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Monday, May 20, 2013

8:00 Chuck Wilkie welcome

Chairperson: Charles Wilkie

Session 1 – Industry and Academics

8:15 Closing the Loop in the FR Community (Pulling the Same Rope Instead of Pushing It)...... 1

James T. Daly,
Business Development Manager, Spartech Color and Specialty Compounds, 11650 Lakeside Crossing Ct., Maryland Heights, MO 63146, Phone/Mobile: 484-951-2557, Office: 314-569-7435, email: jim.daly@spartech.com

This paper will address the needs of the commercial flame retardant production community, compounders, and our relationships with the FR ingredient manufacturers and the academic FR community. BCC is, primarily, an academic conference and has been, traditionally, lightly attended by compounders. It will be my goal herein to build a bridge between these facets and begin a dialogue that gets all parties pulling the rope in the same direction.

Academic conferences are long on theory and statistics, but frequently short on answers to questions that are being asked on the front lines. This makes sense as the academic community is typically insulated from OEM's by the chemical companies and compounders. How do we get the best and brightest creative minds working on the solutions being sought by OEM's? What are the current demands of the FR market going unanswered? The following will be given as examples: The flame-retardant pallet market, FR-UV additives for foamed HIPS in high heat/UV environments, industry standards for the measurement of environmental health-safety, the future of bromine-based FR's, non-halogenated FRs and improved efficiency and cost and performance – effective tests and measurements.

Session 2 – Fire Safety and the Media

8:45 Toxic Gas Evolution from Foam Filled Furnishing Fires: How do Fire Retardants affect the toxicity of smoke? 2

Matthew Blais, Southwest Research Institute, San Antonio, TX. Ph: 210-522-3524. Email: matthew.blais@swri.org

A series of Fire Tests were performed using FR and non FR Foam with and without FR covering fabrics. An ISO Room test was used to measure heat and smoke evolution and the room was sampled with a 2 M gas cell on a Thermo-Fischer FTIR every 15 minutes over the duration of the burn and after the fire had been extinguished. This presentation presents the data and analysis from these experiments with the objective of determining how FR protected materials affect the toxicity of smoke as well as gain additional information on the impact FR on flame spread in foam filled furnishings.

9:15 Fire safety and flame retardants 13

Marcelo M. Hirschler, GBH International, 2 Friars Lane, Mill Valley, CA, 94941, US

In recent years flame retardants have been subjected to a well-organized and persistent public attack in the media. A key area of unfounded criticism is the assertion that flame retardants do not have a significant effect on fire safety. This work will examine the relevant published scientific data on the subject to make an unbiased and technically valid determination of the effectiveness of flame retardants in improving fire safety. The data clearly shows that flame retardants very effective in a variety of areas, including many consumer products (such as upholstered furniture, mattresses and appliances) and building products (such as wall and ceiling linings, insulation and electric cables). In some cases, the use of flame retardants is enough to ensure that ignition does not occur. However, when the proper level of flame retardants is used (to meet an adequate level of fire performance), even if ignition occurs, fire hazard is significantly lowered by decreasing heat release, flame spread and smoke release and, most importantly, time available for escape. Public safety requires that flame retardants remain available as an effective tool for increasing fire safety.

Session 3 – Biopolymers

9:45 **Flame retardancy of stereocomplexed polylactide: processing, characterization and reaction to fire 40**

SERGE BOURBIGOT, ANTOINE GALLOS ET GAËLLE FONTAINE
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

Polylactide (PLA) is synthesized from renewable resources and currently deserves a particular attention in the area of environmentally degradable polymer materials. PLA has good mechanical properties, thermal plasticity and biocompatibility and is thus a promising polymer for various end-use applications (mainly packaging and fibers). Manufacturers expect some durable applications for PLA with targeted applications including electronic, electrotechnic, transportations, etc…. Nevertheless, the major part of these applications requires improvements of the properties of the PLA, like crystallinity, enhanced thermal properties (melting temperature …), etc which cannot be reached by PLA. It can be achieved by the stereocomplexation of L-lactide and D-lactide to make thermally improved polylactides. Stereocomplexed PLA (scPLA) will be prepared by a solvent-free process and in a continuous way by reactive extrusion. It is thus an efficient and ecofriendly way to product polylactides. The resulting material will be fully characterized. In numerous applications of polylactides, flame retardancy is required. Intumescence is a method to provide flame retardancy to polymers and it will be investigated for scPLA. The intumescent additives are incorporated during reactive extrusion and the resulting material is an intumescent scPLA. Reaction to fire of the intumescent scPLA will be examined and discussed in the talk.

10:15 **Improving the fire behavior of biocomposites by fiber surface modification 48**

L. Ferry, G. Dorez, A. Taguet, B. Otazaghine, R. Sonnier, J.M. Lopez Cuesta, *C2MA Material Research Center, Ecole des Mines d'Alès, 6 Av. de Clavières 30319 Alès Cedex (France)*

Biobased materials generate a growing interest in numerous industrial fields (building, transportation, electric equipment…). In these applications, fire performance is a major requirement that limits the use of new materials. The flammability of biopolymers has been investigated by some authors during the last five years. Most of the works have been focused on polylactic acid (PLA) which is the most available biopolymer. Flame retardants tested in PLA involved essentially intumescent systems and/or nanofillers. In sectors where structural properties are needed, biopolymers can be reinforced by natural fibers to offer a green substitution of traditional composites. Only few papers deal with flammability of such biocomposites.

In this work, the fire behavior of biocomposites based of polybutylene succinate (PBS) reinforced by various lignocellulosic natural fibers (cellulose, flax, hemp, bamboo and sugar cane) has been investigated. The improvement of fire behavior by fiber surface modification has been studied on flax fibers using different phosphorous molecules. The reactivity between surface modifiers and the various components of the fiber has first been evaluated using various analytical methods. Then, the flammability of surface treated flax biocomposites has been investigated by microcalorimetry and cone calorimetry.

10:45 – 11:15 COFFEE BREAK

Chairperson: Martin Klatt

11:15 **Synthesis of chitosan derivative flame retardants and their application 53**

Yuan Hu*, Lei Song , State Key Laboratory of Fire Science, University of Science and Technology of China, 96 Jinzai Road, Hefei, Anhui 230026, PR China Tel./fax: 86 551 3601664. E-mail address: yuanhu@ustc.edu.cn.

