



Thermal Decomposition of Styrenic Polymers Modified with Covalently Bound P- and N-containing Groups: Analysis of the Gaseous-Phase Mechanism

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Sunday, June 5, 2022

ARRIVAL AND REGISTRATION

2:30 PM REGISTRATION BEGINS

LECTURE SESSION I

Session Chair: Jamie Grunlan, Texas A&M University

3:15 PM OPENING REMARKS

3:30 PM **Alexander Morgan**, University of Dayton Research Institute
Studying Smoldering to Flaming Transition in Polyurethane Furniture Sub-Assemblies: Effects of Fabrics, Flame Retardants, and Material Type **1**

4:00 PM **Mauro Zammarano**, NIST
Fire Barrier Fabrics in Upholstered Furniture: An Obvious Solution to One of the Most Enduring Problems in Fire Safety **2**

4:30 PM BREAK

4:45 PM **Isaac T. Leventon**, NIST
The NIST Material Flammability Database: Experimental Measurements for Fire Model Calibration and Validation **3**

5:15 PM **Morgan C. Bruns**, St. Mary's University
Development of Automated Calibration Tools for Determining Fire Model Input Parameters **4**

5:45 PM **Natallia Safronava**, Federal Aviation Administration
Microscale Combustion Calorimetry and Material Change Similarity **5**

6:15 PM WELCOME RECEPTION

Monday, June 6, 2022

7:00 AM BREAKFAST | 7AM – 10 AM IN THE HOTEL'S ATRIUM

LECTURE SESSION II

Session Chair: Alexander Morgan, University of Dayton Research Institute

8:30 AM **Anteneh Worku**, Pinfa North America
The Road to Flame Retardant Commercialization **6**

9:00 AM **Sabyasachi Gaan**, EMPA, Switzerland
Hybrid Strategies for Improving the Fire Performance of Epoxy Resin Cured With Aliphatic Hardener **7**

9:30 AM **Svetlana Tretsiakova-McNally**, Ulster University, UK
Thermal Decomposition of Styrenic Polymers Modified with Covalently Bound P- and N-containing Groups: Analysis of the Gaseous-Phase Mechanism **8**

Monday, June 6, 2022, cont'd

10:00 AM	BREAK	
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10:45 AM	Sabine Fuchs , Hamm-Lippstadt University of Applied Science, Germany <i>Halogen-Free Styrene Copolymers With Intrinsic Flame Retardant Properties</i>	10
11:15 AM	Jacques A. De Beer , University of Maryland <i>Milligram-scale Flame Calorimetry: Development of a Pyrolyzer System used for Accurate Emulation of the Burning Behavior of Non-thermally Thin Samples</i>	11
11:45 AM	END AM SESSION, LUNCH ON YOUR OWN	
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4:30 PM	Bernhard Scharfel , BAM Federal Institute for Materials Research and Testing, Germany <i>Non-vegan Flame-Retardant (Adjuvants in) Biocomposites</i>	13
5:00 PM	Helge-Otto Fabritius , Hamm-Lippstadt University of Applied Sciences, Germany <i>Mechanistic Investigations of Wasp Nest Papers: Towards Environmentally Compatible Flame-Retardant Concepts for Synthetic Materials</i>	14
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Tuesday, June 7, 2022

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11:15 AM	Yury Brusentsev , Åbo Akademi University, Finland <i>Sulfenamides, Sulfinamides and Sulfonamides as Flame Retardants – Similarities and Differences in the Mechanism of Action</i>	20
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LECTURE SESSION V		
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4:30 PM	Conor McCoy , University of Maryland <i>Modeling of Flame Spread on Charring, Non-charring, and Flame Retardant Polymers In UL-94V</i>	22
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5:45 PM	Vitus Hupp , Bundesanstalt für Materialforschung und -prüfung (BAM), Germany <i>Adhesive Tapes in Bonded Materials - Fire Risk or Protective Layer?</i>	24
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Wednesday, June 8, 2022

