flame-retardant PA6 composites. The MCA-MMT nanocompound was prepared in our laboratory. Flame retardancy of the PA6 composites was investigated with the vertical burning testing (UL-94), limiting oxygen index (LOI), and cone calorimeter (CC) tests. Thermal stability and brittle fracture surface morphology of the PA6 composites were studied by thermo-gravimetric analysis (TGA) and scanning electron microscopy (SEM). It was found that application of MCA-MMT nanocompound compared with MCA and OMMT can modify fire retardancy and thermal stability of the PA6 composites due to barrier performance of nano-dispersed MMT in polyamide 6.

10:15

Coffee Break

Presiding: SERGE BOURBIGOT

10:45

High Performance Flame Retardant Biodegradable Polymers for 3-D Printing

Yichen Guo, Edward D. Weil, and Miriam Rafailovich, *Department of Materials Science and Engineering, SUNY at Stony Brook, Stony Brook, NY 11794-2275;* Simon Zhuang, *Dublin Jerome High School, Dublin, OH;* Robert Evans, *Division Avenue High School, Levittown, NY*

We have shown that high performance flame retardant biodegradable polymer nanocomposites can be obtained by melt blending poly (lactic acid) (PLA), melamine polyphosphate (MPP) and organically modified clays (C-30B) with specific ratios. The UL-94 tests showed that adding 1% of C-30B was able to prevent dripping which allowed the sample to achieve a V0 designation. Increasing the amount of C-30B to 2% though, resulted in complete failure of the test. Cone calorimetry measurements showed a large drop of the Average Heat Release Rate and Peak Heat Release Rate for all the samples with 17% MPP, with no obvious difference between the samples with and without the C-30B clay. The rheology results showed that the addition of C-30B can cause a pseudo-solid viscoelastic transition for the polymer matrix, and 1% of C-30B was the perfect loading to enable the flow of PLA matrix which assisted the subliming of melamine, and prevent the dripping during the burning.

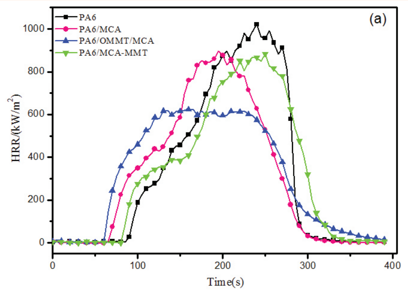


FIGURE 1: Comparison of heat release rate of PA6 composites by CONE

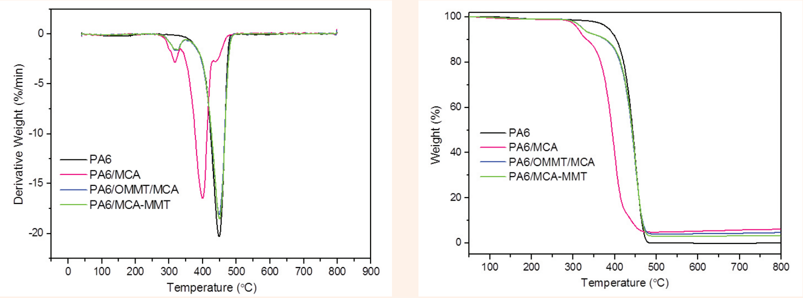


FIGURE 2: TGA and DTG curves of PA6 composites

FORMULATION AND FLAME RETARDANT BEHAVIOUR OF PA6 COMPOSITES

SAMPLES	PA6 (w%)	MCA (w%)	OMMT (w%)	MCA-MMT (w%)	LOI (%)	UL-94 (3.2mm)	t_1 (s)	t_2 (s)	Dripping
PA6	100	0	0	0	21	NR	>30	>30	Yes
PA6/MCA	92	8	0	0	24.6	V-2	6.5	3.5	Yes
PA6/OMMT/MCA	92	4	4	0	21.8	NR	48.5	45	Yes
PA6/MMT-MCA	92	0	0	8	25.1	V-0	2.1	2.0	No

** This work was supported by National Natural Science Foundation of China,Youth Science Found project (No.51303011), Basic Research Foundation of Beijing Institute of Technology (No.20130942002)*

In order to process the nanocomposites into fibers for 3-D printing, it was essential to preserve the ductility of the PLA homopolymer. We therefore first optimized the Izod impact of the nanocomposites, and the results indicated that the flame retardant sample also had the maximum impact, which was the same as that of PLA. Tensile testing also indicated that even though the modulus and the tensile strength of the flame retardant sample increased by 30% and 15% respectively, the elongation at break did not decrease relative to the PLA homopolymer. As a result we show that 1.75 mm fibers of the flame retardant composition were able to be drawn and printed. Preliminary testing of the drawn fibers indicated that the process did not degrade the flame retardant properties, which retained the V0 classification.

SESSION 3: MODELLING

11:15

Physical Modelling of an Aeronautical Composite in Fire

P. Tranchard[1], F. Samyn[1], S. Duquesne[1], J-L. Montes[2], S. Bourbigot[1], *[1] ISP/UMET - UMR/CNRS 8207, Ecole Nationale Supérieure de Chimie de Lille (ENSCL), Bât. C7, Avenue Dimitri Mendeleïev - CS 90108, 59652 Villeneuve d'Ascq Cedex, France; [2] Thermal Tech Center, ESAZT, AIRBUS Opération S.A.S, 316 Route de Bayonne - 31060 Toulouse, France, p.tranchard@laposte.net*

The evaluation of fire behaviour of structural composites is done through experimental tests which are time consuming and costly for the aircraft manufacturers (e.g. ISO 2685 and burnthrough test). Concurrently, the amount of composites in aircraft structures has increased and each type of material has to be fire evaluated accordingly. Currently, the numerical simulation is largely used during the development phase of an aircraft. So, simulation tools are under-development to predict the thermomechanical behaviour of composite exposed to fire. Hence it is paramount to explore in detail the behaviour of composites under fire conditions in order to secure the design and to secure the certification tests to match with the aircraft master planning.

In the talk two approaches will be considered. A novel fire test bench designed to mimic burnthrough test will be first commented and fire behaviour of some composites will be examined. Numerical simulation developed to predict the thermal degradation of the composite coupon will be then presented and fully discussed.

11:45

Modeling Flame Spread on Polymeric Solids: From UL-94 to Room Corner

Stanislav I. Stoliarov, Isaac T. Leventon, Chad M. Lannon, *University of Maryland, Department of Fire Protection Engineering, College Park, MD, 20742, United States; stolia@umd.edu*

A new model of upward flame spread has been developed by coupling the numerical pyrolysis solver ThermaKin2D, whose function is to compute the transient rate of gaseous fuel production of a material in response to external heat flux, with an empirical flame model that predicts a wall flame's heat feedback profile as a function of material mass loss rate. The empirical flame model was initially parameterized to describe flame growth on 4-20 cm tall samples of poly(methyl methacrylate) and subsequently extended through scaling to an arbitrary pyrolyzable solid. The same model development approach was applied to the Room Corner (NFPA 286) testing scenario. The approach generated promising results and revealed that an accurate intermediate scale (20-60 kW m-1) wall flame description is critical for an accurate prediction of the corner fire dynamics. Overall, this research demonstrates feasibility of fast and informative calculation of results of standard flammability tests from fundamental material properties.

