

21st Annual Conference on Recent Advances on Flame Retardancy of Polymeric Materials

**Chairman: Prof. Menachem Lewin
Polytechnic Institute of NYU**

Featuring

**An Intensive Short Course in Selection, Evaluation, and
Commercial Application of Flame Retardants
May 23, 2010**

**Main Conference
May 24-26, 2010**

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21st Annual Recent Advances in Flame Retardancy of Polymeric Materials

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

Organized by BCC Research, 35 Walnut St., Wellesley, MA 02481
Program Chairman: Professor Menachem Lewin, Polymer Research Institute, Polytechnic University



21st Annual Recent Advances in Flame Retardancy of Polymeric Materials

May 24-26, 2010

Holiday Inn Stamford Downtown

Organized by [BCC Research](#)

Featuring an Intensive Short Course: Selection, Evaluation, and Commercial Application of Flame Retardant Polymers, Sunday May 23, 2010.

Course Director: Professor Menachem Lewin, Polymer Research Institute, Polytechnic University



21st Annual Recent Advances in Flame Retardancy of Polymeric Materials

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Holiday Inn Stamford Downtown

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.**



Intensive Short Course

Selection, Evaluation, and Commercial Application of Flame Retardant Polymers

Sunday, May 23, 2010, 8:30 a.m.–5:30 p.m.

Course Director: Professor Menachem Lewin, Polymer Research Institute and Department of Chemical and Biological Science, Polytechnic Institute of NYU, 6 MetroTech center, Brooklyn, NY 11201

The Course Instructors

Edward D. Weil, Professor, Polymer Research Institute, Polytechnic Institute of NYU, Brooklyn, NY

Sergei Levchik, Product Development Manager, ICL-IP America, Ardsley, NY

Marc L. Janssens, Director of the Fire Technology Department, Southwest Research Institute® (SwRI®), San Antonio, TX

Who Should Attend?

Chemists, engineers, physicists, polymer and material scientists involved in research and development, production, marketing, QC, standards, and evaluation of products and their environmental impact; personnel involved in planning and design of products in building, construction, automotive, aircraft, telecommunications, electronics, computers, textile, wood products and pulp and paper and other industries. For both newcomers and practitioners who want to brush up on FR technology practices.

Why Attend?

Flame retardancy of polymers is an active and developing field and involves several disciplines. A systematic introduction to the field is of great importance to colleagues already engaged in R&D, production and marketing of polymeric materials and products, as well as those entering the FR field, and to colleagues beginning their activity in polymer technology. The course will considerably shorten the time needed for getting acquainted with the numerous flame retarding additives, the flammability behavior of the various polymeric materials, the diversified applications of flame-retarded polymers, the consumer, environmental, and regulatory issues involved and the systems and equipment used for production and testing. A comprehensive full-day (8:30 a.m.-5:30 p.m.) intensive, informative program, staffed by a knowledgeable and experienced faculty steeped in academic insight and industrial know-how.

Topics Discussed in the Course

(partial listing)

- Principles of flammability and fire hazards
- Flame retarding polymers
- Review of flame-retardant chemicals
- Mechanisms of flame retardancy
- Fire test methods
- Survey of flame retardancy of all the significant plastics and textile fabrics
- Material flammability
- Standards-setting and regulatory organizations
- Properties measured by fire tests

A Certificate of Participation will be awarded to attendees



21st Annual Recent Advances in Flame Retardancy of Polymeric Materials

Conference Program

Registration—

Sunday, May 23, 6:00-7:30 p.m., Reception

Monday, May 24, 7:30-8:15 a.m.

May 24, 2010

8:15-8:30 a.m.—Opening Remarks

Professor Menachem Lewin

Polymer Research Institute, Polytechnic Institute of NYU



Session I: General Papers and Reviews

Chairperson: Jose Marie Lopez Cuesta, Pôle Matériaux Polymères Avancés, Centre des Matériaux, Ecole des Mines d'Alès, France

8:30 - 9:00

Modeling Pressurization Caused by Thermal Decomposition of Highly Charring Foam in Sealed Containers

K. L. Erickson, A. B. Dodd, R. E. Hogan, Sandia National Laboratories, Albuquerque, NM

Polymer foam encapsulants provide mechanical, electrical, and thermal isolation in engineered systems. In fire environments, foams, such as polyurethanes, can liquefy and flow during thermal decomposition, and evolved gases can cause pressurization and failure of sealed containers. Foam liquefaction and flow can cause serious modeling issues in systems safety and hazard analyses. Highly charring hybrid polyurethane epoxy cyanate ester foam was developed to mitigate modeling issues associated with foam liquefaction and flow. A previous paper discussed the experimental and modeling approach developed to predict radiation and conduction heat transfer through decomposing hybrid foam in vented containers. This paper discusses application of a similar approach to the more difficult problem of predicting heat transfer, foam decomposition, and pressure growth in sealed containers. Model predictions will be compared with results from radiant heat transfer experiments involving encapsulated objects. All model parameters are evaluated from independent laboratory-scale experiments such as TGA and DSC.

9:00-9:30

Smoke and Combustion Products – Recent Progress and Some Issues

Edward D. Weil, Polytechnic Institute of NYU, **Marcelo Hirschler**, GBH International and **Sergei Levchik**, ICL-IP

Methods for smoke reduction in burning plastics will be reviewed with emphasis on recent progress. Visual obscuration, gaseous combustion product toxicology, and soot carcinogenicity will be addressed. The dominant role of carbon monoxide in fire gases is further supported, and the relative contribution of other components such as hydrogen

halides will be discussed. Continued progress is shown in formulating PVC for low smoke by use of inorganic additives, while styrenic systems remain a challenge. An attempt will be made to assess the controversial environmental issues in regard to halogen-containing plastics. A distinction is emphasized between hazard and risk, and a judicious approach to choice of flame retardant is recommended, considering factors such as relative efficiency, emissions in accidental fires and end-of-life issues. Progress in modern waste-to-energy facilities and metal smelters now affords means for safe recovery of values from electrical and electronic scrap, including halogen-containing flame retardant plastics.