7:00 AM BREAKFAST | 7AM – 10 AM IN THE HOTEL'S ATRIUM

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9:30 AM	Igor Jordanov , Ss. Cyril and Methodius University, Macedonia <i>Lignin-Based Multilayer Nanocoating for Flame Retardant Cotton Fabric</i>	28
10:00 AM	BREAK	
10:15 AM	Bob A. Howell , Central Michigan University <i>Iron Additives as Alternatives to Antimony Oxide in Flame-Retardant Formulations</i>	29
10:45 AM	Hatsuo Ishida , Case Western Reserve University <i>Polybenzoxazines: Development of Very High Performance Noncombustible Polymers without the Need of Flame Retarding Additives</i>	30
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LECTURE ABSTRACTS

Fire and Polymers

June 5-8, 2022

Embassy Suites By Hilton Napa Valley

Napa, CA

1.

Studying Smoldering to Flaming Transition in Polyurethane Furniture Sub-Assemblies: Effects of Fabrics, Flame Retardants, and Material Type

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²University of Maryland, College Park, Maryland, United States.

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The transition from smoldering to flaming was studied on fabric, batting, and foam assemblies via an electric spot-ignition source of similar intensity to a cigarette. The materials studied included four different fabrics (cotton, polyester, cotton/polyester blend, flame retardant cotton/polyester blend), two types of batting (cotton, polyester), and three types of polyurethane foam (non-flame retardant, flame retardant by FMVSS 302 testing, flame retardant by BS5852 testing). The results from testing found that materials highly prone to smoldering could propagate smoldering into foams and lead to ignition, whereas materials that tended to melt back from the ignition source did not. Flame retardant fabrics or foam can and do prevent the transition from smoldering to flaming provided sufficient levels of flame retardants are incorporated in the upholstery fabric or foam. Studies on the mechanism of transition to flaming will be discussed, along with heat release measurements on the studied material combinations.

2.

Fire Barrier Fabrics in Upholstered Furniture: An Obvious Solution to One of the Most Enduring Problems in Fire Safety

Mauro Zammarano, Ickchan Kim, Matthew F. Bundy, Rick D. Davis

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Upholstered Furniture (UF) fires persists as the leading cause of residential fire deaths in US, closely followed by cooking fires. About two thirds of UF fire deaths occur after flashover. Recently, regulations introduced in several US states banned or severely limited the use of flame retardants.

The “Low Heat Release Upholstered Furniture” project at the Fire Research Division (FRD) of National Institute of Standards and Technology (NIST) conducts research aimed at helping US industries’ efforts to reduce the fire losses associated with UF fires [1]. NIST studies demonstrated that, in a furnished compartment containing commercial UF, fire barrier fabrics can delay the time to flashover by over 14 min (from approximately 7 min to 21 min) and significantly increase the time for safe egress time and likelihood for fire fighters to prevent flashover occurrence. Noticeably, this decrease in fire hazard was achieved with no chemical fire retardants in the polyurethane foam, cover, barrier fabric or any other component of the UF.

In this presentation, new chair mockup tests with high performance fire barrier fabrics will be discussed. Fire barriers include oxidized polyacrylonitrile and polysilicic based fabrics. These data will be used to identify possible emerging technologies in fire barriers and expand our set of data to further support the ability of the Cube test, a NIST-developed cone-calorimeter based test, to predict full-scale fire performance of UF [2].

[1] <https://www.nist.gov/el/fire-research-division-73300/flammability-reduction-73304/low-heat-release-upholstered-furniture>

[2] Mauro Zammarano, Fire Performance of Upholstery Materials: Correlation between Cube Test and Full-Scale Chair Mock-Ups, NIST TN 2194, <https://doi.org/10.6028/NIST.TN.2194>

3.