12:15

Lunch

Presiding: **WALID AWAD**

2:00

Enhanced Thermal Decomposition and Kinetics of Poly (Lactic Acid) Sacrificial Polymer Catalyzed by Metal Oxide Nanoparticles

Jing Li, *University of New Haven, jli@newhaven.edu*

Poly(lactic acid) (PLA) has been used as sacrificial polymer in the fabrication of battery separators and can be employed in 0D-3D Vaporization of Sacrificial Component (VaSC). In this study, 1wt% PLA/Fe_2O_3, PLA/CuO, PLA/Bi_2O3 composites are prepared by solvent evaporation casting. Scanning Electron Microscopy (SEM) images indicate that the embedded nanoparticles are well dispersed in the polymer matrix, and X-Ray Diffraction (XRD) verifies the crystallinity of these metal oxides (MOs). Thermal stability analysis of PLA and PLA/MO composites is performed using the Thermal Gravity Analyzer (TGA) and Differential Scanning Calorimeter (DSC). The overall heat of combustion is measured by Microscale Combustion Calorimeter (MCC) and is found to be insensitive to the presence of nanoparticles. The overall catalytic effects of the three metal oxides follows: $Bi_2O_3 > Fe_2O_3 >$ CuO inert material. PLA/Bi_2O_3 decomposition onset point (T5%) and maximum mass loss decomposition temperature (T_{max}) are lowered by approximately 75 K and 100 K respectively compared to the neat PLA. The as-synthesized Bi_2O_3 is identified as the most effective additive among those proposed in the literature to catalyze the PLA decomposition process. A numerical pyrolysis modeling tool, ThermaKin, is utilized to analyze thermogravimetric data of all the PLA/MOs' and to produce a description of the decomposition kinetics, which can be utilized for modeling of thermal removal of these sacrificial materials.

SESSION 4: FABRICS AND FOAMS

2:30

From Synthesis to Manufacturing, How FR Apparel Is Engineered

Warren Gerhardt, Jason Spruell, Rajib Mondal, Petr Valenta, *Milliken & Company, Spartanburg, SC, 29303, warren.gerhardt@milliken.com*

As a leader in the protective apparel market, Milliken has a variety of tools available to develop technologies that bring both improved performance and comfort to the wearer. This is accomplished by leveraging innovations at every scale of the textile during its fabrication. The most powerful tool we have in this holistic approach is a phosphorus-based chemistry that is engineered into the garment at the fiber level. Discussed today will be our contributions in the design and synthesis of FR active systems that are based on phosphonium chemistry. An overview of the field and the value of these molecular/polymeric compositions will be given.

3:00

Towards Durable FR Nylon-Cotton Blends for Military Clothing Applications

Ravi Mosurkal[1], Sammaiah Thota[2], Ramaswamy Nagarajan[3], Jayant Kumar[2], [4]; *[1] US Army Natick Soldier Research, Development & Engineering Center, Natick, Massachusetts.; [2] Center for Advanced Materials, University of Massachusetts, Lowell; [3] Department of Plastics Engineering, University of Massachusetts, Lowell. [4] Department of Physics and Applied Physics, University of Massachusetts, Lowell, ravi.mosurkal.civ@mail.mil*

There is a significant need in the Army for improved, cost effective and environmentally safe flame retardant (FR) clothing, due to flame hazards ranging from incidental exposure to threat-generated exposures (i.e. thermal weapons, ballistic, blast, chemical, and directed energy). Current FR protective materials (e.g. FR ACU) do not provide optimum protection against existing and emerging battlefield threats and have inadequate durability. They are both financially and environmentally costly, and many cannot be purchased/manufactured in the US. Current research is focused on developing FR fabrics based on nylon/cotton blend (1:1 nylon:cotton), with comparable FR protection to the FR ACU but with enhanced durability and lower cost.

It is imperative to find ways to convert Nyco fabric into FR fabric for the Army uniforms through effective and convenient surface coating techniques. Although, many researchers, including our group, have been working to develop flame retardant (FR) coatings on cotton and Nyco fabrics using traditional coating methods, including layer-by-layer method, to impart FR properties, these coated fabrics cannot withstand the laundering tests which is essential for soldier clothing applications. Most coatings used currently interact with the fabric through predominantly weak, non-covalent interactions that are not stable during washing. Since fire initiation is a surface phenomenon, development of covalently functionalized conformal coatings will have a direct impact on flammability of the fabric as well as durability of the coating. In this presentation, we address the durability issues of the current FR coatings and present the results from the research work on corona/plasma treatment and chemical functionalization for producing durable FR Nyco.

3:30

Flame Retardant Finishing of the Nylon/Cotton Military Fabrics Using a Reactive Organophosphorus Oligomer: Chemical Bonding and Hydrolysis Resistance

Charles Q. Yang[a] and Qin Chen[b], *[a]Department of Textiles, Merchandising and Interiors, The University of Georgia, Athens, Georgia 30602, U.S.A, cyang@uga.edu; [b]College of Chemistry, Chemical Engineering & Biotechnology, Donghua University, Shanghai 201620, China*

Nylon66/cotton blend fabrics have long been used in military protective clothing. Because fire risk has drastically increased in recent warfare, developing flame retarded military nylon/cotton fabrics becomes extremely important for protecting military personnel. This research focuses on the chemical reactions involved in the flame retardant finishing of cotton/nylon blends. In our previous research, it was discovered that a hydroxy-functional organophosphorus oligomer (HFPO) was bound to nylon when a nylon fabric was treated with the combination of HFPO and dimethyloldihydroxylethyleneurea (DMDHEU). In this research, the bonding mechanism and hydrolysis resistance of HFPO/DMDHEU on the nylon/cotton blend fabrics is investigated. The data indicate that HFPO is bound to the nylon/cotton blend fabrics by (1) forming a HFPO/DMDHEU crosslinked polymeric network on both nylon and cotton fibers (2) forming a DMDHEU bridge between cellulose and HFPO on cotton. The quantity of the HFPO/DMDHEU crosslinked network and that of the DMDHEU-bridging formed on the nylon/cotton blend fabric is determined by both the amount of HFPO and the HFPO/DMDHEU ratio used in the treatment. The data also show that the bonding of HFPO/DMDHEU on the nylon/cotton blend is highly resistant to hydrolysis and it is a durable flame retardant system for the nylon/cotton military blend fabrics. The treated fabrics pass the fabric vertical burning test after 50 home laundering cycles. A nylon/cotton blend fabric with a higher cotton-to-nylon ratio has more HFPO/DMDHEU bound to the fabric and is more hydrolysis-resistant. The changes in the mechanical strength and stiffness of the treated blend fabrics are also discussed.

4:00

Coffee Break

Presiding: TIM REILLY

4:30

Polyelectrolytes as the Basis for Benign Flame Retardant Nanocoatings

Jaime C. Grunlan[a], [b], [c]; *[a] Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-3123, USA, [b]Department of Chemistry, Texas A&M University, College Station, TX 77843-3122, USA, [c] Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843-3122, USA, jgrunlan@tamu.edu*

Layer-by-layer (LbL) assembly is wide-reaching conformal coating “platform” technology capable of imparting a multiplicity of functionalities on nearly any type of surface in a relatively environmentally friendly way. At its core, LbL is a solution deposition technique in which layers of cationic and anionic materials (e.g. colloidal or nano-particles, polymers and even biological molecules) are built up via electrostatic attractions in an alternating fashion, while controlling process variables such as pH, coating time, and concentration. On foam, these coatings can dramatically reduce the heat release rate (HRR) and eliminate melt dripping. We've also developed intumescent recipes that rely on the foaming action of phosphorus and nitrogen-rich molecules. In an effort to impart flame retardant behavior to woven fabrics with fewer processing steps, onepot aqueous polyelectrolyte complexes have also been developed in our lab. These water-based coatings impart self-extinguishing behavior to blends of cotton and nylon (or polyeseter). Reduction of total heat release, measured with a microscale combustion calorimeter (MCC), by more than 80% was accomplished with just 15 wt% added to a woven fabric. This water-based coating technology can be applied quickly and easily in just one or two steps. For more information, please visit our website: *http://nanocomposites.tamu.edu*