In recent years, the natural polysaccharide materials have motivated great interest in the flame retardant field owning to their environmental friendliness, abundant yield and low cost. In our study, chitosan has been chosen to synthesize some novel natural resources based flame retardants and study their effect on thermal and combustible properties of polymeric materials. Some chitosan derivative flame retardants, melamine chitosan phosphate (MPCS) and Nickel chitosan phosphate (NiPCS), have been synthesized and applied into polymer. The results from MCC indicated that both the peak heat release rate (PHRR) and the total heat release (THR) were reduced after introducing MPCS or NiPCS. Thermogravimetric analysis exhibited that the addition of MPCS or NiPCS enhanced the thermal stability of the char residue at high temperature as well as the char yield at 700 ^{o}C. RT-FTIR data confirmed that the chitosan-based flame retardant could promote the dehydration effect as well as accelerated the char formation.

11:45 **Flame retardation of glass fiber reinforced PLA/PC composites 54**

Ling Lin, 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 Tel.& Fax: +86-28-85410259

Poly (lactic acid) (PLA), a bio-based polymer that can be derived from renewable sources, has a great potential to replace conventional petrochemical-based polymers in some fields. In order to widen its applications as engineering plastics, minor component polycarbonate (PC) was blended together with glass fiber (GF) to prepare glass fiber reinforced PLA/PC composites. The mechanical tests showed that the glass fiber reinforced PLA/PC composites had much higher tensile strength, flexural strength, flexural modulus and notched Izod impact strength than PLA. In order to improve the flame retardancy of the multi-component system, some halogen-free flame retardants were used to prepare the flame-retardant composites with maintaining good mechanical properties. This presentation will report the flammability and thermal decomposing behavior of the composites that were evaluated by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimeter and thermogravimetric analyzer.

Session 4 – Instrumentation

12:15 **FTIR-PCFC coupling: A new method to study the combustion of polymers** 66

R. Sonnier[1*], G. Dorez[1], H. Vahabi[2], C. Longuet[1], L. Ferry[1]
[1] *CMGD Material Center, Ecole des Mines d'Alès, Alès (France)*
[2] *Laboratoire MOPS,CNRS UMR 7132,Université de Lorraine, Saint Avold (France)*

The analysis of gases released during the thermal degradation of a polymer is usually performed by two well-known methods, namely thermogravimetric analysis (TGA) coupled to FTIR and cone calorimeter coupled to FTIR. Nevertheless, the former method allows analyzing gases released during pyrolysis without further combustion: TG analysis is generally performed under nitrogen flow. Even if oxidative pyrolysis could be carried out, the polymer is degraded at relatively low temperature (most often lower than 500°C) and combustion does not occur. FTIR-cone calorimeter coupling allows analyzing gases after combustion but this combustion is not controlled. Combustion efficiency is generally close to 1 (complete combustion) except when flame inhibitors are incorporated into the polymer.

Pyrolysis-Combustion Flow Calorimeter (PCFC) has two main differences compared to these both techniques. First pyrolysis and combustion are well-separated phenomena in this apparatus. Second, combustion conditions could be precisely monitored to obtain a more or less complete combustion[1]. In this work, we have equipped our PCFC with a FTIR spectroscopy apparatus. To the best of our knowledge, no such coupling has been tested yet. The preliminary results allowed detecting several gases: CO, CO_2, CH_4, HCl, HCN, NO, N_2O, NO_2, C_2H_2, C_2H_4, acetaldehyde… The presence of these gases versus the combustion temperature has been investigated for various virgin and flame retarded polymers. The role of flame inhibitors has also been pointed out.

[1] R. Sonnier, B. Otazaghine, L. Ferry, J-M. Lopez-Cuesta, *Monitoring the combustion efficiency in Pyrolysis Combustion Flow Calorimeter (PCFC) – Correlation with Cone Calorimeter*, BCC 2012, Stamford

LUNCH 12:45 – 2:00

Chairperson: Charles Manzi-Nshuti

2:00 **Modifying Cone Calorimeters for Testing Materials with Low Heat Release Rates 69**

Tim Earl, GBH International, Sean Gregory, Sandra Pasantes, Andrew Green, FTT Ltd, Stephen J Grayson, Suresh Kumar, Interscience Communications Ltd

The cone calorimeter was designed to measure heat release from combustible materials such as wood plastics and building products. These typically have peak heat release rates (HRR) of 250- 2000 kW/m^2. Traditionally, the results have been either used directly or as data for flame spread and other numerical models.

More recently, some nations have issued standards and regulations which use HRR as measured in the cone. Some of the performance criteria specified in these new regulations are so low as to be within the currently allowable noise and drift levels of the instrument.

A recent study identified three methods which could be used to improve upon noise and drift and make the cone calorimeter a more appropriate tool for low heat release measurements:

- **Reduce analyzer noise and drift by specifying a lower performance requirement**
- *Tighten laboratory practice to remove interfering influences*
- ***Increase the oxygen depletion levels (for example by using a larger cone heater)***

This paper identifies improvement areas in all of the above areas but will focus on primarily on increasing oxygen depletion levels. A recent development in that area is the use of a larger cone heater which gives a uniform heat flux over the whole surface area of a much larger (150 x 150mm specimen). This paper will discuss the larger cone heater in more detail.

2:30 **Effect of Moisture on Ignition Delay of Polymers...... 78**

Natallia Safronava[a], Richard E. Lyon[b], Sean B. Crowley[b], Stanislav I. Stoliarov[c]
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A previous study of poly(arlyether-ether-ketone) (PEEK) showed that the ignitability of this high temperature engineering plastic is sensitive to the presence of absorbed moisture. The present research extends this work to include five other engineering plastics: polycarbonate (PC), polyoxymethylene (POM), polyethyleneterephthalate (PET), polyphenylsulfone (PPSU) and polyhexamethyleneadipamide (PA66). Separate batches of each polymer were conditioned in boiling water (hot/wet), 50% relative humidity (ambient), or vacuum oven (dry) environments and tested in a cone calorimeter at heat fluxes between 20 and 70 kW/m^2. The hygrothermally-conditioned samples were also examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to determine the effect of moisture on the phase transition and thermal decomposition temperatures, respectively. It was found that absorbed moisture is released as microscopic surface bubbles at the softening temperature of the polymer (glass transition or melting temperature), resulting in significantly shorter ignition times. An attempt was made to model the moisture-sensitive ignition delay using the thermo-kinetic pyrolysis model ThermaKin.

3:00 **The role of nanoparticle synergies in the enhancement of the thermal conductivity and the flame retardant properties of polymer blends 94**

Kai Yang[1], Steven Krim[2], Rebecca Trojanowski[3],Thomas Butcher[3] ,Gerald Alessio[4],Miriam Rafailovich[1];
[1]Materials Science and Engineering, SUNY-Stony Brook, Stony Brook, New York;
[2]Lawrence High School, Cedarhurst, New York;
[3]Energy Division, Brookhaven National Laboratory, Upton, New York.
[4]ICL-Industrial Products, Ardsley, New York.