9:30-10:00

Phosphorus Sulfur Compounds as Flame Retardants

Manfred Doering, Michael Ciesielski, Jochen Wagner, Institute for Technical Chemistry, Karlsruhe Research Center, Germany

Commercially available phosphorus flame retardants are mostly phosphorus oxygen compounds and can provide condensed-phase or gas-phase activities. Replacing oxygen against sulphur in the phosphorus flame retardants the gas-phase efficiency will be increased in epoxy resins. Recently, phosphorus compounds together with sulfur were described as non-halogenated flame retardants for polystyrene. We will introduce new phosphorus sulphur compounds, which are particularly generated by a direct reaction of phosphorus compounds with sulfur and discuss their synergetic flame-retardant effect with sulphur compounds.

10:00-10:30 Coffee

Chairperson: Gerald Kirschenbaum, Consultant

10:30-11:00

Parameter Sensitivity of Condensed-Phase Burning Modeling

Nicolas Bal, Guillermo Rein, BRE Centre for Fire Safety Engineering, The University of Edinburgh

A one-dimensional numerical model describing the phenomena occurring up to ignition for a solid fuel is used to study which mechanisms are more important. The model solves the heat transfer equation and accounts for mass loss via multiple pyrolysis reactions. Ignition is specified by a critical mass criterion. The model is deliberately simple and follows the rule that simplifications are required where higher precision is not warranted. Comparison with a large dataset of experimental measurements for PMMA show that the model can predict the time to ignition in or a wide range of heat fluxes from 10 to 200 kW/m². The numerical sensitivity study shows that four parameters (kinetic parameters, specific heat, density and in-depth-radiation coefficient) are very important. Variations of the other parameters, in comparison, produce negligible changes to the time to ignition.

11:00-11:30

Fire Retardant Polyamides- Present Technologies and Challenges

Kelvin K. Shen, Saied Kochesfahani, and Frédéric Jouffret, Rio Tinto Minerals, Denver, USA

Polyamides (PA) engineering plastics display excellent mechanical properties (such as high strength at high temperatures, toughness at low temperatures, and good wear/abrasion resistance), moldability, and chemical resistance. They have been used in automotive parts, electrical/electronic components, and industrial markets. PA 66, PA 6, and a variety of high temperature PA such as PA 6T/66, PA 6T/M, PA 46, and PA 9T are commonly used for producing molded electrical parts such as electrical connectors, circuit breakers, relay switches, and bobbing. In these applications, PA has to meet a variety of flammability tests such as UL 94, Comparative Tracking Index, and Glow Wire Test (GWFI/GWIT). This paper will review briefly present halogen-containing PA technologies and issues in electrical/electronic application. More importantly, recent advances in halogen-free PA will be presented. Special emphasis will be on the use of aluminum diethylphosphinate, melamine polyphosphate, melamine cyanurate, red phosphorus, ammonium sulfamate, Firebrake@Zinc Borates, boron phosphate, silicone, and talc in PA. Mode of actions of these flame retardants in PA will be discussed as well.

11:30-12:00

Environmentally Safe Flame Retardant Materials

Ravi Mosurkal, Jason W. Soares, Romy Kirby, Wayne S. Muller, U.S. Army Natick Soldier Research Development and Engineering Center Natick, MA

Jayant Kumar, Center for Advanced Materials, University of Massachusetts Lowell Lowell, MA

Halogen-based flame-retardant (FR) polymers and additives have been a cost-effective solution for FR applications. However, there is now an increased global emphasis on discontinuing the use of halogenated compounds due to the release of toxic gases upon combustion that is harmful to both humans and the environment. Thus, there exists the need to develop human and environmentally safe, economical polymers with efficient FR properties. We have recently shown that enzymatically and non-enzymatically synthesized polyborosiloxane copolymers have great potential as FR materials. We will present simple eco-friendly synthesis, characterization including thermal properties, surface analysis of char, and the thermal degradation mechanism of the organic-inorganic hybrid siloxane copolymers. Furthermore, we will present data on new siloxane-based nanocomposites.

12:00-12:30

Molecular Dynamics of Backbone Scission in Polyolefins

Stanislav Stoliarov, Department of Fire Protection Engineering, University of Maryland, College Park, MD; **Kenneth Smith**, United Technologies; **Morgan Burns**, University of Texas at Austin; **Phillip Westmoreland**, North Carolina State University; **Richard Lyon**, Federal Aviation Administration; and **Marc Nyden** National Institute of Standards and Technology

The past work on development and application of classical molecular dynamics (MD) to simulation of chemical reactions is reviewed. The next generation approach to reactive MD called

RxnMD is introduced. In both the old and new methodologies, potential energy surfaces of chemical reactions are constructed from functions and parameters of a traditional (non-reactive) force field. However, rather than predicting reactions on the basis of a bond breaking/making algorithm, RxnMD models pre-defined reaction types accurately by smoothly interpolating between non-reactive potential energy terms describing reactants, transition states, and products. The new methodology was applied to a system of ethylene oligomers of various degrees of polymerization. The results indicate that the size of the molecule is clearly a factor affecting its stability. Thus, at least for certain types of reaction, the knowledge of kinetics obtained from the studies of small gas-phase molecules is not directly applicable to polymer degradation.