5:00

A Novel Efficient Flame Retardant for Resolving the "Candlewick Effect" of Ramie Fiber Reinforced PP Composites

Cong Deng, Shuang-Lan Du, 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*

A novel mono-component intumescent flame retardant, ETA-APP, was used to flame-retard PP/ramie fiber (PP/RF) composite. Due to the existence of a large amount of hydroxyl groups at the surface of ramie fibers, the in-situ functionalization of RF was realized through hydrogen bonding between RF and ETA-APP during melting processing. Scanning electron microscope (SEM), energy dispersive X-ray (EDX), and X-ray diffraction (XRD) illustrated that core-shell RFs were in-situ formed in PP/RF/ETA-APP composite after melt blending, in which the RFs and ETA-APP acted as the core and shell, respectively. X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared spectroscopy (FTIR) confirmed that the hydrogen bonding between RF and ETA-APP was formed in the PP/RF/ETA-APP composite after the melt blending. The resulting PP/RF/ETA-APP composite had much better flame retardancy than PP/RF containing a traditional highly-efficient intumescent flame retardant (TIFR) which cannot functionalize RFs. The in-situ accumulated ETA-APP at the surface of RF was charred during the combustion process, and the formed char layer efficiently prohibited the combustion-supporting "wicking action" resulting from the wetting, spreading, and flowing of polymer melt along the RF, leading to the formation of a compact char layer containing the backbones consisting of the residue of RFs. Therefore, the highly-efficient flame retardation of PP/RF/ETA-APP was achieved.

5:30-7:00
Reception

TUESDAY,
MAY 24, 2016

7:00-8:00
Breakfast

SESSION 5: TESTING

Presiding: JOHN YAO

8:00

Combustion Products of Polymers at Constant Fuel/Oxygen Ratio in the Microscale Combustion Calorimeter

Richard N. Walters, Richard E. Lyon, Natallia Safronava and Louise Speitel, *Federal Aviation Administration, W.J. Hughes Technical Center, Atlantic City International Airport, NJ 08405, Richard.e.lyon@faa.gov*

When materials burn, the products of combustion depend on the chemical composition of the volatile fuel, the temperature of the combustion process and the availability of oxygen. Incomplete combustion leads to products that can be toxic or irritating to the respiratory system (CO, HCN, NO_x, unburned hydrocarbons, etc.) when inhaled and these are generated when the combustion temperature is low, radical scavengers are present to inhibit the gas phase reaction, or the oxygen concentration is insufficient to convert the fuel gases to complete combustion products (e.g., CO_2, H_2O, N_2 and mineral acids). The FAA's microscale combustion calorimeter (MCC) was modified to provide a constant fuel/oxygen mass ratio during the entire course of polymer thermal decomposition in a constant heating rate experiment and was connected to a Fourier transform infrared spectrometer (FTIR) for quantitative analysis of the combustion products. With this new capability, the combustion temperature and fuel/oxygen ratio can be separately controlled and the combustion products accurately measured for polymers, flame-retardants and flame retardant polymers. Results will be presented for the combustion products of a variety of materials generated at fuel/oxygen ratios ranging from fuel-lean to fuel-rich.

8:30

Rapid Mass Calorimeter

S. Rabe, B. Schartel, *Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany, Sebastian.Rabe@bam.de, Bernhard.Schartel@bam.de*

Modern flame retardant polymeric materials often stand for multicomponent systems consisting of different ingredients. Using a variety of flame retardants, fillers, additives, synergists and adjuvants as well as applying different concentrations, particle size distributions, encapsulation, and so forth lead to a vast multidimensional matrix of possible formulations. Actual, comprehensive elucidations are no longer possible due to time, material and cost limitations. The task is dying for accelerated procedures, for high-throughput methods. Therefore we developed the Rapid Mass Calorimeter based on a Mass Loss Calorimeter with attached thermopile chimney and a linear motion unit for semi-automatic sample change. Together with the reduction in specimen size (2 cm x 2 cm), a saving of time around 70% and a saving of material of 96% is achieved not considering the strongly reduced calibration and maintenance efforts required for the Mass Loss Calorimeter. The correlations between the results of the Rapid Mass Calorimeter and the Cone Calorimeter as well as to the Oxygen Index and UL94 classification are described; the effects such as when reducing the specimen size are discussed.

9:00
Combustion of Flame Retardant Compounds and Polymers in the Microscale Combustion Calorimeter

Natallia Safronava[a], Richard E Lyon[b], Richard N Walters[b;]
[a]Technology and Management International, LLC, 1433 Hooper Ave, Toms River, NJ 08753; [b]FAA, WJHTC Atlantic City International Airport, NJ 08405, natalia.safronava@faa.gov

The FAA's microscale combustion calorimeter (MCC) was modified to study gas phase combustion of polymers by adding CO and CO$_2$ analyzers to the standard O$_2$ analyzer and extending the combustor temperature capability to the lower-limit flame temperature (<1100°C). Previous work (BCC Conference, 2013) showed that bromine-containing compounds and polymers exhibited gas phase activity, as indicated by low oxidation rates of the volatiles in the combustor and the presence of carbon monoxide (CO) in the combustion products even at the highest temperatures. In contrast, phosphorus-containing polymers showed no gas phase activity by either of these measures. One explanation for these earlier results was that phosphorus remained behind in the solid residue (char) rather than entering the combustor (gas phase). In order to address this possibility, pure, low molecular weight organophosphorus compounds and flame-retardants spanning the entire range of P-oxidation states were completely volatilized into the combustor during the standard heating program. These organophosphorus compounds and flame-retardants had oxidation rates and product yields in excess oxygen that were typical of pure hydrocarbons—indicating little or no gas phase activity for phosphorus.

9:30
Standardized Fire Testing and Understanding Its Limitations

Matthew S. Blais, *SWRI, San Antonio, Texas, matthew.blais.swri.org*

Many standardized fire tests originate in the 1960's using old technology and are designed to measure specific properties. Due to their long history, these tests have been used by authorities having jurisdiction to make permitting decisions for years. Unfortunately some of these tests are misapplied and result in poor decisions for materials use. It is critical to understand the origin and correct application of standardized tests. In this presentation we will discuss the origins, strengths and weaknesses of Standardized tests such as ASTM E84, E162, and E662.

10:00
Coffee Break

Presiding: **MAURO ZAMMARANO**

10:30
Fire Tests Used for Regulation: Are We Testing the Correct Fire Property?

Tim Earl, *GBH International, tearl@gbhinternational.com*

Fire tests are used extensively for regulation. The process by which a fire test comes to be referenced in codes and regulation is fairly complex. The choice of which fire test to reference is influenced by many factors, including:

- Existing available test methods
- A desire to simulate the fire conditions the regulation is designed to address
- The limits of currently available technology
- The cost of the required test equipment
- The ability to quantify the test results in a manner which will be easily understood by users and regulatory officials.

As such, the actual fire property being measured in the regulatory fire test may not be intuitive. This paper consists of two parts: Part I will describe the different properties that fire tests can measure and the test methods which measure them. Part II will discuss fire safety regulations and which test methods are referenced, with some historical background of how those tests were chosen.

11:00
Use and Misuse of Steiner Tunnel Test for Building Products

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

The Steiner tunnel test, developed at UL in the 1940s to assess flame spread of traditional materials, has, in the ensuing decades been used to test multiple kinds of materials, for both flame spread and smoke development. The test is intended to provide comparative surface burning characteristics of materials (or the associated composite products).

Since the test is now used for products for which it was not designed, various ingenious techniques have been used to generate test results that are not within the spirit (and often not often within the words) of the standard. The result is the approval of materials without the corresponding fire safety.

The test was never expected to provide results for fire safety engineering (or fire hazard) calculations but it was expected to be used for regulatory purposes, and it still is used that way.