Condensing boilers achieve very high efficiency levels by recovering heat from the flue gas before it is discarded. The recovery of latent heat from the water vapor in the humid gas is a very important part of the total heat recovery process. When biofuels are used, such as biodiesel, the condensate formed is corrosive – leading to the need for expensive alloys in the heat exchanger. In order to develop biofuels as a practical alternative to fossil fuel for home heating applications, it is necessary to replace the metallic alloys in the condensing section of these boilers with polymeric materials. The requirements for selecting the polymer are fairly rigorous and cannot be satisfied by any polymer alone; the polymer must withstand relatively high temperatures (T~250C) and be resistant to degradation in the presence of the sulfuric acid environment found in condensates produced from conventional oil combustion. Furthermore, even though the polymer is not in contact with fire, its proximity to an open flame and to the ignition electronics found in boilers, building code regulations require that the materials must be flame retardant, and conform at least to UL94-V0 or V2 requirements. Since no single polymeric material can satisfy these criteria, the focus of this research was to develop organic-inorganic polymer blend nanocomposites, with multiple types of nanoparticle fillers, such as RDP coated montmorilonite clays, Halloysite nanotubes, graphene and carbon nanotubes which in combination are used to tailor the mechanical, chemical, and thermal properties to meet the specific requirements for optimal boiler construction.

COFFEE BREAK 3:30 – 4:00

Chairperson: Manfred Doering

Session 5 – Fabrics and Foams

4:00 **Polycarboxylic Acids as New Condensed Phase Flame Retardants for Cotton 95**

Charles Q. Yang, Department of Textiles, Merchandising and Interiors, the University of Georgia, Athens, GA 3060. USA

Polycarboxylic acids have been used as crosslinking agents for both cotton and wood cellulose and are applied as durable press finishing agents for cotton fabrics. In our previous research, we discovered that polycarboxylic acids, such as succinic acid (SUA) and 1,2,3,4-butane tetracarboxylic acid (BTCA), also function as a flame retardant for cotton when they esterify cotton. In this research, we studied the mechanism and performance of those nontraditional flame retardants. The esterification of cotton by a polycarboxylic acid reduces peak heat release rate and increase percent char yield. Thus, a polycarboxylic acid functions as condensed phase flame retardant to facilitate the dehydration and to enhance the char formation of cotton cellulose. A polyarboxylic acid does not function as a flame retardant without a curing process. Polycarboxylic acids are effective in reducing the 45º flammability of cotton fleece, but they are less effective in reducing the flammability of cotton as measured by vertical burning test or LOI than the traditional phosphorus-based flame retardants. For unsaturated polycarboxylic acids such as maleic acid (MA), we found that sodium hypophosphite, used as the catalyst for esterification, can be bound to cotton by its addition to the carbon-carbon double bonds of MA, thus further reducing cotton's flammability.

4:30 **Multilayer Nanocoatings for Gas Barrier and Fire Protection 96**

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., polyallylamine) 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 6 chitosan (CH), as the cationic layer, and pH 10 montmorillonite (MMT) as the anionic layer, were deposited on foam (30 nm thick and added 4 wt%). 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. In related work, cotton fabric was treated with intumescent nanocoatings, composed of chitosan and phytic acid (PA). 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. Micro cone calorimetry revealed a 4X reduction in total heat release and a 2X reduction in peak heat release rate, compared to the uncoated fabric. This study marks the first fully renewable, intumescent nanocoating. With crosslinking, these coatings have also been shown to survive 10+ wash cycles. Some additional results using sulfonated molecules will also be described if there is time.

5:00 **Nanocoating of Halogen-free Polymeric Materials on Nylon/Cotton blend for Flame Retardant Clothing Applications** 116

Mahesh Narkhede[1, 2], Sammaiah Thota[2], Ravi Mosurkal[*, 2, 3], Jayant Kumar[*, 2, 4]

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Of late, there has been tremendous interest in the area of halogen-free fire retardant fabrics by means of inventive and innovative surface coating techniques. Electrostatic layer-by- layer (LbL) adsorption of materials is a simple and versatile process for imparting desired properties to surfaces.[1] Recently, Grunlan et al explored this coating technique using phosphorous and amine containing electrolytes for developing flame retardant cotton fabric. [2] In the past, we have shown that organic-inorganic hybrid polysiloxane copolymers have great potential as FR materials. [3] In this presentation, we report the development of nanocoating of these Siloxane based materials using LbL adsorption on

Nyco (nylon/cotton, 50:50) fabric. For these coatings, we have used amine containing polysiloxanes and phosphorous based materials as cationic and anionic electrolytes respectively. LbL adsorption process is monitored by Fourier- transform infra-red spectroscopy. The thermal and flame retardant properties were measured by thermo-gravimetric analysis (TGA), pyrolysis-combustion flow calorimetry (PCFC) and vertical flame tests (VFT) and compared with untreated Nyco fabric as a control sample. We observed extinguishing properties in these coated fabrics. Weave structures of coated fabrics and burnt fabric residues after vertical flame tests are studied by scanning electron microscopy. LbL coating process, characterization, thermal and flame retardant properties of Nyco coated fabrics and surface analysis of intumescent char will be presented.

References

1. Decher, G.; Hong, J. D. and Schmitt, J. *Thin Solid Films,* **1992,** 210/211, 831–35
2. Li Y; Mannen, S; Morgan, A; Chang, S; Yang, Y; Condon, B and Grunlan, J. C. *Adv. Mater.* **2011**, 23, 3926–3931
3. Mosurkal, R.; Kirby, R.; Muller, W.S.; Soares, J.W. and Kumar, J., *Green Chem.*, **2011**, 13, 659

5:30 **Novel P-N Bonded Flame Retardants..... 117**

Sabyasachi Gaan, Matthias Neisius, Timea Stelzig, Shuyu Liang, Henri Mispreuve*, Perler Heribert*
Chemistry Group, Advanced Fibers, EMPA Swiss Federal Laboratories for Materials Science and Technology
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There has always been a strong interest in flame retardant community in developing P-N bonded structures. Their excellent flame retardant properties have been attributed to P-N synergism phenomena. Most of these P-N bonded structures like phosphoramidates have been shown to have condensed phase action. We have recently developed novel P-N bonded structures (Phosphonamidates) derived from 9, 10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide (DOPO). Phosphonamidates of varying thermal stability were prepared by varying the substituents on the amino group. These phosphonamidates have been shown to primarily exhibit gas-phase flame inhibition. This presentation will focus on the synthesis, evaluation of thermal properties and fire retardant applications of these novel phosphonamidate compounds as flame retardants in flexible polyurethane foams and other polymers.