The NIST Material Flammability Database: Experimental Measurements for Fire Model Calibration and Validation

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The National Institute of Standards and Technology (NIST) is developing a series of experimental and analytical tools to allow for: (a) calibration of the material properties used as inputs to fire models and (b) the validation of their ability to predict flammability response across a range of configurations and scales (i.e., 0D thermal decomposition of mg-scale samples, 1D gasification and burning of g-scale/coupon-sized slabs, and 2D flame spread over 2.45 m walls). Initial tests have characterized the burning behavior of 17 unique materials (synthetic polymers and copolymers, fiber-reinforced composite materials, porous polymer foams, and natural- and engineered-wood-products) with a wide range of chemistries and burning behaviors (e.g., char formation, sooting tendency, and structural deformations). This presentation provides an overview of the systematic methodology by which these experiments are performed, the measurement data obtained in each experiment, and the infrastructure and metadata needed to maintain this information in a unified database.

4.

Development of Automated Calibration Tools for Determining Fire Model Input Parameters

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Computational fire models such as the Fire Dynamics Simulator have proven to be highly effective at predicting the transport of smoke and heat in building fire scenarios. However, application of these models for predicting fire growth requires the specification of a relatively large number of material properties. Much work has been done to demonstrate methods for estimating these required properties from milligram and gram scale tests, but the analysis of this small-scale data requires a significant amount of human effort. As there are a vast array of flammable polymers being used in our built environment, the determination of these material properties presents a significant challenge. In order to streamline this process, a suite of automated computational tools is being developed. This talk will describe the design and demonstrate the application of these tools for analyzing thermogravimetric analysis, microcombustion calorimetry, and differential scanning calorimetry data of several polymeric materials.

5.

Microscale Combustion Calorimetry and Material Change Similarity

Natallia Safronava, Richard E. Lyon and Richard N. Walters

Federal Aviation Administration

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Small changes in the composition of certified aircraft cabin constructions are often necessitated by the unavailability, performance characteristics, or environmental regulation of the original constituents-requiring costly recertification of all constructions and assemblies containing these constituents (e.g., adhesives, films, fibers, resins, thermoplastics, coatings, pigments, potting compounds, etc.). In response to this issue, the FAA in cooperation with the aviation industry, developed a microscale method and parameter to measure and compare the intrinsic flammability of constituent materials at the 10 milligram scale. This microscale test method and combustion parameter were codified as ASTM D7309-21b Standard Test Method for Determining Flammability Characteristics of Plastics and Other Combustible Solid Materials Using Microscale Combustion Calorimetry/*MCC*. The *MCC* combustion parameter called the fire growth capacity/*FGC*, includes ignitability and heat release, and was derived from a continuum-level unsteady burning model*. In this paper we present an empirical microscale/*FGC* criterion for flammability of substitute components of aircraft cabin materials that will provide similar 14 CFR 25 fire performance in bench scale tests. In particular, we demonstrated that the relative change in *FGC* of a substitute component should be similar to the expected variation of fire test results of cabin materials at the 95% confidence level.

*R.E. Lyon, N. Safronava, S. Crowley and R.N. Walters, A Molecular-Level Fire Growth Parameter, *Polymer Degradation and Stability*, **186**, 109478 (2021).

6.

The Road to Flame Retardant Commercialization

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Thousands of flame retardant additives, reactives and resins have been discovered and evaluated in academic, government and industry labs over the past several decades. However, only a low percentage has been successfully commercialized. This paper will go through steps and hurdles that a new FR molecule/formulation/idea has to go through before it is commercial. The paper is not a detailed deep drill of each step but will show some critical considerations in discovery, development and commercialization phases. FR R&D is a multidisciplinary effort and requires an all hands on deck approach and collaboration throughout the “idea to commercialization” process. The paper will attempt to bring industry, academia and regulatory bodies to a common understanding of the challenges that each team has to overcome to deliver a flame retardant product that has FR performance while keeping a balance of properties of end-user product, cost and health and environmental aspects.

7.