The original standard, ASTM E84, does not give mandatory details describing how materials or products need to be mounted for testing. In order to prevent misuse of the Steiner tunnel, three strategies have been used: (a) changing the wording in ASTM E84, (b) creating standard practices for specimen preparation and mounting of specific

materials and products, which are then referenced in ASTM E84 and (c) developing new tests with variations specific for some items.

Key changes to ASTM E84 wording include details on specimen width and thickness, mandates to use standard practices and minimization of the use of non-mandatory appendix guidance.

Standard practices have been issued for specimen preparation and mounting of many materials, including wall/ceiling coverings, water resistive barriers, pipe and duct insulation, wood products, site-fabricated stretch systems, reflective insulation materials, radiant barrier materials, vinyl stretch systems, tapes and caulks, sealants and various veneered systems.

Alternate test standards exist, as variations of the Steiner tunnel, that apply to various products for use in plenums (including wires and cables, sprinkler pipes, pneumatic tubing, plastic cable raceways and plastic water piping) as well as fire retardant treated wood and loose fill insulation.

This paper presents an update by discussing both the appropriate and inappropriate use of the Steiner tunnel and describing areas where work is still needed.

11:30

Testing Polymer Flammability by Microscale Combustion Calorimetry

Thomas Fabian, *Research Manager, Commercial & Industrial R & D, Distinguished Member of Technical Staff, UL, Northbrook, IL Thomas.fabian@ul.com*

A relatively new test method, microscale combustion calorimeter (MCC) is being used to characterize material flammability on milligram-sized test specimen. MCC's quantitative nature can provide unparalleled insight into the influence of polymer formulation on flammability characteristics. This offers an incredible advantage over other methods such as UL94 or Cone Calorimeter where required sample molding may also affect test results. As a result, MCC's quantitative nature coupled with small sample requirement can be used to more strategically design plastic compounds as well as easily determine continued production consistency and compliance.

12:00

Comparison of Materials Flammability Results Between Method A and B of the Micro-scale Combustion Calorimeter, ASTM D7309

Hsinjin Edwin Yang, *Pioneer Scientific Solutions, LLC*, Frederick P. Schall, *Deatak Inc, fred.schall@deatak.com;* T. Yang, I. B. Rufus, A. Paeglis, *GAF*

Recently, the Micro-scale Combustion Calorimeter (MCC) has been well developed to scientifically and quantitatively study polymer flammability characteristics such as: ignition temperature (T_i), combustion temperature, heat release rate (HRR), heat release capacity (HRC), and total heat of combustion (HOC). The standard test method—**ASTM D7309**—with two different test techniques, method A and method B, have been developed for the test methodology of the MCC. It is of great interest to study the

flammability behavior and flammability index (F_{index}) of materials applying MCC with the method A and B, and compare their results for high and low flammability.

The results showed that high flammability materials with method A have much higher value for most of the MCC results, e.g. T_i, h_c, HRR and HOC than with method B. The heat release capacity of method A is about two times higher than method B for the most high flammability materials. The flammability results displayed smaller differences between methods A and B for low flammability materials. The discrepancy of the MCC flammability results especially for high flammability materials between method A and B will be discussed in terms of the pyrolysis and combustion processes, and the degree of flammability.

12:30
Lunch

SESSION 6: SPECIFIC POLYMERS AND FLAME RETARDANTS

Presiding: STAS STOLIAROV

2:00
Flame-Retardant Epoxy Resins and Composites

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

This presentation provides a general overview about the application of phosphorus containing flame retardants with different chemical environment in epoxy resins. These compounds comprise in particular reactive phosphorus compounds, phosphorus containing salts as well as bridged and polymeric phosphorus additives. The efficiency of mainly gas phase and condensed phase active flame retardants will be compared in different neat epoxy resins and their reinforced composites. New efficient flame retardants and epoxy formulations for different applications will be introduced.

Reactive phosphorus compounds

Principally, phosphorus compounds can be incorporated in an epoxy network via the resin or the hardener [1]. In the first case this is realized also in industrial scale by the so-called preformulation wherein an epoxy resin reacts with reactive phosphorus compounds, bearing P-H- or OH-functionalities. On the other hand, P-containing diamines and novolaces have been synthesized as curing agents, and recently a first example has been commercialized. Changing the chemical environment around phosphorus the activity of the flame retardant can adapt to the requirements of the resin or the composite.

Phosphorus Containing Salts

Due to their good flame-retardant efficiency and minimal influence on the material properties of the matrix polymers phosphorus containing salts are widely used as flame retardant additives. Particularly aluminum salts of dialkylphosphinic acids and aluminum hypophosphite are commercially available flame retardants for thermoplastics as well as epoxy resins [2]. Melamine phosphinate, phosphonates and phosphates are described as additive flame retardants for epoxy resins and often used in synergistic formulations together with melamine polyphosphate, melamine cyanurate or aluminum hydroxide [3, 4]. Here we discuss the different flame-retardant efficiency and the melamine reactivity in epoxies and composites.

Bridged and Polymeric Phosphorus Derivatives

Compared to spherical monofunctional phosphorus compounds rod-like or star-shaped di- and multifunctional compounds have higher thermal stability depending on the chemical environment of the phosphorus atom, lower surfactant effect, and less migration [5]. This applies in particular for oligomeric and polymeric phosphorus compounds. The flame-retardant efficiency of bridged phosphorus compounds with different chemical environment around phosphorus in different neat epoxy resins and carbon fiber reinforced composites will be compared.

Recently, new phosphorus based oligomeric flame retardants, particularly suitable for resin transfer molding procedures, are commercially available and their efficiency as well their reactivity against epoxy resins will be discussed.

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[4] Neumeyer, T; Bonotto, G; Krämer, J; Altstädt, V; Döring, M; Fire behavior and mechanical properties of an epoxy hot-melt resin for aircraft interiors; Composite Interfaces 2013, 1-13

[5] Klinkowski, C, Wagner, S; Ciesielski, M; Döring, M; Bridged phosphorylated diamines: Synthesis, thermal stability and flame retarding properties in epoxy resins; Polymer Degradation and Stability 2014 (106) 122-128

2:30
Tailored DOPO-Based Flame Retardant Additives for Thermoplastics

Sabyasachi Gaan, Additives and Chemistry Group, Advanced Fibers, Empa Swiss Federal Laboratories for Materials Science and Technology, Switzerland, Sabyasachi.Gaan@empa.ch

The reactivity of 9, 10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide (DOPO) offers possibilities for its chemical modifications. Various P-C, P-O and P-N bonded DOPO derivatives have been synthesized and their compatibility with high temperature polymers like PA, PA66, PET and PBT has been evaluated. P-N and P-C bonded DOPO compounds have been found to be compatible with polyamides whereas P-O bonded DOPO derivatives were compatible with polyesters. This presentation will address suitability of such additives for engineering plastics and fiber applications. These additives are meltable, act as plasticizers in processing of thermoplastics and thus ensure good mixing however careful attention has to be paid to process parameters like humidity control and temperature of processing. With addition of such additives to above mentioned polymer one can achieve satisfactory mechanical and excellent flame retardant properties in UL 94 and other vertical burning tests.

3:00

Synthesis of Novel Phosphorus-Containing Compounds and Investigation on Flame Retardancy and Mechanism for Unsaturated Polyester Resin

Bihe Yuan, Ying Lin, Lei Song, Zhou Gui, Yuan Hu, *State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, China, yuanhu@ustc.edu.cn.*

Unsaturated polyesters (UPR) are widely used as resin components for composites in the field of transportation, electrical engineering and construction etc. However, typical UPR has very poor resistance to fire during burning with high smoke density because of its intrinsic chemical composition and molecular structure.