Tuesday, May 21, 2013

Chairperson: Bernhard Schartel

Session 6 – FR from a different point of view

8:15 **Flame Retardancy from a Polymer and Plastic Manufacturer Perspective – Uses, Needs, and Requirements** 123

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Flame retardancy is an important subject to many plastics and polymer manufacturers. They are often challenged in meeting the multiple and sometimes exclusive requirements of processing, cost, effectiveness, third-party certifications, and customer acceptance. The effect on the performance of the plastic or polymer must not be significantly affected or degraded by the incorporation of flame retardant additives. Finding the right flame retardant approach whether it is a polymer additive, an inherently flame retarded polymer, a topically applied additive or an installation or construction technique can be critical to a product's acceptance in various applications. This paper will discuss these issues along with some needs from the perspective of a polymer and plastics manufacturer.

Session 7 – Work on Some Specific Polymers

8:45 Fundamental Understanding of Burning Behavior of UV-Cured Thiol-Ene Networks 151

Sergei Nazarenko and Charles Manzi-Nshuti**,**
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The field of photocurable polymers is rapidly growing and expanding into new applications. A success of UV-curing was largely determined by its inherent advantages such as high reactive efficiency, eco-friendly formulations that do not emit VOCs, the possibility of using a variety of processing techniques , i.e. spraying, dipping, or rolling of a reactive mixture on a substrate prior to curing which occurs in seconds with UV light. In particular photocurable thiol-ene networks recently brought considerable attention due to the fact that curing reaction in these systems proceeds via a unique radical mediated step growth mechanism which defines the uniformity of a network structure, leads to low shrinkage and insensitivity to oxygen inhibition as compared to traditional photocurable acrylate and methyl methacrylate networks which are prone to these problems. Because of these additional advantages the thiol-ene networks can potentially replace acrylate and methyl methacryalate based systems in certain applications.

In order to develop a better understanding of fire related hazard associated with the application of thiol-ene network polymers we have been conducting an extensive investigation of burning behavior of these systems using a cone calorimeter. Nine model UV-curable thiol-ene have been prepared from chemically similar di, tri, and tetra thiol propionate ester monomers and three chemically different multifunctional ene monomers (allyl ether, allyl triazine, and an allyl isocyanurate) with the same functionality three. This thiol-ene network components selection allowed investigating the effect of thiol functionality and ene rigidity on fire retardant properties. A tandem of various techniques such as cone calorimetry, DSC, TGA, optical microscopy and scanning electron microscopy allowed a detailed investigation of the changes that occur in both the condensed phase and the char residues of the networks during different stages of burning.

9:15 Synthesis of novel hyperbranched polymers containing phosphorus, nitrogen, and silicon and study of their application in UV curable flame retardant coatings 152

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Novel hyperbranched polymers containing phosphorus, nitrogen, silicon on the backbones and acryl as the surface groups were successfully synthesized via the Michael addition polymerization of phosphate monomers with multifunctional amines, and their structure were clarified by nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) spectra and gel permeation chromatography (GPC). Then a series of UV-curable flame retardant coatings were prepared by the incorporation of these hyperbranched polymers into epoxy acrylate (EA). The transparency of all the flame retardant EA resins to visible light can match pure epoxy acrylate. The results of microscale combustion calorimetry (MCC) revealed that as-prepared polymers could effectively reduce peak heat release rate and total heat release. The thermal degradation of the flame retardant resins was studied using thermogravimetric analysis (TGA), real time Fourier transform infrared (RTFTIR) and thermogravimetric analysis-infrared spectrometry (TGA-IR). It was found that the modified epoxy acrylates presented much higher thermal stability and left more char residues above certain temperature compared with that of pure EA resin, in the spite of lower initial decomposition temperatures.

9:45 Weathering of an epoxy based fire protective intumescent coating 153

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Passive fire protection systems are widely used by the oil, gas and chemical industries to protect steel against fire. However, there are concerns that the performance of these systems in a fire may be deteriorated because of weathering. In this study, an intumescent fire retardant epoxy based coating containing ammonium polyphosphate (APP), melamine and titanium dioxide was chosen as model system. The coating was exposed to immersion tests in distilled and salted water. Immersion in distilled water for 1 month shows a slight decrease of the protective properties: APP turns on coating extreme surface into polyphosphoric acid, which, combined with the mechanical erosion effect of water, is dissolved/detached in water. The coatings immersed for 1 month in the salted water bath however show very poor protection of the steel plate and no intumescence is observed. The mechanisms involved in the loss of fire protection by the salted water will be further discussed during the conference.

10:15 Phosphorus containing salts as flame retardants in epoxy resins and engineering plastics 163

Manfred Döring, Bettina Burk
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Due to their good flame-retardant efficiency and minimal influence on the material properties 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[1].

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[2].

Due to the less thermal stability of these melamine salts they are not recommended for use in engineering plastic. Zinc complexes of these phosphorus compounds represent coordination polymers and are extremely thermally and chemically stable[3]. So, they are particularly suited in synergistic formulation for use in engineering plastics.

Here we describe the synthesis and structure of these coordination compounds, and their flame protection effects in polyamides and polyesters.

References

(1) E. Weil, S. Levchik; Flame Retardants for Plastics and Textiles: Practical Applications; Hanser Gardner Publications 2009

(2) M. Döring, M. Ciesielski, C. Heinzmann; "Synergistic Flame Retardant Mixtures in Epoxy Resins" in Fire and Polymers VI, ACS Symposium Series Volume 1118; edited by A. Morgan, C. Wilkie, G. Nelson; Oxford University Press 2013

(3) M. Döring, C. Kollann, U. Storzer, M. Ciesielski, U. Dittrich, B. Just, H. Keller, E. Meusel, K. Heinemann; "New Phosphorus-containing Flame Retardants for Thermoplastics"; BCC conference on Flame Retardancy, Stamford 2005

COFFEE BREAK 10:45 – 11:15

Chairperson: Serge Bourbigot

11:15 **Synthesis of DOPO-substitued organophosphorus oligomers as effective flame retardants for epoxy composites 170**