Hybrid strategies for improving the fire performance of epoxy resin cured with aliphatic hardener

Aurelio Bifulco², Sabyasachi Gaan^{1,*}

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The use of aliphatic amines as hardeners is preferable over the toxic aromatic amines, however, their incorporation increases the flammability of the resin ¹. This presentation will summarize different hybrid strategies (Figure1) which we have recently developed to flame retard bisphenol A diglycidyl ether (DGEBA) resin cured with a cycloaliphatic amine. The synthesis of in-situ sol-gel silica nanoparticles in the epoxy resin followed by incorporation of two DOPO based flame retardants in combination with other synergists or the use of humic acid and ammonium polyphosphate, could help achieve non-dripping V0 classification in UL 94 tests with low phosphorous loadings (e.g. 1, 2 wt%) ²⁻⁵. The formation of a hybrid silica-epoxy network guarantees a better dispersion of more polar additives in the hydrophobic resin, leading to tailored interphases. These strategies enable to boost the flame retardancy of the matrix, without compromise in mechanical and thermal properties of the composites.

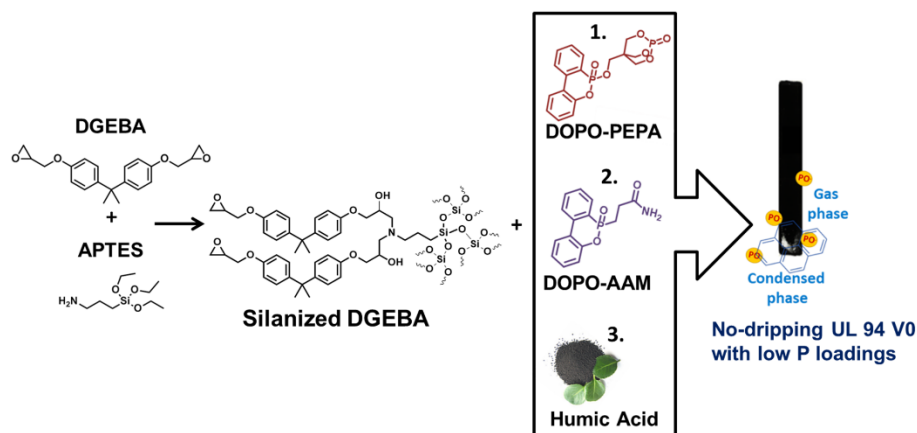


Figure 1. Hybrid routes for flame retardant improvement of epoxy systems

References

1. Mestry, S.; Mhaske, S. T., Synthesis of epoxy resins using phosphorus-based precursors for flame-retardant coating. *J. Coat. Technol. Res.* **2019**, *16* (3), 807-818.
2. Branda, F.; Bifulco, A.; Jehnichen, D.; Parida, D.; Pauer, R.; Passaro, J.; Gaan, S.; Pospiech, D.; Durante, M., Structure and Bottom-up Formation Mechanism of Multisheet Silica-Based Nanoparticles Formed in an Epoxy Matrix through an In Situ Process. *Langmuir* **2021**, *37* (29), 8886-8893.
3. Bifulco, A.; Parida, D.; Salmeia, K.; Lehner, S.; Stämpfli, R.; Markus, H.; Malucelli, G.; Branda, F.; Gaan, S., Improving Flame Retardancy of in-situ Silica-Epoxy Nanocomposites cured with Aliphatic Hardener: Combined effect of DOPO-based flame-retardant and Melamine. *Composites Part C: Open Access* **2020**, *2*.
4. Bifulco, A.; Parida, D.; Salmeia, K. A.; Nazir, R.; Lehner, S.; Stämpfli, R.; Markus, H.; Malucelli, G.; Branda, F.; Gaan, S., Fire and mechanical properties of DGEBA-based epoxy resin cured with a cycloaliphatic hardener: Combined action of silica, melamine and DOPO-derivative. *Mater Design* **2020**, *193*, 108862-108862.
5. Venezia, V.; Matta, S.; Lehner, S.; Vitiello, G.; Costantini, A.; Gaan, S.; Malucelli, G.; Branda, F.; Luciani, G.; Bifulco, A., Detailed Thermal, Fire, and Mechanical Study of Silicon-Modified Epoxy Resin Containing Humic Acid and Other Additives. *ACS Applied Polymer Materials* **2021**.

8.