Aiming at overcoming the limitations and shortcomings of the present study of flame retardant UPR, a series of phosphorus-, nitrogen-, sulfur-containing and silicon-containing novel compounds were synthesized and well characterized, including additive and reactive types of flame retardants, by the method of the molecular design, on the basis of the latest research progress on the halogen-free flame retardant polymers.

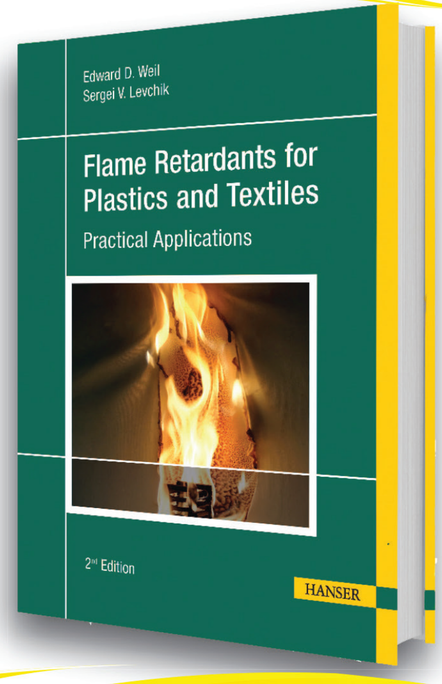
The synthesized additive and reactive flame retardants were incorporated into UPR by physical blending and copolymerization methods, respectively. Furthermore, some reactive flame retardant monomers were used as both diluting and crosslinking agent to substitute a portion of styrene in UPR. The thermal degradation and flammability behaviors of UPR composites and the flame retardant mechanism were investigated and discussed.

3:30

Flame Retardant Properties of Phosphonate Oligomers In Thermoset Applications

Lawino Kagumba, Morgan Pilkenton, *FRX Polymers Inc., Chelmsford, MA 02139, lkagumba@frxpolymers.com*

Oligomeric phosphonates can be used as non-reactive or reactive additives in a variety of thermoplastic and thermoset resins to impart good flame retardancy. In thermoset systems, the flame retardant and resulting product properties such as thermal, mechanical and electrical properties can be enhanced by reacting the phosphonate oligomers into the resin. In order to optimize these properties, the reaction and processing conditions of each system must be well understood. This session will highlight the reaction chemistry and processing conditions such as cure time and temperatures required to incorporate phosphonate oligomers into thermoset systems. Examples of studies will include unsaturated polyesters, epoxy resins and polyurethanes. Flame retardant performance and resulting properties of systems



containing phosphonate oligomers will be presented and compared to some of the commercial halogen-free flame retardant systems like resorcinol bis(diphenyl phosphate) (RDP) and fillers like Aluminum Trihydroxide (ATH). The combination of phosphorus and nitrogen-based flame retardant additives with phosphonate oligomers to improve processability and flame retardant properties will also be demonstrated.

4:00

Coffee Break

Presiding: ANTENNEH WORKU

4:30

Resin Properties as a Function of Ethane-1,2-bis(pentabromophenyl) (EBP) Particle Size

Rajeev Mathur, *Albemarle Corp, Baton Rouge, LA. rajeev.mathur@albemarle.com*

Ethane-1,2-bis(pentabromophenyl) (EBP) is a versatile flame retardant used in myriad polymer applications, ranging from automotive to consumer electronics to textile to wire and cable. Due to its high melting point, EBP behaves as a reinforcing filler, in addition to providing flame retardancy. For a non-melt blendable additive like EBP, the particle size distribution is critical in that there is an optimum range which provides the best performance while minimizing the potential for dust exposure in the compounding environment.

We present studies on how EBP's particle size distribution influences various resin properties. These include mechanical properties (IZOD, flexural, tensile), physical properties (MFI, color, gloss), electrical properties (dissipation factor, dielectric strength), and flammability (UL94, LOI), among others.

Based on these studies, we propose a particle size range best suited for general compounding of EBP as a polymer additive.

Presiding: CHUCK WILKIE

5:00

Introduction to the Poster Session

Each poster presenter (9 posters) will be allotted 2 or 3 minutes to highlight their poster.

5:30 – 7:30

Poster Session/Reception

P-1. Low-Flammable Expandable Polystyrene Foams Prepared Via Three Novel Flame-Retardant Adhesives

Zong-Min Zhu, Wang Liao, Ying-Jun Xu, Yu-Zhong Wang*, *Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemical Engineering, 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*

Three novel flame retardant adhesives were synthesized via a sol-gel method. Their chemical structures were characterized by Fourier transform infrared spectroscopy (FT-IR) and 1H, 31P NMR. Flame retardant expandable polystyrene foams (EPS) were prepared with the three novel adhesives. The flammability of EPS/FRs was investigated by limiting oxygen index (LOI), UL-94 vertical burning test and cone calorimeter (CC). EPS with 40% loading of flame retardant adhesives had a limiting oxygen index (LOI) of 27, and obtained the UL-94 rating V-0; its peak heat release rate (PHRR) decreased by 57.3%. A possible flame retardant mechanism was proposed. Furthermore, these low-flammable expandable polystyrene foams maintained their good mechanical properties.

P-2. A Flame-Retardant Polyester Blend Via Reactive Blending and Solid State Polymerization

Xue-Wu Yin, Xiu-Li Wang, Yu-Zhong Wang, *Center for Degradable and Flame-Retardant Polymeric Materials, College of Light Industry, Textile and Food Engineering College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials, Sichuan University, Chengdu 610064, China, yzwang@scu.edu.cn*

A polyester blend with high flame retardance was prepared by melt extrusion using phosphorus-containing PET-based copolyester (CPET) and a thermotropic liquid crystal copolyester TLCP(P_{10}PDT) in the presence of pyromellitic dianhydride (PMDA, a cross-link agent). The blend with the mass ratio of CPET: P_{10}PDT: PMDA=90: 10: 0.1 showed a LOI value of 30% and lower peak value of heat release rate. Due to the presence of PMDA, some cross-link reactions or transesterification between CPET and P_{10}PDT occurred, which was reflected by the torque rheometer, resulting in a good compatibility of CPET with P_{10}PDT. Besides, compared with neat CPET, the blend showed good crystallization, beneficial to its further application. TLCP has the potential to make the flame-retardant polyester bend fiber have high tensile strength due to its in *situ* fibrillation in polyester matrix during the process of fiber formation.

P-3. Phosphorus Containing Polyhedral Oligomeric Silsesquioxanes (POSSs) of Perfect T8 Caged Structures As Flame Retardants for Epoxy Resin

Zhi Qi, Wenchao Zhang, Xiangdong He, Rongjie Yang, *National Engineering Technology Research Center of Flame Retardant Materials, School of Materials, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, 100081 Beijing, P. R. China, yrj@bit.edu.cn*

Phosphorus containing polyhedral oligomeric silsesquioxanes (POSSs) of perfect T8 caged structures was designed as a new class of flame retardant. Phosphorus containing POSS combine several advantages from phosphorus based flame retardant and nanostructure inorganic-organic hybrid materials. Three phosphorus containing POSSs were synthesized by the addition reaction of octa vinyl POSS with diphenylphosphine (DPP), diphenylphosphine oxide (DPOP), and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), respectively. The impact of DPP-POSS, DPOP-POSS, and DOPO-POSS on the pyrolysis and fire behavior of an epoxy resin (DGEBA/DDS) were investigated under temperature programmed heating (TGA-FTIR), forced flaming conditions (cone calorimeter) and small flame conditions (LOI and UL-94). The flame retardant performance and mechanisms of DPP-POSS, DPOP-POSS, and DOPO-POSS were assessed and discussed in detail based on TGA-FTIR, XPS, and FTIR. The main flame retardant activity of DPP-POSS, DPOP-POSS, and DOPO-POSS are in the especially strong condensed phase activity through charring and intumescence due to the synergistic between phosphorus and silicon in these POSSs.