Xin Wang*, Lei Song, Yuan Hu

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A wide variety of flame retardant epoxy resins with 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) and its derivatives have attracted extensive attention in recent years. However, these DOPO-containing compounds reported are mostly small molecular flame retardants, which exists some drawbacks, such as leaching and low phosphorus content. Therefore, the polymeric flame retardants, possessing high phosphorus content and rich aromatic structure, are highly noting. In this work, we synthesized several novel organophosphorus oligomers, and incorporated them into the flame retardant epoxy resins. LOI values increased significantly for the epoxy resins containing the organophosphorus oligomers compared to the pure resins, and UL-94 V-0 rating could also be achieved. The addition of the organophosphorus oligomers obviously decreased the value of peak heat release rate and total heat release of the epoxy resins. TGA results indicated that incorporating the organophosphorus oligomers significantly enhanced the char yield and the thermal stability of char layer at higher temperature. Thermogravimetric analysis/infrared spectrometry (TG–IR) and direct pyrolysis/mass (DP–MS) analysis were employed to explore the thermal degradation mechanism of the flame retardant epoxy composites. The results suggested that introducing the organophosphorus oligomers could reduce the release of combustible gas, trap the H and OH radicals by releasing the PO radical and induce the formation of char layer, thus retard the polymer degradation and combustion process.

11:45 **Novel Ecolabel Compliant Flame Retarded Polymer Formulations 171**

Subramaniam Narayan, Marshall Moore, Great Lakes Solutions, A Chemtura Business, West Lafayette, Indiana, Subramaniam.Narayan@chemtura.com

Flame retardants in polymers play a significant role in protecting lives and reducing damage in the event of a fire. Typically brominated flame retardants (BFR) require a synergist such as antimony trioxide (ATO) that enables lower loadings of the BFR in polymer formulations. This combination works in a vapor phase mechanism through the formation of flame quenching antimony trihalide. However currently under the European Classification and Labeling requirements there is a hazard phrase assigned to ATO which limits its potential use in products which are marketed with the EU Ecolabel, a.k.a. the “Ecoflower”. The result has been that plastics formulated with non-halogen flame retardant systems, which do not require the use of ATO, have replaced flame retarded Acrylonitrile-Butadiene-Styrene (ABS) or high impact polystyrene (HIPS) formulated with BFRs and ATO in the housings of consumer electronics in models designed to meet the Ecolabel criteria. Additionally, long term cost fluctuation of antimony metal has been reported as a driver for a search for alternatives to ATO.

Although non-halogenated flame retardants do not require an ATO synergist, the use of those too have been affected by ecolabel criteria. As an example, the current European Classification and Labeling requirements for Bisphenol A diphenyl phosphate (BAPP, BDP or BPADP) call for a hazard classification related to its ecotoxicity that is not allowed under the Ecolabel criteria. Recent work by the Environmental Protection Agency (EPA) on the use of flame retardants in plastics suggests that brominated flame retardants that are based on polymeric or oligomeric substrates have generally low toxicity concerns because they cannot be absorbed or easily metabolized. The same work also shows that they generally have low ecotoxicity hazards. If such a flame retardant can function by itself, without the need for an ATO synergist and without restrictive hazard phrases, it would be an attractive solution for Ecolabel compliance, both from an environmental and economics point of view.

This work describes the replacement of ATO in formulations containing a newly developed flame retardant, Great Lakes Solutions’ Emerald Innovation™ 1000 (FR1) for polymers used in used in electrical and electronics applications. Evaluations have shown that when combined with a char forming polymer like polyphenylene ether (PPE), FR1 functions as an effective flame retardant in high impact polystyrene (HIPS) without the need for ATO synergist. Similarly a small amount of FR1 works efficiently in blends of PPE/HIPS at 1:1 and 1:3 ratios, once again without any ATO synergist. Further, the mechanical properties of the blend system are not affected by the introduction of the flame retardant. In polycarbonate (PC)/ABS systems, this innovative new flame retardant also shows good flame retardancy without the need for ATO synergist. Results of this study demonstrate that FR1 can be used PC/ABS combinations ranging from 80% to 30% PC. In addition, PC/ABS formulations based on FR1 provides a good balance of mechanical, thermal and other physical properties compared to commercial formulations, in contrast to liquid phosphate flame retardants which can plasticize the system resulting in poor impact strength and/or thermal properties.

Our findings indicate that In addition to the benefit of simply being an ATO-free formulation, PC/ABS formulations based on FR1 potentially meet performance requirements that bis-phosphate based formulation cannot. For example, in PC/ABS parts with thin wall thicknesses, e.g. 0.8mm, customers report that liquid phosphate esters fail to meet flammability requirements. FR1 works efficiently @ 0.8mm thickness without requiring ATO synergist, resulting in V-0 ratings on the UL-94V flammability test.

12:15 **GAS PHASE COMBUSTION STUDIES OF FLAME RETARDANT POLYMERS IN THE MICROSCALE COMBUSTION CALORIMETER 179**

Richard E. Lyon, Richard N. Walters and Sean Crowley, Federal Aviation Administration
Fire Safety Branch ANG-E21, William J. Hughes Technical Center, Atlantic City International Airport, NJ 08405

A microscale combustion calorimeter (MCC) was modified to measure carbon monoxide and carbon dioxide in the exhaust gases in order to study gas phase combustion chemistry of flame retardant polymers. The temperature of the MCC combustor was systematically reduced from the ASTM D7309 value for complete oxidation of hydrocarbon fuel gases (900±100°C) in order to effect incomplete combustion of flame retardant polymers during the 9-second residence time. A two-step reaction model with carbon monoxide as an intermediate species was used to calculate the extent of reaction from the oxygen depletion as a function of combustor temperature. From these data, global kinetic parameters for thermal oxidation of the pyrolysis gases in excess oxygen were obtained and used to calculate the chemical reaction time in the diffusion flame of an over-ventilated cone calorimeter. These chemical reaction times increased by orders of magnitude when halogens were present in the polymer backbone or as additives. When the computed chemical reaction times at flame temperatures exceeded the computed residence time of the gases in the diffusion zone of the flame, low combustion efficiency was observed in the cone calorimeter, suggesting a possible method for screening flame retardants for gas phase activity.