12:30-1:30 Lunch



Session II: Halogen and Non-Halogen Flame Retardants

Chairperson: Marc Nyden, National Institute of Standards and Technology

1:30-2:00

A New Sustainable Polymeric Fire Safety Solution for Thermoplastics and Elastomers

Kumar G. Kumar, Albemarle Corporation

Albemarle is introducing its new generation of High Performance Polymeric flame-retardants. Designed for use in a broad range of plastics, this break-through technology yields products that can be tailored to offer a unique set of physical and flame retardant properties in a “single-package” solution. Thanks to their non-bio accumulative, non-toxic and excellent recyclability profiles, these products are ideal candidates for an industry striving for more environmentally friendly and sustainable fire safety solutions.

2:00-2:30

Polymeric Flame Retardants

S. Levchik, ICL-IP America, NY; **P. Georlette, Y. Bar-Yaakov, Ita Finberg, Yaniv Hirschsohn**, 2ICL-IP, Beer Sheva, Israel

Polymeric flame retardants are sustainable products in the view of many national and international human health and environmental regulations. This presentation will overview existing and new polymeric bromine and phosphorus based flame retardants. Special attention will be given to new applications with the focus on physical properties and safety of use of these flame retardants thanks to their high thermal stability and excellent permanence in the polymers.

2:30-3:00

Halogenated Dioxasiloles as Precursors to Flame Retardant Polymers

Bob A. Howell and **Young-Jun Cho**, Center for Applications in Polymer Science and Department of Chemistry Central Michigan University, Mt. Pleasant, MI

Certain five-membered dioxaheterocycles (heteroatoms may be P,Si,S,etc.) contain a strained carbon-carbon bond which may undergo homolytic thermolysis at modest temperatures to generate a diradical capable of initiating vinyl polymerization. If substituents contain flame retarding moieties this represents a convenient method

for imparting flame retardancy to a polymeric material. One such heterocycle is 2,2-diphenyl-4,4,5,5-tetra(3,5-dibromophenyl)-1,3-dioxo-2-silole. This compound may be prepared by treatment of a multibrominated precursor diol with diphenyl-chlorosilane. It may be used to generate oligomers/polymers with flame retardant properties.

3:00-3:30 Coffee

Chairperson: Charles Wilkie, Marquette University

3:30-4:00

Flame Retardant Synergies with Organic Phosphinates

Wolfgang Wanzke, Elke Schlosser, Sebastian Hoerold, Bernd Nass, Clariant Produkte, Deutschland; BU Additives, Development Flame Retardants, Gersthofen, Germany

Fire Retardants based on organic metal phosphinates were fully commercialized in 2004, representing a new class of halogen free systems offered in the market. The main area of application was glass fiber reinforced polyamides at that time. In the past six years a lot of other uses, especially in engineering plastics and elastomers were developed. Flame retardant polyester resins is the newest market segment with extended use of phosphinates in a variety of compounds. The electrical and electronics industry recognized and appreciated the property profile of phosphinate based polyesters as a replacement for established FR materials. More applications including adhesives and thermosets have been added as well. As shown by previous analytical studies, phosphinates can work by different mechanisms making them versatile in polymer specific recipes. Showing a significant portion of gas phase action when used on their own, a shift to more solid state activity by char formation can be observed when using nitrogen containing synergists and/or char stabilizing components. The most recent work concerning metal phosphinates in combination with different synergists in thermoplastic and elastomeric applications will be reviewed.

4:00-4:30

Novel Phosphorus-based Flame Retardants for Epoxy Resins and Carbon Fiber Composites: Decomposition Mechanisms and Fire Behavior

Brigit Perret, Bernhard Schartel, BAM Federal Institute for Materials Research and Testing, Berlin, Germany; **Kai StöB, Jan Diederichs, Michael Ciesielski, Manfred Döring,** Institute of Technical Chemistry, Karlsruhe Research Center GmbH, Karlsruhe, Germany; **Johannes Krämer, Volker Altstädt,** Department of Polymer Engineering, University of Bayreuth, Bayreuth, Germany

The flame retarding action of different novel phosphorus-based flame retardants in different epoxy resins and their carbon fiber reinforced equivalents suitable for automotive and aviation industry was investigated. Pyrolysis was studied by means of thermal analysis (thermogravimetry, TG), evolved gas analysis (TG-FTIR) and condensed phase analysis (linkam hot stage cell coupled with FTIR). The fire behavior was studied by means of reaction to a small flame (flammability, LOI and UL 94) and forced flaming behavior (cone calorimeter). All flame retarded epoxy resins with and without carbon fibers show significant better results in forced flaming behavior and flammability compared to the non-protected epoxy resins. Interactions between flame retardant and epoxy matrix were found and mechanisms and efficiency of the flame retardants strongly depends on the epoxy matrix in which they are inserted. Furthermore the influence of the carbon fibers during combustion is of great importance.

4:30-5:00

Phosphorus-containing Syrenic Monomers for the Preparation of Flame Retardant Polymeric Materials

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

Effective phosphorus flame retardants are attractive replacements for organohalogen compounds which have come under increasing scrutiny because of their tendency to bioaccumulate when released into the environment and to pose potential health risks. In this instance, five new phosphorus-containing styrene monomers have been prepared, fully characterized, and used to generate styrene copolymers containing various levels of flame-retarding comonomer. The effectiveness of the comonomers in imparting flame retardance to the copolymers is reflected in the char yields upon thermal degradation and decreased peak heat release values when subjected to combustion.