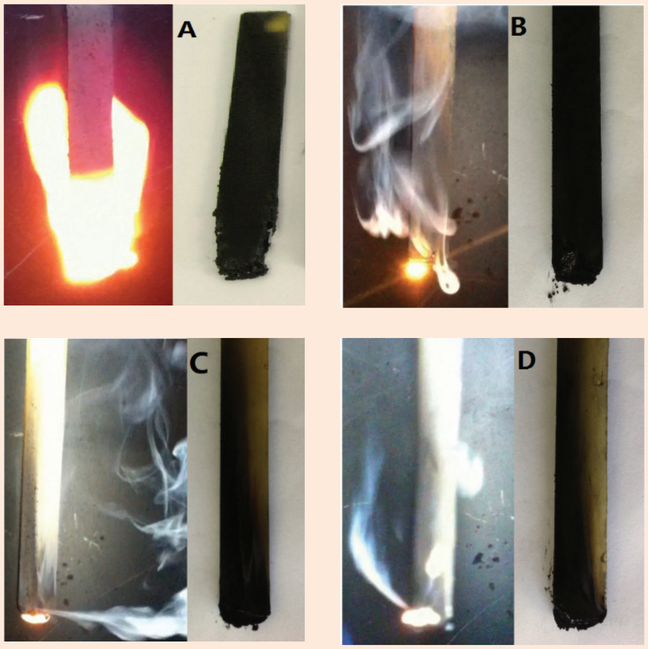


FIGURE 1 Video screen shots and photos of bars after UL-94 test of Pure EP (A), EP/DPP-POSS (B), EP/DPOP-POSS (C), and EP/DOPO-POSS (D).

TABLE 1 FLAME RETARDANCY OF EP COMPOSITES.

			LOI (%)	UL-94 (3.2 mm)	$^{t}1$(s)	$^{t}1$(s)	Dripping
Pure EP	0	0	23.0	NR	>30	/	Yes
EP/DPP-POSS	0.52	0.58	33.2	V-0	6	3	No
EP/DPOP-POSS	0.50	0.55	29.3	V-1	25	5	No
EP/DOPO-POSS	0.47	0.52	30.0	V-1	20	5	No

P-4. Isosorbide bis-Acrylate as a Source of Phosphorus Flame Retardants

Yoseph G. Daniel and Bob A. Howell, *Science of Advanced Materials, Center for applications in Polymer Science, Department of Chemistry and Biochemistry, Central Michigan University, Mt. Pleasant, MI, 48859-0001, danie1yg@cmich.edu*

The increasing concern about the potential negative health effects of traditional organohalogen flame retardants have placed these compounds under increasing regulatory pressure around the world. There is a growing need to develop new, nontoxic, biocompatible or biodegradable flame retardant agents. Phosphorus compounds derived from renewable biosources offer great potential to meet this need. Isosorbide is a dihydroxy ether available from starch. It may be readily converted to the corresponding bis-acrylate ester. This compound undergoes Michael addition of phosphites to provide a number of phosphorus compounds which display good flame retardancy (LOI, PCFC, UL94) in DGEBA epoxy.

P-5. Thermal Degradation Mechanism Development for Multi-Constituent Polymer-Based Systems with Chemical Interactions

Yan Ding [1], Stanislav I. Stoliarov [1], [1] *Department of Fire Protection Engineering, University of Maryland, College Park, MD, USA; yanding@umd.edu*

A systematic methodology has been developed to obtain the reaction kinetics and thermodynamics of the thermal degradation of solid polymeric materials. This methodology has been successfully applied to multiple neat polymers. This study extends this methodology to multi-constituent systems with chemical interactions. The studied materials include three neat materials (Polylactic Acid (PLA), Ammonium Polyphosphate (APP), Melamine (MEL)) and their blends. A comprehensive pyrolysis model (ThermaKin) was utilized to obtain reaction kinetics, thermodynamics, and heats of combustion of gaseous products by conducting inverse analyses on the data collected through the Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Microscale Combustion Calorimetry (MCC). Each neat material was individually parameterized to build a thermo-kinetic reaction mechanism. Subsequently, these three reaction mechanisms were merged together and additional reactions were incorporated into this merged mechanism to capture the interactions between the constituents of the blends. This methodology may enable us to intelligently design multi-constituent fire-resistant materials that meet the specific flammability requirements while significantly reduce the material manufacturing and experimentation cost

P-6. Functionalization of Graphene Oxide with Phosphazene Flame Retardant and Ni(OH)2 Nanosheets for Improving Flame Retardancy of Polypropylene

Bihe Yuan[1],[2], Lei Song[1], Kim Meow Liew[2], Yuan Hu*,[1]. [1] *State Key Laboratory of Fire Science, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, P. R. China. yuanhu@ustc.edu.cn; yuanbh@mail.ustc.edu.cn.* [2] *Department of Architecture and Civil Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong.*

Graphene has captured enormous attention in the area of polymer nanocomposites, due to its impressive properties. Many studies have demonstrated that effective dispersion of bare graphene in polyolefin is challenging, due to the marked discrepancy in polarity and compatibility. The functionalization of graphene with nanomaterials or organic modifiers has been proven to be an effective approach to improving its dispersion in polymers. Graphene provides a platform for anchoring foreign nanomaterials because of its two-dimensional structure and high surface area. It is of great importance to modify the surface characteristic of graphene, proving more active sites for the loading of nanomaterials. As with other two-dimensional nanomaterials, graphene has also been developed to reduce fire risk of polymers. However, flame retardant effect of the virgin graphene is not marked. To improve flame retardant property, the issue of graphene (oxide) dispersion must be addressed and the functionalization of graphene (oxide) with flame retardant moiety is preferred.

In this work, to improve the dispersion and flame retardant efficiency, graphene oxide was modified with a phosphazene flame retardant and $Ni(OH)_2$ nanosheets. The removal of oxygen functional groups of graphene oxide and grafting of flame retardant are achieved synchronously. Phosphazene materials are a class of high performance flame retardant, due to the synergistic effect between phosphorus and nitrogen. The NH_2 groups in this phosphazene flame retardant shows strong affinity to Ni^{2+} and thus the decoration of $Ni(OH)_2$ nanosheets is enhanced. The effect of functionalized graphene oxide (FGO) on the combustion property of polypropylene is investigated and the enhancement mechanism is clearly demonstrated.

P-7. Properties and Characterization of Two Flame Retardant Poly(butylene terephthalate) Compounds

David A. Schiraldi, Kimberly DeGracia, *Department of Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, OH 44106, USA, kcd27@case.edu*

Poly(butylene terephthalate) (PBT) is a polyester produced in high volume and is used in the electrical, electronics, and automotive industries. These applications require flame retardant (FR) PBT systems, but the most commonly used contain bromine and an antimony source which are known to cause health and environmental complications. In addition, PBT poses technical challenges as it depolymerizes and dehydrates to butadiene at fire temperatures, giving off flammable gas.

We have investigated two FR PBT-based compounds found in industry. The compositions, mechanical and thermal properties, and flammability performances were studied. These experimental parameters were compared to those reported by industry. Oven-aging studies are currently being conducted to determine the change in mechanical and thermal properties, crystallinity, and flammability of the FR systems. We hope that these studies will aid in the ongoing research to develop alternative non-halogenated FR systems that are effective and can be produced in high volume.