LUNCH 12:45 – 2:00

Session 8 – Composites and Nanocomposites

Chairperson: Richard Lyon

2:00 **APP/CaMMT Nanocompounds and Their Intumescent Flame Retardancy on Polypropylene 193**

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Calcium ion based montmorillonite (CaMMT) is a natural mineral without experiencing an ionic exchange with sodium ion. Nanocompounds (APP-CaMMT) of ammonium polyphosphate with CaMMT were prepared through in-situ polymerization. According to XRD, the CaMMT layers in APP were completely exfoliated, and APP was in crystal forms I and II. The APP-CaMMT nanocompounds with dipentaerythritol (DPER) together were applied to intumescent flame retarded polypropylene (PP/IFR) composites with a comparison with APP (crystal form II) and a mixture of APP with micro-CaMMT. These PP composites (PP/APP-CaMMT/DPER, PP/APP/DPER, and PP/APP/DPER/micro-CaMMT) were studied by using limited oxygen index (LOI) measurements, UL-94 flame testing, thermogravimetric analysis (TGA) and Cone calorimeter. It was found that the APP-CaMMT nanocompounds enhanced the flame retardancy of the PP/IFR compared with the form II APP and the mixture of APP and micro-CaMMT by increasing LOI, decreasing pHRR, and passing UL94 V0 rating.

2:30 **Flame Retardancy of Composites Tailored for Different Applications 196**

Bernhard Schartel
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Fibre reinforced polymers are used for diverse applications such as electronics and electrical engineering, transportation (railway vehicles, shipping, aviation) and construction. The fire behaviour of composites differs in comparison to polymers. Fibres behave often inert with respect to pyrolysis, but they change the melt flow and dripping behaviour, the heat absorption and transfer, the amount and properties of the fire residue and so on. Flame retardancy concepts are needed not only suitable for composites, but also tailored for the different applications and fire protection goals.

The field is illuminated by examples taken from different projects carried out in the group of the author in the recent years.[1-8] The examples target on different applications through achieving V0 in UL 94 testing (reaction to small flame controlling the fire risks in the beginning of a fire), reducing heat release rate and fire load in the cone calorimeter (fire risks under forced flaming combusting controlling the contribution to developing fires) and investigating the structure integrity when a severe flame is directly applied (key property in fully developed fires). Approaches to halogen-free flame retardancy in glass fibre reinforced thermoplastics and carbon fibre reinforced thermosets are presented as well as building up a bench and intermediate scale testing of composites applying mechanical load and direct flame simultaneously.

The understanding of fire behaviour and flame retardancy mechanisms in composites is a promising basis for target-oriented development. Using suitable fire tests and testing specimen target on the different protection goals, whereas additional investigations such as thermal analysis, rheological experiments, residue analysis, etc feed us with valuable information about the mechanisms and the structure-property-relationships.

Successful concepts are presented for flame retardancy tailored for different application as well as general guidelines for future development. Different phosphorus flame retardants are proposed to achieve halogen-free flame retardancy in applications demanding limited fire risks with respect to ignition and developing fires. Advanced testing is presented for addressing the structure integrity of composite in fire that is believed to be the most important fire risk for structural applications tested against fully developed fire.

[1] U. Braun, A.I. Balabanovich, B. Schartel, et al. Polymer, 47, 8495-8508, 2006
[2] B. Schartel, A.I. Balabanovich, U. Braun, et al. J. Appl. Polym. Sci., 104, 2260-2269, 2007
[3] U. Braun, B. Schartel, M.A. Fichera, C. Jäger. Polym. Degrad. Stab., 92, 1528-1545, 2007
[4] U. Braun, H. Bahr, H. Sturm, B. Schartel. Polym. Adv. Technol., 19, 680-692, 2008
[5] B. Perret, B. Schartel, K. Stöß, et al. Macromol. Mater. Engin., 296, 14-30, 2011
[6] B. Perret, B. Schartel, K. Stöß, et al. Eur. Polym. J., 47, 1081-1089, 2011
[7] B. Schartel, J.K. Humphrey, A.G. Gibson et al. in preparation
[8] A. Hörold, B. Schartel, V. Trappe et al. in preparation

3:00 Covalent functionalization of carbon nanotubes with polyhedral oligomeric silsequioxane for fire retardant nanocomposites 197

Fei Liang[1], Yong Tang[1], Jihua Gou[1*], Yuan Hu[2]
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Keywords: Carbon nanotubes, POSS, buckypaper, superhydrophobicity, flame retardancy

Multi-walled carbon nanotubes (MWCNTs) were covalently functionalized with polyhedral oligomeric silsequioxane (POSS). The results of Fourier Transform Infrared Spectroscopy, Raman spectroscopy and Transmission Electron Microscopy revealed that POSS particles were grafted onto MWCNTs. The POSS content determined by thermo-gravimetric analysis (TGA) was estimated to be approximately 25 wt%. A stable and superhydrophobic surface characteristic was observed for the film made of MWCNTs grafted with POSS (MWCNT-g-POSS) even after an exposure to a high-humidity environment for three weeks. The water contact angle of the sample was measured to be 160.5±1.1º. Buckypapers were made from both pristine MWCNTs and chemically converted to MWCNT-g-POSS. The pore structures of the buckypapers were characterized by mercury intrusion porosimetry and scanning electron microscopy. The flame retardant performance of the buckypaper based composites was evaluated by TGA and microscale combustion calorimetry (MCC) test. The TGA test results indicated that the MWCNT-g-POSS dramatically increased the char residues of the composite. Approximately 72 % reduction in peak heat release rate was achieved for the MWCNT-g-POSS /resin composite from the MCC testing. Such reduction was due to the smaller median pore size of the MWCNT-g-POSS buckypaper and high char yield during combustion, which limited the diffusion of flammable gases generated from the pyrolysis of resin.

3:30 Advanced Flame Resistant Carbon Fiber Reinforced Composites 198

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Efforts to replace metals with composites in shipboard structures have emphasized the use of brominated vinyl esters as fire-retardant polymers. However halogenated polymers produce toxic and potentially carcinogenic compounds during combustion, thus there is a need for environmentally benign and affordable resin system that offers desired fire, smoke and toxicity (FST) behavior, processability and structural performance, which are also compatible with carbon fibers for composites production . An inherent flame- retardant epoxy system was successfully developed by chemically integrating phosphorous- and silicon-containing compounds to render synergistic effects that significantly improve the FST behavior. This refined epoxy resin offers low viscosity and amenability to room-temperature cure, and enables room-temperature manufacturing of composites via vacuum assisted resin transfer molding (VARTM). The flame retardant properties of composites fabricated using the refined epoxy resin system matched those of brominated vinyl ester. The flame resistance was achieved without compromising the desirable mechanical performance of the base epoxy system, which is superior to those of brominated vinyl ester. This important advantage can be used to design lighter and lower-cost shipboard structures.

4:00 – 4:30 COFFEE BREAK

Chairperson: Kelvin Shen

4:30 **Fullerene: a potential flame retardant for polyolefins 209**

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Fullerene (C_{60}) behaves as an electron-deficient compound and is known as a radical sponge. Most of polymers experience a free radical chain scission process during combustion. Thus, the presence of C_{60} may reduce the flammability of polymers by trapping the free radicals.