5:00-5:30

Materials in Navy Applications

Usman Sorathia, Naval Surface Warfare Center, Carderock Division

There is a need for new bedding component materials in the U.S. Navy vessels. The current bedding components and their specifications are being upgraded to permit newer commercially available materials. There is a concern for fire, smoke, and toxicity of these materials. In order to permit these new materials in the Navy construction, fire performance criteria are being established for many applications. This paper will discuss such criteria for bedding components, including mattress, blankets, and pillows.

5:30-6:00

Morphologically Unique Magnesium Hydroxide – Preparation and Performance in Halogen-free Flame-retardant EVA

Lijuan Li^a, Zhiqi Liu ^{a,b}

a. Key Laboratory of Salt Lake Resources and Chemistry, Qinghai Institute of Salt Lakes, CAS, Qinghai, Xining810008, China;

b. Graduate University, CAS, Beijing100049, China;

Magnesium hydroxide as an ecologically sound flame retardant has been widely used to fire-retard many polymers for its high decomposition temperature, smoke suppression, non-toxicity and ability to neutralize with acidic gases from polymer combustion. The shape, particle size and size distribution of magnesium hydroxide have a great influence on the flame retardancy, smoke suppression and mechanical properties of a flame-retardant polymeric composite. In this paper, the magnesium hydroxide with special morphological features was prepared by hydrothermal modification using technical magnesium hydroxide as the raw material. The influence of the morphology-transforming agent and hydrothermal conditions on the magnesium hydroxide shape and size distribution was investigated. The mechanical properties, flame property and electrical property of the EVA compounds are shown to be remarkably improved by means of adding such morphologically unique magnesium hydroxide. The SEM images and the particle size distribution of magnesium hydroxide obtained under different morphology-transforming agent and hydrothermal conditions. The EVA compounds and their composition. Mechanical properties, flame property and electrical property of EVA and composites.

6:00-7:30 Reception

May 25, 2010



Session III: Nanocomposites and Flame Retardancy

Chairperson: Kelvin Shen, Rio Tinto Minerals

8:30-9:00

Time to Ignition of Nanocomposites an Unpredictable Puzzling Trend to be Understood

A. Fina, A. Alongi, D. Battezzore, G. Camino, Politecnico di Torino, Alessandria site, Alessandria, Italy

Although the performance of polymer nanocomposites in forced combustion tests is well known and discussed, a limited knowledge is so far available on fundamental mechanisms beyond the bare results. In particular, variable trends for time to ignition (TTI) of nanocomposites have been reported: a reduction of TTI compared to neat polymers is often observed, but the opposite effect is also reported in many cases.

A number of proposals have been made to interpret reduction of TTI in nanocomposites when it occurs, such as thermal instability of nanofiller organic modifiers and/or of polymer-nanoparticles compatibiliser, enhanced radiant heat absorption, improved thermal conductivity as well as viscosity increase hindering convective flow in the molten polymer. However, none of the interpretations supplied so far in the literature, results in a general rule and no solid experimental evidences are reported. The results of a thorough investigation on ignition, by the measurement of ignition temperatures related to thermal behaviour of polymers and nanocomposites, will be reported.

9:00-9:30

New Features in Flame Retarding PA-6 with Bromine-based Additives in the Presence or Absence of Layered Silicates

Menachem Lewin^{1*}, Jin Zhang¹, Eli Pearce¹, Mauro Zammarano²
1. Polytechnic Institute of NYU, 6 MetroTech Center, Brooklyn, NY 11201.

2. Building and Fire Research Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-8665, USA

*Correspondence to: Professor M. Lewin, E-mail: mlewin@duke.poly.edu.

Tel.: +1-718-260-31632.

Several new features encountered during the flame retardation of polyamide 6 (PA6) with bromine-based additives are discussed in light of recent results obtained in this laboratory with pentabromobenzyl acrylate (PMA). Bromine FRs were surprisingly found to behave similarly to clay: 1) they decrease PHRR by 2.7% for 1 wt% PMA, as compared to 9.7% for organically layered silicates; 2) the time of ignition for 10 wt% PMA containing PA6 decreases to 39s as compared to 55s for pristine PA6. It is postulated that the bromine-based FRs migrate to the surface during pyrolysis and form part of the surface barrier during combustion, thus decreasing the thermal conductivity which is responsible for time of ignition. 3) in the presence of 1 wt% organically layered montmorillonite (OMMT), the high ratings obtained with UL-94 are retained along with the 47% decrease in PHRR. Increasing OMMT to 3 and 5 wt% brings about a drastic decrease in FR ratings. This is accompanied by a strong increase in the size and mass of drops formed in the UL-94 test, indicating an increase in density and viscosity of the pyrolysing melt; 4) the use of Na+MMT instead of OMMT retains the FR ratings, a high time of ignition and the mechanical properties.

9:30-10:00

Investigation on Synergistic Effects on Fire Retardancy Using Submicronic Boehmite and Kaolinite

José-Marie Lopez Cuesta, Sayyed-Hossein Vahabi, Claire Longuet, Rodolphe Sommier, Pôle Matériaux Polymères Avancés, Centre des Matériaux, Ecole des Mines d'Alès, Alès, France

Submicronic kaolinite and boehmite are investigated as fire retardant fillers in PC, PC/PMMA and PC/ABS alloys. Various combinations with conventional flame retardant such as phosphates and hydrated fillers are studied in order to achieve synergistic effects. A particular attention is focused on the influence of interfacial treatments and modifications of kaolinite and boehmite on the thermal degradation of the above polymers. Nanocomposites are elaborated using a microcompounder and characterized using scanning and transmission electron microscope, thermogravimetric analysis, X-Rays diffractometry, cone calorimeter, combustion micro-calorimeter, epi-radiateur test, and limiting oxygen index. Results show that water contained in the submicronic fillers enhances the thermal degradation of polycarbonate. This can be reduced by the incorporation of PMMA as minor component in PC/PMMA blends. Moreover, an intercalation process involving DMSO, methanol and dodecylamine is also carried out on kaolinite. After polymerization of kaolinite/Methyl MethAcrylate compositions, the resulting kaolinite/PMMA nanocomposites are incorporated in PC. An improvement of fire behaviour and transparency is noticed in comparison with PC/PMMA blends produced by melt blending.