Thermal Decomposition of Styrenic Polymers Modified with Covalently Bound P- and N-containing Groups: Analysis of the Gaseous-Phase Mechanism

Svetlana Tretsiakova-McNally^{1,*}, *Paul Joseph*², *Aloshy Baby*¹, *Doris Pospiech*³, *Eileen Schierz*³, *Albena Lederer*³, *Malavika Arun*²

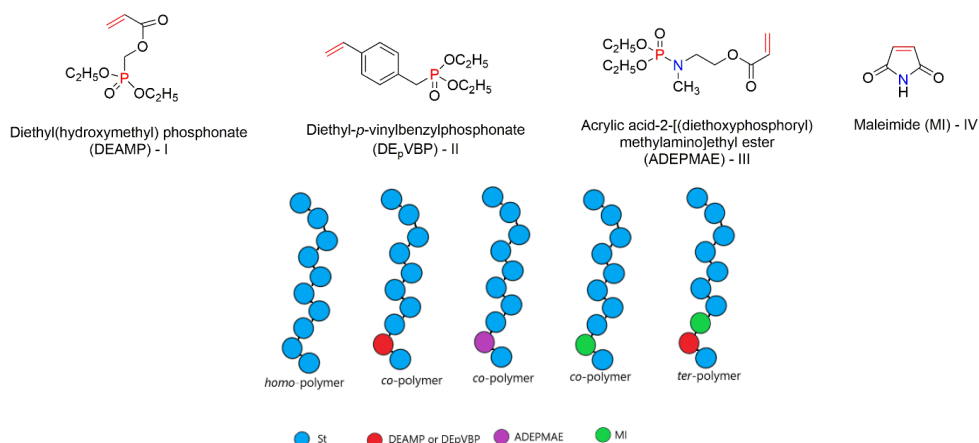
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Through the present study, we have modified polystyrene chains by chemically binding nominal amounts of P- and/or N-containing monomers *via* a free radical polymerization. The selected monomers included: diethyl(hydroxymethyl)phosphonate (DEAMP), diethyl-*p*-vinylbenzyl phosphonate (DEpVBP), acrylic acid-2-[(diethoxyphosphoryl)methylamino]ethyl ester (ADEPMAE) and maleimide (MI). The purpose of these chemical modifications was to enhance the fire retardance in the resultant *co*- and *ter*-polymers prepared *via* a solution polymerization technique. Thermogravimetric (TGA) and pyrolysis combustion flow calorimetry (PCFC) investigations found that the modified systems exhibited an improved propensity to form char residues and had lower heat release rates, as compared to the control homopolymer. Furthermore, pyrolysis/GC-MS was employed to identify the major volatile products formed upon the thermal decomposition of the polymers. For instance, ethanol, benzaldehyde, acetophenone triethylphosphate, as well as styrene and styrene oligomers were detected in the gaseous phase emanating from the pyrolysis reaction(s) of the modified polymers, indicating a significantly altered decomposition mechanism.



9.

Designing Oligo- and Polymeric Flame Retardants for High Char Yields

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This presentation will describe the synthesis of new oligomeric and polymeric compositions which, despite the lack of halogenated or phosphorus-based components, exhibit both exceptionally low heat release properties (by calorimetric measurements) and non-flammability (by vertical burn tests). The ketone-rich aromatic polymers, deoxybenzoins, and related structures will be described were obtained *via* 1) attachment to core molecules to afford small, multifunctional structures and 2) step-growth polymerization chemistry to give linear and branched polymers that may be employed as stand-alone materials or as additives to commodity polymers. Calorimetric measurements show the fire growth capacity (FGC) values of these new structures to be under 100 J/g-K, while several versions are readily integrated into reactive processing methods with polymers containing useful partner functional groups.

10.

Halogen-free styrene copolymers with intrinsic flame retardant properties

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Equipping styrene homopolymers and copolymers with flame retardant properties is important for a variety of applications. These include polystyrene particle foams (EPS) and extruded foams (XPS) to insulate building facades as well as injection-molded parts made from HIPS, ABS, ASA, etc., for use in the E&E sector. Brominated flame retardants for styrenic polymers [1] are increasingly coming under criticism due to the release of corrosive gases in the event of a fire and a potentially persistent environmental behavior [2]. In comparison, halogen-free flame retardants for styrene (co)polymers are not currently represented in the market because their flame retardant efficiency is either insufficient for the stated applications, or they provide unfavorable properties such as coloring or odors [3].