The flame retardancy of polypropylene/fullerene (PP/C_{60}) nanocomposites was investigated by cone calorimetry. The results show that the presence of C_{60} in PP matrix not only prolonged the t_{ign} (time to ignition) but also considerably reduce the PHRR (peak heat release rate). PP/2.0 wt% C_{60} showed a t_{ign} of 36s, which was much longer than that of pure PP, this implied that C_{60} could delay the start of combustion. Furthermore, the PHRR of PP/C_{60} nanocomposites was around 60% (1.0 wt% of C_{60}) and 55% (2.0 wt% of C_{60}) of pure PP, demonstrating that the addition of C_{60} improved the flame retardancy of PP. C_{60} reduced the flammability of PP by trapping free radicals in the gas phase and in situ forming a gelled-ball crosslink network to improve the flame retardancy of PP in the condensed phase.

To get more information about the flame retardant mechanism of C_{60}, the influence of C_{60} on the flame retardancy of high density polyethylene (HDPE), polypropylene (PP), polymethyl methacrylate (PMMA), and bisphenol A polycarbonate (PC) have been studied by using microscale combustion calorimetry (MCC). The results showed C_{60} had different effects on the flammability of different polymer matrices. Compared with pure HDPE, the PHRR of HDPE/C_{60} nanocomposites were given a reduction 18% (1.0 wt% of C_{60}) and 26% (2.0 wt% of C_{60}). No obvious changes of PHRR were found with the addition of C_{60} in PP, PMMA and PC. Among these polymers, more side groups were found in PP and PMMA. When PP and PMMA exposed to high temperature, C_{60} was able to trap the alkyl radicals produced by the thermal decomposition of PP and PMMA. However, the bond dissociation energy of C-C in the side chain is smaller than that of C-C in the backbone. At higher temperature, more fuel gases were formed by the decomposition of side chains and C_{60} could not inhibit the decomposition of PP and PMMA. As for PC, the degradation mechanisms were different from HDPE, PP and PMMA. The main volatile products collected during thermal degradation of PC were phenol and bisphenol A, which did not react with C_{60}. As a result, C_{60} did not have flame retardant effect for PC.

As C_{60} showed good flame retardancy in HDPE matrix, we further studied the influence of C_{60} on the thermal behavior of HDPE, which could further illuminate the mechanism for the influence of C_{60} on the flame retardancy of polymers. The results showed that in N_2 the onset decomposition temperature of HDPE increased by about 9 ºC independent of C_{60} concentration. Thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TG/FTIR) and Py-GC-MS results showed that C_{60} could trap the carbon-centered radicals originated by carbon-

carbon bond scission of HDPE to delay the degradation. However, the degradation mechanism of HDPE did not change with the addition of C_{60}. In air, when the content of C_{60} was above certain threshold value, the thermal stability of HDPE was remarkably improved, with increased onset and peak decomposition temperatures. From the dynamic temperature scanning, it was found that the reaction between C_{60} and HDPE took place at 245 ºC. At this temperature, more alkylperoxide radicals ($RO_2^\bullet$) were formed by the oxidative degradation of HDPE and C_{60} could trap $RO_2^\bullet$ to form RO_2C_{60} thus inhibited the degradation of HDPE. Also C_{60} could trap $RO^\bullet$ originated by the O-O bond scission of $ROOC_{60}$ or ROOR at higher temperature.

The above result indicated that C_{60} can be used as a synergistic flame retardant to improve the thermal stability of polyolefins at the early stage of thermal oxidative degradation.

Acknowledgements

Financial support from the National Natural Science Foundation of China (No. 51073140) and the Natural Science Foundation of Ningbo (No. 2011A610124) are acknowledged.

5:00 **Natural halloysite and goethite as versatile and highly effective green flame retardants for thermoplastic compounds,** Chris DeArmitt, **Applied Minerals Inc., 110 Greene Street, Suite 1101, New York, N.Y. 10012, 212-226-4254, 917-210-4077 office, 601-620-8080 mobile,** cdearmitt@appliedminerals.com 211

The market is moving steadily away from chemical FR solutions accelerated by regulatory changes that mandate the phase out of brominated additives in particular. This has caused a shift to products including minerals such as ATH and MDH but those are limited in their applicability due to low decomposition temperature. Thus, a large part of the thermoplastics market remains unaddressed. Halloysite has been proven effective in many polymer and elastomer systems where it can be used alone, or as a synergist, to provide a combination of FR functionality, mechanical reinforcement and productivity enhancement. The high water-loss temperature, above 420ºC, enables it to be processed into virtually any type of polymer. Moreover, a recent evaluation revealed Dragonite Halloysite to be an extremely friendly solution making it the preferred alternative for environmentally conscious customers.

Goethite is a special type of iron oxide with the formula FeOOH which has long need recognized for its extreme efficacy as an FR and smoke suppressant in chlorinated polymers like CPE, PVC and CPVC. Dragonite IO is an extremely pure, natural Goethite which provides an economically appealing alternative. We will show how Goethite, normally used as a pigment, can provide excellent FR performance rivaling, or even surpassing, other more well known alternatives.

Wednesday, May 22, 2013

Session 9 – New Developments in FR

Chairperson: Marshall Moore

8:15 **New Developments in Inorganic Tin Fire Retardant Systems 212**

Paul Cusack, ITRI Limited, St Albans, UK

Although a wide range of chemicals have found use as fire retardants over the years, many are facing increasing scrutiny either because of their inherent toxicity or their negative impacts in the environment. In view of a clear industrial demand for safer fire retardants, ITRI commenced its work on tin-based FR additives in the mid-1980s.

ITRI's research led to the commercial introduction of two specific tin compounds – zinc hydroxystannate (ZHS) and zinc stannate (ZS) – as novel fire-retardant additives with the additional benefit of smoke suppression, and markets for these compounds have increased steadily over the past 20 years or so.

Initially developed as safe alternatives to antimony trioxide for use in PVC and other halogen-containing polymeric materials, recent advances have focused on their application in halogen-free polymers and market growth is evident in the European and Japanese electronic sectors.

This paper gives an overview of recent work carried out at ITRI covering applications in halogen-free electronics, cables and fire-protective coatings, with particular reference to the development of novel tin additives, based on proprietary nano-particulate and coating technologies.