10:00-10:30 Coffee

Chairperson: Marcelo M. Hirschler, GBH International

10:30-11:00

(Chemically Modified) Nanoparticles for Flame Retarded Polymeric Materials

Gaelle Fontaine, Serge Bourbigot, Equipe Procédés d'Elaboration des Revêtements Fonctionnels (PERF), Ecole Nationale Supérieure de Chimie de Lille (ENSCL), France

The talk will investigate the reaction to fire of flame retarded polymers containing novel functionalized nanoparticles. Those nanoparticles are incorporated in various polymers including thermoplastic polyurethane (TPU), polylactic acid (PLA), and epoxy resin containing flame retardants or not. The synthesis of chemically modified particles like carbon nanotubes (MWNT), polyhedral silsesquioxanes (POSS), or graphene will be presented. The effect of the chemical modifications will be examined in terms of dispersion and of performance. The mechanisms of action as well as synergistic aspects between the nanoparticles and the flame retardant will be also investigated and discussed during the talk.

11:00-11:30

Synthesis, Thermal Behavior and Combustion of the Novel UV-Cured Flame Retardant Nanocomposite Coatings

Yuan Hu, Weiyi Xing, Lei Song, State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui, China

The novel organo-phosphorus acrylate containing acid and carbon source (BTP) was synthesized successfully. Meanwhile the novel UV-cured nanocomposite coatings containing organically modified alpha-zirconium phosphate (OZrP) was prepared through UV irradiation, and the synergistic effect of OZrP based on UV-cured flame retardant nanocomposite coating was also studied. The structure was characterized by FTIR, ¹H NMR, XRD and TEM. The combustion properties of the cured films were evaluated by LOI, MCC and cone calorimeter. Thermal behavior and degradation of the cured films were studied by TGA, and TGA-IR. The LOI value for BTP was 39. The

char yield was 36% at 800°C. The results of XRD and TEM indicated that an intercalated structure or exfoliated structure was formed. The results of MCC revealed that the HRR of the films decreased with the contents of organic α -ZrP (OZrP). The TGA results indicated that with increasing the contents of OZrP, the char yields of UV-cured films were enhanced. Thermal stability of flame retardant coating could be improved by adding OZrP. Cone tests indicated that the addition of OZrP in flame retardant systems could reduce PHRR by 29%.

11:30-12:00

Characterizing Particle Emissions from Burning Polymer Nanocomposites

Marc R. Nyden and **Nathan D. Marsh**, Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD

Carbon nanotubes (CNT) and fibers (CNF) may pose significant health and environmental risks due to their small size and ability to interact with biological molecules. It has recently been suggested that the morphology of the nanoparticles may have a special influence on the above risks. The health risks increase with in exposure to fire or other forms of intense energy. In an effort to gain a better understanding of the potential hazards associated with the commercialization of polymer nanocomposites, we have undertaken an investigation into the nature of the particles released when these materials are burned. The first question we hope to answer is whether significant amounts of nanoscale additives are released (in addition to soot, which is a ubiquitous byproduct of gas phase combustion) when polymer nanocomposites are burned.

12:00-12:30

An Efficiently Flame-Retardant Polycarbonate System Prepared from a Novel Silicon- and Phosphorus-Containing Flame Retardant and Montmorillonite

Zhi Hu, **Yu-Zhong Wang**, Center for Degradable and Flame-Retardant Polymeric Materials (ERCEPM-MoE), College of Chemistry, State Key Laboratory of Polymer Materials Engineering, Sichuan University, China

A novel silicon- and phosphorus-containing flame retardant, P-PSi, was used to prepare flame-retardant polycarbonate (PC) together with montmorillonite (MMT) via melt blending. The resulting flame-retardant PC/P-PSi/MMT organic-inorganic hybrids have good comprehensive properties. The thermal degradation behavior and flame retardancy of those hybrids were investigated with TGA, limiting oxygen index (LOI), vertical burning test (UL-94), and cone calorimeter. The LOI value of the flame-retardant PC systems could reach 32.8 when the content of P-PSi was 5wt%. When 2wt% MMT was added into the hybrids containing 5wt% P-PSi, the UL-94 rating reached V-0. Various cone parameters also showed that PC/P-PSi/MMT hybrid is a good flame retardant system. A possible flame retardant mode of MMT was studied via the dynamic rheological properties and the morphology of the char of samples obtained after the LOI test and the cone calorimeter test.

12:30-1:30 Lunch

Chairperson: Richard Lyon, Federal Aviation Administration, NJ

1:30-2:00

Recent Advances In Nanocomposites in Fire Retardancy

Charles A. Wilkie, Department of Chemistry and the Fire Retardant Research Facility, Marquette University, WI 53201

For the past several years, my laboratory has studied the utilization of nanocomposites in fire retardancy; this has included investigations of the effect of the various organic modifications on montmorillonites, layered double hydroxides and other clays; the use of carbon nanotubes; the processes by which these may be effective; potentially synergistic combinations of nano-dimensional materials with other fire retardant materials, etc. In this talk, I will discuss new work coming out from this laboratory and its implications for the future.