To avoid the mentioned disadvantages, a novel set of halogen-free styrene copolymers was synthesized in a versatile building-block approach (fig. 1), characterized, and tested for use in B&C applications. Depending on the synthetic route applied, the obtained copolymers exhibited molar masses of 20 – 150 kDa, glass transition temperatures of 83 – 101 °C, decomposition temperatures of 304 - 375 °C, and were able to pass DIN 4102 (B2) flame test without any additional flame retardants added.

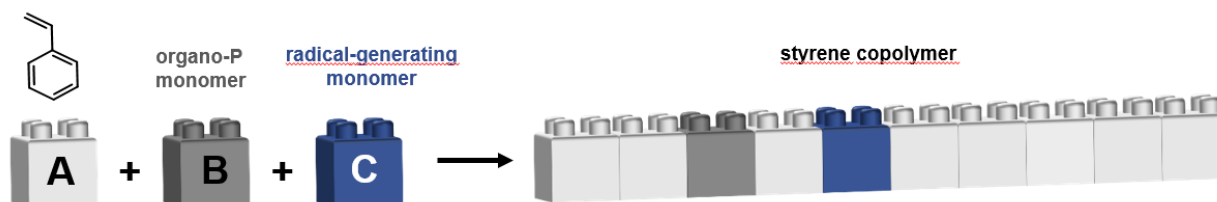


Fig. 1: Synthetic building-block approach towards halogen-free intrinsically flame retardant styrene copolymers.

¹ Hahn, K.; Kriha, O.; Bellin, I.; Braun, F.; Spies, P.; Sandler, J.; Kurt, W.; Janssens, G.; Fischer, J.; Fleckenstein, C.: „Flame-protected polymer foams“, WO2011/073141 A1, 13.12.2010.

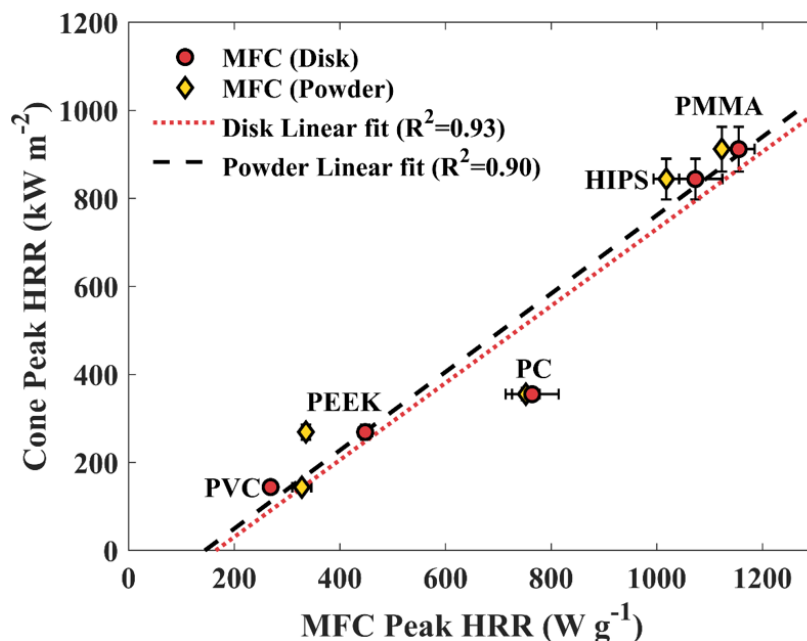
² Directive 2006/1907/EC: REACH, *Offic. J. Eur. Union* **2006**, 396, 1-849.

³ J. Wagner, P. Deglmann, S. Fuchs, M. Ciesielski, C. Fleckenstein, M. Döring, *Polym. Degr. Stability* **2016**, 129, 63-76.