8:45 **New Developments in Brominated and Halogen-Free Flame Retardants** 219

A. Desikan[1], S. Levchik[1] and M. Leifer[2].
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With a broad portfolio of brominated, organophosphorus and inorganic flame retardants, ICL Industrial Products (ICL-IP) is engaged in the development of new flame retardants by exploiting the synergism between bromine based, phosphorus based and other halogen-free flame retardants. ICL-IP is also focusing on the development of polymeric and reactive flame retardants. This paper will give examples of existing and new polymeric and reactive products for applications in thermoplastics, thermosets and polyurethane foam. This paper will also show examples of phosphorus-bromine synergism allowing partial or complete elimination of antimony trioxide in many thermoplastics for electronic applications. New synergistic combinations of magnesium hydroxide with phosphorus and other halogen-free FRs will be presented.

9:15 **Multifunctional deoxybenzoin-based monomers and polymers for reducing materials flammability** 220

Justin Timmons, Zhan Yang, Allen Lesser, Bryan Coughlin and Todd Emrick*
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003

This presentation will describe the synthesis of novel multifunctional deoxybenzoin-containing structures, including their use as cross-linkers in cured resins and adhesives. Utilizing a platform of intermediates identified from the synthesis of aromatic anti-oxidants, we have prepared a wide range of deoxybenzoin derivatives, and applied them in adhesive resin formulations. These monomers and resulting network structures were characterized by thermogravimetric analysis (TGA) and pyrolysis combustion flow calorimetry (PCFC), and seen to exhibit very low heat release values (HRC of ~55 J/(g-K)) and higher char residues (38%) relative to conventional epoxy resins. Moreover, structure-property relationships were identified for a range of related deoxybenzoin-containing structures. The presentation will be set in the broader context of polymer materials flammability, including the identification of new monomers, polymers, and composite materials approaches to the topic.

9:45 – 10:15 COFFEE BREAK

Chairperson: Qiang Yao

10:15 **Flame Retardancy of High Temperature Polymers Such As Polycarbonate and Poly(Cyclohexylene dimethyl terephthalate) 221**

Jinhwan Kim, Department of Polymer Sci. and Eng.,Sungkyunkwan University, 300 Cheoncheon-dong, Jangan-gu, Suwon, Gyeonggi-do 440-746, Korea. e-mail: jhkim@skku.edu

In an attempt to develop an efficient FR for high temperature polymers, two engineering plastics are selected as model polymers: one is a charring polycarbonate (PC) and the other is non-charring poly(ethylene terephthalate) (PET).

A series of organo phosphorus flame retardants (FRs) based on aromatic phosphate and cyclic phosphate, mainly phloroglucinol diphenyl phosphate (PDP), were synthesized for polycarbonate. Their thermal stability and flame retarding efficiency as a single-component additive were investigated and compared with resorcinol bis(diphenyl phosphate) (RDP). The thermogravimetric analysis results revealed that PDP shows a higher thermal degradation temperature and better flame retardancy even though it has a lower P content than cyclic phosphate-based FRs. The flame retarding efficiency was evaluated by the UL-94 test method. The V-0 rating was achieved at a PDP loading of 2 wt% for polycarbonate, which is far better than that of resorcinol bis(diphenyl phosphate) and cyclic phosphate-based FRs. The high thermal stability and P–OH generation tendency is responsible for the better flame-retarding performance of PDP. The degradation path of PDP is also discussed.

Recently, lots of attention have been paid to partly aromatic polyester, poly(cyclohexylene dimethylene terephthalate) (PCT), having higher heat resistance and hydrothermal stability compared to PET and PBT; the structure of PCT is shown in Figure 1. When the thermal properties of three polymers are determined by a differential scanning calorimetry (DSC), the crystalline melting temperature (T_m) of PBT, PET, and PCT are 227, 243, and 289 ^{o}C, respectively. PCT's high T_m and good hydrothermal stability coming from its inherent cycloaliphatic structural unit find its application as an adequate material for the "reflector", the molded part of LED devices such as high power lighting. Since PCT is used in electric and electronic applications, the impartment of flame retardancy is essential and the development of effective halogen-free system is very demanding. However, no publication has been reported on this subject. In this study, the pyrolysis and flame behavior of PCT are investigated by employing the metal (Aluminum) complex of alkyl phosphinate as a main FR. The results are compared with the flame retardancy behavior of PBT system. The flame retarding performances of various formulations are studied by the UL-94 and TGA. The charred residues are investigated by FT-IR (ATR) spectrophotometry and scanning microscope (SEM). A decomposition mechanism is also postulated on the basis of experimental results.

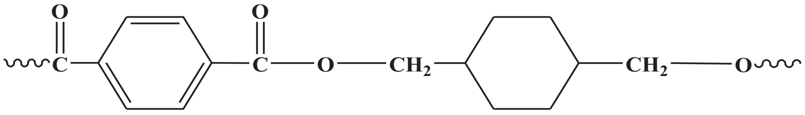

Figure 1. Structural formula of PCT

10:45 **The Potential of Phosphorus-containing Poly(ester)s for Flame Retardancy** 232

Bob A. Howell, Center for Applications in Polymer Science, Department of Chemistry, Central Michigan University, Mt. Pleasant, MI 48859-000. bob.a.howell@cmich.edu

The growing concerns about the potential negative environmental and health impacts of organohalogen flame retardants has prompted efforts to find suitable replacements. Most generally, replacements are organophosphorus compounds. To be widely applicable these compounds should be non-migrating, i.e., they should not be readily released from the polymer matrix that they are intended to protect, either during processing or after ultimate disposal in the environment. In this regard, oligomeric materials offer advantages over small molecules. In particular, poly(ester)s containing phosphorus moieties, either as pendants or components of the mainchain (or both), would seem to be attractive new flame retardants. Some materials of this kind are commercial products, others are under development. Methods by which such materials may be prepared will be explored.

11:15 **Some New Sulfur-Containing Materials as Putative Fire Retardants 235**

Charles A. Wilkie and Jiyu He, Marquette University, Milwaukee, WI 53201

More than a century ago, Gay-Lussac suggested that ammonium phosphate be used as a fire retardant for theatre curtains and he later changed this to ammonium sulfate. Even though this was one of the earliest fire retardants, there is a dearth of sulfur-containing materials except for those used in polycarbonate. We have felt for some time that sulfur was an element under-appreciated in the FR world and finally began an investigation of some sulfur compounds. We have examined three compounds, 2-(1-pyridino-)-1-propane sulfonate, sodium diphenylamine-4-sulfonate and ammonium sulfamate with both PMMA and PS. These have been studied both alone and combined with organically-modified clays (montmorillonites). The results of this investigation will be discussed in this presentation.

11:45 Closing of Conference – Chuck Wilkie

12:00 – 1:00 Lunch