2:00-2:30

Non-halogenated Flame Retardant Formulations for Biodegradable Polymer Blends*

S. Pack, **M. Rafailovich**, Department of Materials Science, SUNY at Stony Brook, NY 11794-2275
N. Muir, Uniondale High School, Uniondale, NY

Recently a great deal of effort has been placed in developing biodegradable blends to replace standard polymer blends in as many applications as possible. Of concern through, have been applications where the polymers had to meet specific standards for being flame retardant. In this case it was feared that as the polymer degrades, the FR formulations are released into the soil where they can leach into nearby water supplies. As a result, the development of new and environmentally safe formulations for biodegradable materials was required. Here we present several options, using functionalized clays in combination with other nanoparticles which have been effective in rendering biodegradable; polymer blends flame retardant with UL-94 VO designation.

* Supported in part by the NSF-MRSEC program

2:30-3:00

Morphology, Thermal Stability, and Flammability Behavior of Polymer Composites Coated with Graphite Nanoplatelets Nanopapers

Yong Tang, **Jinfeng Zhuge**, **Jihua Gou**, Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL

In this study, a hybrid nanopaper consisting of graphite nanoplatelets (GNP) and ammonium polyphosphate (APP), has been fabricated through the papermaking process. The as-prepared hybrid nanopaper was then coated onto the surface of glass fiber reinforced polymer matrix composites through resin transfer molding (RTM) process. The morphologies of hybrid nanopapers with and without the polymer resin were characterized with scanning electron microscopy (SEM). It can be seen that the nanopaper had a porous structure and the APP particles were homogeneously dispersed within the hybrid nanopaper. The polymer resin penetrated the entire nanopapers under a high-pressure compressed air system. The thermal decomposition behavior of hybrid nanopapers and nanocomposites was studied with real-time thermogravimetric analysis/flourier transform infrared spectrometry (TGA/FTIR). The test results indicate that the addition of APP increased the char residues of the nanocomposites. The fire retardant performance of composite laminate coated with hybrid nanopaper was evaluated with cone calorimeter test using a radiated heat flux of 50 kW/m². The cone test results indicate that the peak heat release rate (PHRR) decreased dramatically in the GNP-APP nanopaper coated composite laminates. The combustion behaviors of these samples were also examined by microscale combustion calorimetry (MCC). The HRR obtained from MCC was consistent with the results obtained from cone calorimeter test.

3:00-3:30 Coffee break



Session IV: Consumer Focus and Industrial Applications

Chairperson: Guenther Byer, Kabelwerk Eupen AG, Belgium

3:30-4:00

Intumescence for the Flame Retardancy of Polylactide

Serge Bourbigot, Gaëlle Fontaine and Sophie Duquesne, Equipe Procédés d'Elaboration des Revêtements Fonctionnels (PERF), Ecole Nationale Supérieure de Chimie de Lille, France

Poly(lactide) (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. In numerous applications of PLA, flame retardancy is very often required. Intumescence is a method to provide flame retardancy to polymers and it will be investigated for PLA. Novel systems will be examined including formulations based on 'green' products. Synergistic effects are observed using nanoparticles and they will be discussed in the talk. Finally mechanism of action will be also examined.

4:00-4:30

Intumescent Coatings for the Fire Protection of Steel - Influence of Inorganic Fillers on Char Structure

Sophie Duquesne, Serge Bourbigot, Equipe Procédés d'Elaboration des Revêtements Fonctionnels (PERF), Ecole Nationale Supérieure de Chimie de Lille, France

Intumescent coatings are widely used in the field of fire protection of steel structures due to their high efficiency and easy of process. Their composition is usually based on a combination between ammonium polyphosphate (APP), pentaerythritol and melamine. Moreover, in most of the cases, inorganic fillers such as for example titanium dioxide or zinc borate are added in the formulation for various reasons. It has been demonstrated that APP is very reactive and can react with most of those inorganic fillers leading to thermally stable phosphates. The objective of this study is to investigate how the presence of those fillers will affect the formation and the structure of the intumescent protective char. The influence of various inorganic fillers on the mechanism of intumescence will be reviewed, followed by a discussion on how to select the fillers for optimal properties.

4:30-5:00

Preparation of Ammonium Polyphosphate with Crystal Form type-V from Phosphorus Acid

Gousheng Liu, School of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China

As halogen-free and intumescent flame retardant, ammonium polyphosphate (APP) has been extensively applied in the field of flame retardant materials in recent decades. In the six different kinds of crystal forms from form-I to form-VI, more attentions have been paid to form-I and form-II at home and abroad. Except form-I and form-II, form-V APP has better stability. Until now, less study has been found for APP with crystal form-V. In this study, APP with crystal form-V has

been prepared. Phosphorus acid is the main raw material, melamine is the condensing agent. The two chemicals are mixed, heated and melted at high temperature under a dry ammonia atmosphere. Some effects, such as chemical ratio, heating temperature, time of heating and condensing, flow and pressure of dry ammonia atmosphere are investigated. Structural characterization of prepared product is carried out through XRD, SEM, and IR. Compared with the patterns of industrial-grade APP with crystal form-I, form-II, form-V and cited from literature, it is identified that the prepared product is APP with crystal form-V.

5:00-5:30

New P-based flame retardant for flexible polyurethane foams

Alexander Koenig, Polymers and Additives Environmental Engineering, Fraunhofer Institut für Chemische Technologie, Joseph-von-Fraunhofer Str. 7, 76327 Pfinztal

The chemical nature of the flexible polyurethane foams (PUF), their high air permeability and the high inner surface area of the foam structure cause this material to be highly flammable. In this study, the influencing variables on the burning behavior of flexible PUF are investigated. Additionally the synthesis, formulation, characterization and testing of a new Phosphorus flame retardant methyl-DOPO 9,10-Dihydro-9-oxa-methylphosphaphenthren-10-oxid in flexible PUF with low density is performed. The new flame retardant shows an excellent flame retarding behavior by acting mainly in the gas phase. Here the vaporization of methyl-DOPO occurs in the same temperature region like the depolymerization of the urethane and the bisubstituted urea groups during pyrolysis of the foam. Furthermore TG-MS measurements revealed the release of high concentrations of low molecular species like HPO, CH₃PO or PO₂ in the mentioned temperature region. This species are able to scavenge the H- and OH-radicals in the radical chain mechanism of the flame leading to a significant increase of the CO/CO₂ ratio during cone calorimeter experiments.