Milligram-scale Flame Calorimetry: Development of a Pyrolyzer System used for Accurate Emulation of the Burning Behavior of Non-Thermally Thin Samples

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A new Milligram-scale Flame Calorimetry (MFC) pyrolyzer system was developed to more accurately emulate the burning behavior of samples in gram-scale tests, such as cone calorimetry. The pyrolyzer system comprises a flat heating coil operated in a constant power mode closely replicating the constant heater temperature conditions of cone calorimetry. A comparative study using five representative materials was performed in MFC, microscale combustion calorimetry, and cone calorimetry. All methods produced similar final solid residue yields. The correlation between the peak heat release rate (HRR) data from the newly-designed MFC and cone calorimeter was found to be near-linear. This was also the case when comparing the MFC airborne particulate yield and cone average extinction area data. The heat of combustion (HOC) data from MFC and cone calorimetry was nearly identical. The newly-designed MFC generates accurate relative flammability data using samples three orders of magnitude smaller than used in cone calorimetry tests.



12.

Surface functionalization Strategies for Fire Retardant

Nylon, Cotton and Nyco

Sourabh Kulkarni^{1,4}, *Shiran Yu*², *Zhiyu Xia*², *Alexander B. Morgan*⁵, *Jayant Kumar*^{3,4},
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A 50/50 blend of nylon and cotton (Nyco) is widely used by the US Armed forces for Army Combat Uniforms (ACU) due to its excellent combination of mechanical properties, comfort, and low cost. Despite these excellent properties Nyco is inherently flammable. The burning behavior is also unique due to the combination of a natural fiber (cotton) and a thermoplastic polymer (nylon) in the fiber blend which gives rise to the scaffolding effect. To address the flammability of Nyco fabric, several approaches have been developed for Nylon and cotton fabrics separately to impart flame retardancy. For Nylon fabric, polyphenols have been explored as char forming flame retardant. Polyphenols such as tannic acid can be coated onto the surface of the fabrics via acid dyeing techniques. The attachment of tannic acid on nylon helps improve the thermal stability and impart flame retardancy. Cellulosic fabrics on the other hand require phosphorus based flame retardant compounds for self-extinguishing characteristics. Various chemistries and processes were developed to covalently functionalize phosphorus based compounds on to cotton fabric. These compounds help in catalyzing the carbonization of cellulose, increasing the char formation, and giving rise to self-extinguishing fabrics with a char length of less than 4 inches in standard vertical flame tests. For Nyco fabrics, the combination of polyphenols along with a phosphorous containing compounds can impart FR characteristics. A systematic approach to functionalizing Nylon, Cotton and Nyco will be presented, and lessons learnt will be discussed. Detailed spectroscopic and thermal characterization of nylon, cotton and Nyco fabric as well as assessment of launder durability will also be presented.

Cancel

Coffee Biowastes as Sustainable Flame Retardants for Polymers

Henri VAHABI

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Development of biobased and cost-effective flame retardants has attracted the attention of researchers for developing safe and sustainable materials [1]. Various types of biowastes such as oyster shell powder or eggshell have been already incorporated into polymers to control their flammability. In this work, the coffee biowaste was chemically modified with phytic acid and dimethyl phosphite molecules and then incorporated into epoxy and polylactic acid (PLA). PLA and epoxy composites containing different loading percentage of unmodified/modified coffee biowaste were investigated using thermogravimetric analysis (TGA), cone calorimetry and pyrolysis combustion flow calorimeter analysis (PCFC) and UL94 tests. The chemical modification led to a significant increase in the char content up to 60% as detected by TGA. The results clearly showed the effectiveness of the modified coffee biowaste as flame retardant additive, as signaled by a low peak of heat release rate (pHRR) in cone calorimetry and the self-extinguishable character of materials observed in UL94 test.