P-8. The Contrastive Study on the Gas Pyrolysis and Condensed Phase Structure of Different PC /POSS Composites

BaoFa Cheng, XiangMeiLi*, WenChao Zhang, JiangWeiHao, RongJie Yang, *School of MaterialScience and Engineering, Beijing Institute of Technology, National Engineering Research Center of Flame Retardant Material, Beijing 100081, China, bjlglxm@126.com, Tel.:+86 10 68943961*

Polyhedral Oligomeric Silsesquioxane containing 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS), octaphenyl polyhedral oligomericsilsesquioxanes (OPS) and Polyphenylsilsesquioxane (PPSQ) were synthesized by our lab. 4 wt% DOPO-POSS and 6 wt% OPS were mixed with PC by the twin-screw extruder to prepare the composites. The pyrolysis product analysis of PC/DOPO-POSS and PC/OPS composites was measured by Py-GC/MS, FTIR and SEM-EDS were used to analyze the condensed phase structure and element components of the char residue. The results of Py-GC/MS show that OPS release amount of gaseous phase of benzene and SiO_2. DOPO-POSS has a complicated pyrolytic process compared with OPS, and the main pyrolysis product of DOPO-POSS is DOPO which can reaches 26wt%. The total mass spectrum shows that PC/DOPO-POSS and PC/OPS composites release amounts of micromolecule gaseous products during the pyrolysis process, and those micromolecule gaseous products swell the char during the combustion. In the aspect of condensed phase, the results of FTIR show that the internal char residue structure of PC/DOPO-POSS and PC/OPS are both composed of inorganic carbon. The external char residue structure of PC/DOPO-POSS contain amount of -P (=O)-O-Si- and a little of Si-O structure. The external char residue structure of PC/OPS contain amount of -O-Si-O- structure and a little of polyaromatic carbons and Si-C structures. The analysis of SEM-EDS indicates that the char residue of PC/DOPO-POSS composite is composed of C, O, Si and P elements, and the char residue of PC/OPS composite is composed of C, O, and Si elements.

TG-FTIR result indicates that PPSQ make the initial thermal decomposition of PC happen fast and slowly in the next moment, and evolving gaseous products during the pyrolysis and infrared spectrums such as CO_2, ester groups, aromatic components and isopropyl groups are found. Py-GC/MS results show that more micromolecule gas products are released than that of PC, which is beneficial to create an intumescent and firm char layer. FTIR analysis indicates that the condensed phase structure of PC/PPSQ composite are composed by Si-O, C=O and Si-C. EDS shows the condensed phase of char residue is composed by C, O and Si, and large amount of Si existence in the char layer shows that PPSQ promote molten PC cross-linking and charring fast.

P-9. Thermal Properties and Flammability Performance of Polymer Composites with Carbon Nanotubes-Layered Compound Hybrids

Hongdian Lu, Benghong Yang, Wei Yang, Hongyan Xie, *Department of Chemical and Materials Engineering, Hefei University, Hefei, Anhui, 230601, P. R. China; *Corresponding author E-mail: hdlu@ustc.edu.cn; Tel: 86-551-62158393*

** This work was supported by National Natural Science Foundation of China,Youth Science Found project (No.51303011), Basic Research Foundation of Beijing Institute of Technology (No.20130942002)*

Nanohybrids of carbon nanotubes and layered double hydroxides (CNTs-LDHs) have been successfully fabricated through liquid phase methods. The structural characterization and morphological observation demonstrated that the nanohybrids could display various hetero-structures. The influence of CNTs-LDHs on the thermal stability and flammability performance of polymers including polyurethane and poly(ethylene-co-vinyl acetate) were studied. It was established that incorporation of CNTs-LDHs could enhance fire safety properties of the materials, including the improved thermal stability, flame retardancy and smoke suppression properties. The mechanisms of the flame retardancy for the materials were discussed.

WEDNESDAY, MAY 25, 2016

7:00-8:00

Breakfast

Presiding: **KELVIN SHEN**

8:00

Carbon Nanotubes for Innovative Eco-Friendly Flame Retardant Solutions

D. Bonduel, M.Hurtgen, A.Rul and M. Claes, *Nanocyl S.A, rue de l'essor 4, Sambreville 5060, Belgium. E-mail: michael.claes@nanocyl.com*

Literature has reported many times 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 Re¬tardant (FR) polymer solutions to foresee those modifications of regulations.

In collaboration with different partners (within EU granted DEROCA project), Nanocyl has built a great know-how leading to solutions for fire resistant thermoplastics. In the last development, novel approach using design of experiment (DoE) has been undertaken to satisfy on multifunctional performances for market oriented solution including commodity application.

The developments using this DoE approach show clear synergism between some conventional flames retardant such as metal hydroxide or phosphorus based compound. In addition to the

good flame retardant behavior, other key performances such as mechanical, electrical properties could be enhanced. Successful case studies will be shown to address those technical successes in the field of Wire & Cable, industrial tubes and molded parts.

ACKNOWLEDGMENT
The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n°308391

8:30

Natural Synergist Additives for Halogen-Free Fire Retardant Systems

Julio Santaren and Antonio Esteban, *TOLSA, Madrid, Spain, aesteban@tolsa.com*

Last generations of flame retardants, especially halogen free solutions, have demonstrated a better performance compared to former solutions, limiting the fire propagation and reducing the heat and smoke release. However, new and more restrictive regulations represent a new challenge for the present technologies.

ADINS is the trade name for a range of synergistic additives for FR based on ultrafine organically modified natural silicate with a needle-like morphology (sepiolite). Its special structure provides a synergistic effect with most of the flame retardant systems. These additives strongly boost the char formation, and improve its properties during combustion, thus protecting the polymer from further fire propagation. In particular, ADINS additives have proved to be very effective in halogen-free fire retardant (HFFR) systems.

In this presentation, the results of these additives in combination with two of the most frequently used HFFR systems (metal hydroxides and intumescent FR) in two different polymer systems (EVA and PP) are shown.

ADINS in percentages of as low as 3% in combination with ATH in EVA leads to a significant decrease of the peak of maximum heat release rate (PHRR), compared to pure ATH. It also delays the fire propagation, and reduces smoke production. Furthermore, this additive shows an antidripping effect, most likely due to its needle-like morphology.

The addition of 2% ADINS to PP flame retarded with a typical APP intumescent system allows to improve the UL-94 rating from V-2 to V-0. ADINS improves the stability and mechanical properties of the intumescent char layer and, as a consequence, the smoke production is significantly reduced.

In summary, ADINS synergistic additives in combination with different HFFR provide a more solid char with much better mechanical properties which decreases flame propagation, avoids polymer dripping, and significantly reduces smoke production.

SESSION 7: COATINGS

Presiding: MARCELO HIRSCHLER

9:00

Novel Dynamic Method for Evaluating the Char Strength of Intumescent Coatings

Serge Bourbigot, Anil D. Naik, Sophie Duquesne, *R_2Fire group/UMET - UMR CNRS 8207, Ecole Nationale Supérieure de Chimie de Lille (ENSCL), Avenue Dimitri Mendeleïev - Bât. C7a, CS 90108, 59652 Villeneuve d'Ascq Cedex, France*

Intumescent coatings is a method of passive fire protection. Their main purpose is to protect construction materials such as steel and wood, in case of fire. The result of the intumescence process is a foamed cellular charred layer on the surface which protects the underlying material from the action of the heat flux or the flame. 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). A significant aspect of intumescent formulations is the mechanical strength of the intumescent char. In the conditions of a fire, char destruction can proceed not only by means of ablation and heterogeneous surface burning but also by means of an external influence such as mechanical action of the fire or convective air flows. Mechanical strength of char is generally estimated after fire testing at room temperature by empirical methods (e.g. finger touch, piston rod …) and also using a rheometer as a function of temperature thanks to a method developed in our group. Nevertheless, it has never been measured in real dynamic conditions (fire conditions) while it is a crucial parameter determining the performance of the intumescent char.