5:30-6:00

Flame Retardant Olefinic Polymers Containing Metal Hydroxides - Fire Performance vs. Other Properties Optimization by Surface Modification

Tong Chen, Alex Isarov, J. M. Huber Corporation, Fairmount, GA 30139

Metal hydroxides such as alumina trihydrate (ATH) and magnesium hydroxide (MDH) are used to achieve low-smoke and fire resistant polymer compositions, which often are halogen-free. The requirement for high loading levels when using the metal hydroxides continues to present concerns and challenges for industrial applications due to undesirable reduction in mechanical properties and processing ease. Efforts have been made to design the metal hydroxide products such that the property or performance loss as related to the high loadings may be controlled to an acceptable range, while at same time, the fire performance is sustained or even enhanced. One means to achieving such unique metal hydroxide products is to chemically modify the surface of the hydroxides. This paper will discuss recent results by J. M. Huber Corporation in exploiting surface modification of ATH and MDH to enable performance optimization of the fire retardant polyolefins compositions.

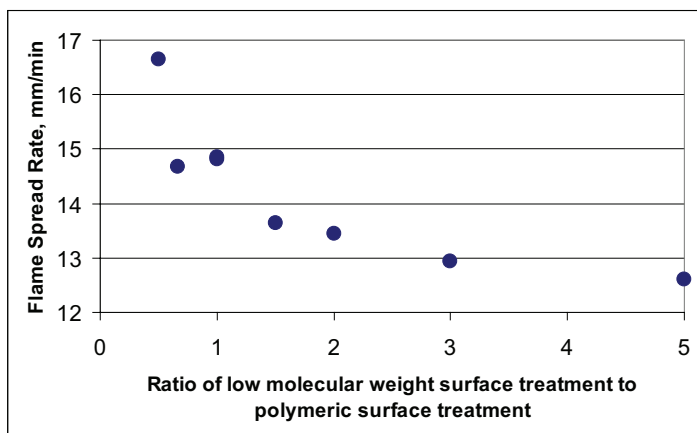


Figure 1. Flame spread rate as a function of the ratio of two components of surface treatment (40% magnesium hydroxide in polypropylene).

May 26, 2010



Session IV: Consumer Focus and Industrial Applications - continued

Chairperson: Serge Bourbigot, Ecole Nationale Supérieure de Chimie de Lille, France

8:30-9:00

Progress with Nanocomposites as a Flame Retardant Concept

Guenter Beyer, Kabelwerk Eupen AG, Belgium

We will report different nanostructured fillers to generate under industrial conditions EVA-, LDPE- and PVC-nanocomposites. An important aspect for PVC as polymer matrix was to avoid the very early degradation of PVC by quaternary ammonium compounds often used in organoclays. The fire performances of the compounds were investigated by Cone calorimeter and TGA under oxidative conditions. Other intercalants than quaternary ammonium compounds were investigated. We will report about the FR properties of different PE compounds with organoclays by extrusion trials. XRD and TEM results will be presented and also the FR properties by cone calorimeter will be reported. In Europe new flame tests are introduced by the European directive CPD (construction product directive). New test results will be presented which indicate the excellent flame retardant properties by nanocomposites which opens the possibility to optimize products.

9:00-9:30

Applications of Micro-scale Combustion Calorimetry to Flame Retardant Textiles Research

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Evaluating and analyzing the performance of flame retardant (FR) textiles is a critical part of research and development of new FR textile products by the industry. The testing methods commonly

used in the industry have significant limitations. Most analytical and testing techniques are not able to measure heat release rate (HRR), the single most important parameter in evaluating the fire hazard of materials. It is difficult to measure HRR of textile fabrics using cone calorimetry because textile fabrics are dimensionally thin samples. The recently developed micro-scale calorimetry (MCC) is able to measure the following flammability parameters for textiles: heat release capacity, HRR, temperature at PHRR, total heat release and char yield using milligram sample size. In this research, we applied MCC to evaluate the flammability of different textile fabrics including cotton, rayon, cellulose acetate, silk, nylon, polyester, polypropylene, acrylic fibers, Nomex and Kevlar. We also studied the textile fabrics and blends treated with different flame retardants. We found that MCC is able to differentiate small differences in flammability of textile materials treated with flame retardants. We were also able to calculate the limiting oxygen index (LOI) using the thermal combustion properties of various textile samples measured by the MCC. The calculated LOI data have yielded good agreement with experimental LOI results. Thus, we conclude that MCC is an effective new analytical technique for measuring textile flammability and has great potentials in the research and development of new flame retardants for textiles. The MCC studies of blend fabrics will also be included.