In this talk, a novel dynamic protocol for measuring the char strength of intumescence coating during fire testing will be presented. It was done at a reduced scale in a furnace fitting the ramp of temperature of a hydrocarbon fire (UL 1709) and cellulosic fire (ISO 834). The furnace is equipped with an air-jet system delivering hot air flow simulating air turbulence circulating around char or fluid impacting the surface of the char. This new concept of testing char strength during fire test gives two criteria: (i) examination of char fragments during air jet and (ii) time to reach 500°C when the char is subjected to airjet (it gives an indirect measurement of char strength). Commercial intumescent coatings and novel intumescent silicone-based coating will be examined using the airjet test and the behavior of the coating will be discussed.

9:30

A Simple Engineering Fire Performance Model for Intumescent Fire Retardant Coatings

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This paper presents an engineering practical model to predict the fire performance of Intumescent Fire Retardant (IFR) coatings by applying them to a 5.0 mm inert steel substrate in Cone Calorimeter experiments. The IFR coating layer (about 100μm thick) is thermally


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thin and the char layer formed by its expansion has negligible heat capacity. The proposed simple model, compared with existing models, eliminates the requirement for determination of numerous expansion parameters and thermal properties for the IFR coating and its ensuing char. Instead, to represent the thermal and insulation behavior of the expanding IFR coating the model shows that the ratio of the heat flux imposed on the surface of the expanding char to the heat flux received by the substrate is a function of height of the expanding char. In addition, the expansion height is expressed as a function of the mass loss of IFR which is obtained based on the degradation of the thermally thin IFR coating as a function of its temperature where the mass degradation rate equation is obtained from TGA measurements of the intumescent coating. The accuracy and robustness of the model are validated by comparing its predictions with Cone Calorimeter experiments for two IFR coatings under three heat flux levels each.

10:00
Coffee Break

10:30
Silicone-Based Backcoating for Smoldering and Open-Flame Resistant Upholstered Furniture

Mauro Zammarano[§], Valeria Cazzetta[*§], Shonali Nazaré[§], J. Randy Shields[§], Yeon Seok Kim[§], Alfonso Maffezzoli[*], Rick Davis[§], [§] *Flammability Reduction Group, Engineering Laboratory, National Institute of Standards and Technology, USA. * Dept. of Engineering for Innovation, University of Salento, Italy, mzam@nist.gov*

Upholstered furniture (UF) is the single largest cause of deaths (about 18%) in U.S. residential fires. Of the 6,300 UF fires, about half are initiated by a smoldering source (e.g., cigarette) and the other half by an open-flame source (e.g., candle). Thus, a reduction in the residential fire hazard requires UF that is both smoldering and open-flame resistant.

This is a challenging problem because in carbon-based polymers commonly used in UF (e.g., textiles and polyurethane foams) there is generally a trade-off between smoldering and open-flame resistance: a flame retardant that reduces the flammability by promoting charring reactions will also likely promote smoldering.

Halogenated flame retardants can be effective in reducing the smoldering and open-flame hazard of UF. However, concerns about the potential environment and health safety of some halogenated compounds have caused the market/community to look for alternative approaches to improved fire safety.

This talk will discuss environment, health, and fire safe silicone-based coatings that drastically improve the open-flame and smoldering resistance of UF covering fabrics. In a single step, the coating is applied to the back side of dry cover fabrics (e.g., by knife coating at lab scale). The coating has no noticeable impact on the fabric color, hand or general appearance. The fabrics and the coatings remain flexible and durable to normal end-use wear and tear. The backcoated fabrics show excellent open-flame and smoldering resistance in component and composite fire testing. Compared to the multi-layer approach (cover fabric, polyester batting and a fire blocking barrier fabrics) currently considered in UF, the backcoated fabric could drastically simplify the manufacture process of UF and provide a higher level of ignition resistance.

SESSION 8: PHOSPHORUS

11:00
Pushing the Limits—Recent Advances with Phosphorus-Based FRs

Volker Butz, Kyle Mitchell and Jérôme De Boysère,
Thor Specialties Inc., 50 Waterview Drive. Shelton, CT 06484, jdb@thor.com, kmitchell@thorsp.com

Building on more than 30 years expertise in phosphorus chemistry and flame retardants (FRs) for textiles, Thor (www.thor.com) has in recent years developed an extensive range of non-halogenated FRs dedicated to plastics applications.

The paper will review the latest innovations involving the Aflammit PCO range of phosphonate based FRs (REACh and TSCA registered new substances) and their synergistic combinations with particular radical generators, which are distinguished by an unsurpassed FR performance, similar or higher than traditional halogenated solutions.

In a second part, the paper will introduce the latest developments in the growing family of intumescent FRs marketed under the Aflammit PPN trademark, highlighting new grades for extrusion or injection molding applications (mainly designed for PP and Thermoplastic Elastomers). Besides thermoplastics, the presentation will also briefly address special grades developed for thermosetting resins and gelcoat applications

11:30
A Rigid Phosphate Plasticizer and Flame Retardant

Kai Huang, Qiang Yao, *Department of Polymer Composites, Ningbo Institute of Materials, Technology and Engineering, CAS, Ningbo, Zhejiang 315201, P.R.China, yaoqiang@nimte.ac.cn*

With the increasing complexity and miniaturization of electronic parts, both low viscosity of polymer melts and good thermal property are critical. Phosphate flame retardants have difficulty to achieve good balance thus far. In an effort to harmonize these two drastically different properties, a phosphate (PDP) possessing both a flexible and a special rigid structures was synthesized. It was tested in polycarbonate and the results were compared with those obtained by resorcinol bis(diphenyl phosphate) (RDP). At a similar low phosphorus loading, both PDP and RDP achieved excellent flame retardancy. However, there was a remarkable difference of the viscosity performance with temperature. At a temperature below 180oC, the viscosity of PC/PDP was closer to that of PC and was much higher than that of PC/RDP. The former also had a higher value of HDT. At high temperatures, although the viscosities of both PC/PDP and PC/RDP were lessened, the degree of reduction of viscosity of PC/PDP was more than that of PC/RDP. The melt index of PC/PDP was also higher than that PC/RDP. In contrary to RDP, PDP showed the ability to retain the good thermal property while dramatically improving the processability of PC.

12:00

Formulation of Flame Retardant Aliphatic and Semi-Aromatic Polyamide Compounds

Timothy Reilly, *Clariant Plastics and Coatings, Charlotte, NC USA, timothy.reilly@clariant@clariant.com*

Polyamides are a versatile engineering plastic used in a growing number of applications including automotive. This presentation will cover the performance properties of halogen-free flame retardants used in the commercially important grades of aliphatic and semi-aromatic polyamides. Compound performance properties, new developments and future opportunities will be discussed. The latest developments from Clariant concerning aluminum phosphinate will also be reviewed.

12:30

Bio-Based FR of Polyethylene & Polypropylene

David A. Schiraldi, Taneisha Deans, Yuqin Li, *Department of Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, OH 44106, USA. das44@case.edu*

Flame retardation of polyolefins, such as polyethylene and polypropylene (PE and PP), usually relies upon inorganic additives, which can negatively impact processability and mechanical properties of the materials, and in many cases requires high loadings. Taking a page from nature, we have identified renewable families of materials which can be directly harvested from agriculture, can be compounded into PE and PP under normal processing conditions at modest levels, and which provide UL(94) V(0) self-extinguishing behavior, with little impact upon processing or mechanical properties. The compositions, mechanical and flammability performances, and initial thoughts on mechanisms of action will be presented.

1:00

Conclusion of the Meeting

CHUCK WILKIE

1:15

Boxed Lunch To Go

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