Session V: Testing and Standardization

Chairperson: Giovanni Camino, Politecnico di Torino, Alessandria, Italy

9:30-10:00

Differences of Polymer Nanocomposites Burning in Horizontal Compared to Vertical Orientation

S.Ukleja, M. McKee, J.P. Zhang, M.A. Delichatsios, Fire Safety Engineering Research and Technology Center, University of Ulster

Although experiments are generally conducted in the cone calorimeter in the horizontal orientation, tests in the vertical orientation can and should be conducted for the case when the final geometry (large-scale) of the materials is vertical and when the material may be melting. This study examines how the sample orientation affects the burning behaviors of a polymer nanocomposite (polypropylene modified with nanoclay, PP+NC) in the cone calorimeter. Tests are conducted at various heat fluxes and a comparative analysis of the results is performed in terms of ignition time, mass loss rate, heat release rate and production of toxic gases (CO, CO₂ and smoke). No dripping occurs in a vertical orientation. Ignition time is twice as long. The transient HRRs are lower. Transient results for the toxic gases are lower. Several causes of these differences are discussed. A numerical model to explain the differences between the orientations is described.

10:00-10:30 Coffee

10:30-11:00

Fire Testing for Code Use: Steiner Tunnel Test Variations

Marcelo M. Hirschler, GBH International

The Steiner tunnel is the fire test most commonly used for regulatory use in the USA. The standard test, ASTM E 84, is quite vague in the explanation of how materials or products need to be mounted

for testing. This has led to tests being conducted, and materials or products being approved, without the proper associated fire safety. This was initially addressed by developing specific variations of the test that applied to wires and cables (for use in plenums), sprinkler pipes, pneumatic tubing and plastic cable raceways. In recent years standard practices have been issued for specimen preparation and mounting of wall/ceiling coverings, pipe and duct insulation, wood products, site-fabricated stretch systems and reflective insulation materials. Other changes have been made, or are in progress, addressing specimen width and thickness. This paper will present an update and indicate areas where added work is still needed.

11:00-11:30

Effects of an Enclosure on Burning Behavior in the Cone Calorimeter

M. Janssens and **C. Gomez**, Southwest Research Institute, San Antonio, TX

This paper reports on a systematic study to evaluate the effects of the enclosure on the burning behavior in the Cone Calorimeter for a range of materials. Specimens of seven materials were tested in air at the same heat fluxes, with and without enclosure. Some preliminary tests were conducted to determine the maximum airflow through the enclosure. The flow was found to be unstable at 180 L/min, which is the high limit on the flow meters, and a flow rate of 150 L/min was used in the experiments. Specimens of seven materials (black PMMA, brominated FRP, carpet, flexible PVC, FR treated and untreated Douglas fir plywood and rigid polyisocyanurate foam) were tested at 50 and 75 kW/m². The effects of the enclosure on ignition time, heat release and smoke production rates were found to be statistically insignificant. Tests could not be conducted at 100 kW/m² to avoid overheating of the enclosure.

11:30-12:00

The Limiting Oxygen Index Test (Revisited)

R.E. Lyon, **M.R. Fullmer**, **S. Crowley** and **R.N. Walters**, Federal Aviation Administration, Airport and Aircraft Safety R&D Division, Atlantic City International Airport, NJ

Heat release rate measurements were made using oxygen consumption calorimetry for several commercial plastics during the standard ASTM D 2863 test to measure the minimum oxygen concentration to support candle-like combustion of plastics/oxygen index. An energy balance at the sample surface for flaming combustion can account for the downward burning rate and extinction condition (limiting oxygen index) in terms of the thermal combustion properties of the material and the effect of oxygen on flame heat flux.

12:00-12:30

New EU regulations for fire safety in railways: comparison with presently existing regulations.

J. W. Mitchell, **F. Schutz**, **S. Collot**, **F-X. Blet**, Rhodia Polyamide, Saint Fons, France

The new regulations for trains in Europe are discussed. This method replaces the previous national regulations concerning fire

and fume. The new regulations appear to be of vital importance to resin manufacturers. The previous French regulations were based on a Fire resistance part "T" using Glow wire and LOI as the main test methods and a Fume/toxicity part "F" using both toxicity and opacity methods. The new norm will have 3 Hazard levels (HL) based on type of transport and an R levels based on the type of applications and the risk. The most critical R levels are discussed for E&E applications. It is estimated that around 80-90% of application use will be covered if HL2 level is actually reached. This paper will compare results and ratings achieved using the old French regulation with new results and draft ratings made in accordance to the new CEN/TS 45545 regulation.

12:30-1:30 Lunch

Chairperson: Manfred Doering

1:30-2:00

Ten Decades of Flame Retardancy Testing at the Forest Products Laboratory

Robert H. White and **Susan L. LeVan-Green**, U.S. Forest Service, Madison, WI

The development or adoption of advances in flammability test equipment played a critical role in facilitating ten decades of FPL research to improve the flammability of wood products. FPL equipment developments include the 1912-15 work of R.E. Prince to expose specimens to constant temperatures to determine the times for ignition, the fire tube apparatus in 1920's, and the 8-ft tunnel in 1950's. In the 1960's, considerable fundamental research was conducted using thermogravimetric and differential thermal analysis. As an early promoter of the use of heat release rate as a measure of relative flammability, FPL developed an apparatus in the 1960's to measure the heat released by a burning material. As better technologies were developed to measure heat release rate, FPL obtained such equipment to continue its efforts to properly measure the potential contribution of wood products to a fire and facilitate the development of new fire-retardant-treated wood products.

2:00-2:15

Heat Release Testing with the OSU Apparatus

Timothy T. Earl, GBH International

For more than 20 years, the Federal Aviation Administration has required certain materials used in the interior of passenger aircraft to meet maximum heat release limits. The prescribed test method utilizes the Ohio State University Rate of Heat Release Apparatus. Since then, the cone calorimeter has become much more common, and interest in the OSU outside of the aviation industry has waned. As a result, many current fire researchers have little knowledge of this instrument which is used as a regulatory tool in a critical application. This paper will discuss the different configurations of the OSU as specified by standards and regulations issued by the FAA, ASTM, and Airbus.