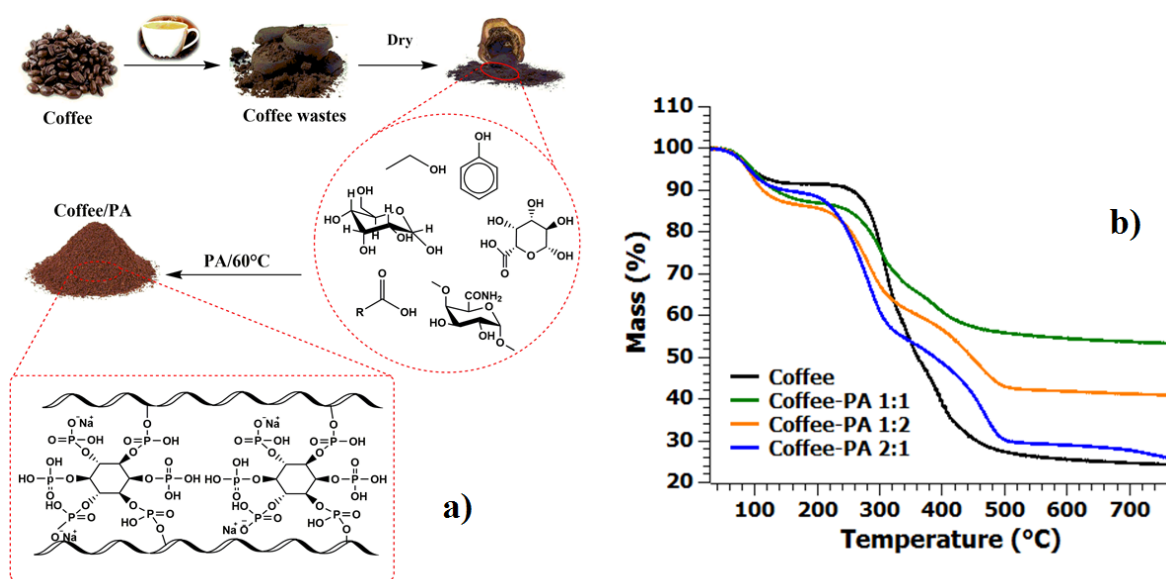


Figure 1: Scheme of chemical modification of coffee waste using phytic acid (a), thermogravimetric analysis (TGA) curves for coffee waste and modified coffee waste with different ratios of phytic acid (b).

Reference:

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13.

Non-vegan Flame-Retardant (Adjuvants in) Biocomposites

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Emanating from developing flame retarded biocomposites, we have proposed renewable natural fibers (including keratin) taken from industrial waste as an authentic sustainable approach.[1,2] More recently, we have investigated *non-vegan flame retardant* approaches. This paper loves to give you an insight into our ongoing projects on biogenic industrial wastes like leather, bone meal, and insects.[3-5] Materials were characterized multi-methodically, flame retardant modes of action quantified, decomposition mechanism proposed, and synergisms explained.

Considering the large quantities of leather waste (LW) in industrial-scale production, we underline LW as multifunctional bio-adjuvants. LW enhances the flame retardancy of poly(ethylene-vinyl acetate) (EVA) containing phosphorus flame retardants (P-FR).

Products/by-products of the invertebrate and vertebrate farming, respectively, are promising bio-based adjuvants in flame retarded bio-epoxy thermosets. While the addition of bone meal yields the formation of an inorganic shield, protein-based powders from insects provide an intumescent behavior. In combination with a P-FR superior charring and self-extinguishing are obtained.

Acknowledgement: In part of this work was supported by the Volkswagen Foundation grant “Experiment!” No. 97437.

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14.

Mechanistic investigations of wasp nest papers: Towards environmentally compatible flame-retardant concepts for synthetic materials

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Fire is common in many ecosystems and has led to evolutionary adaptations of organisms and their structures. Wasps build nests from paper-like materials consisting of chewed wood particles and their protein-rich saliva, whose composition influences the properties of their building material. We show that the flammability of these bio-papers is significantly inhibited compared to synthetic papers. The microstructure of egg-cells and shells built by the animals differs in saliva quantity and how densely it covers the wood particles (Fig. 1). This leads to different flame-retardancy properties and influences the stability of the charred residues after flame testing. Investigation of biomimetic papers synthesized using various amounts of commercial proteins like gluten and wood particles from different tree species indicate a similar role of the proteins. First transfer attempts to synthetic materials by incorporating the design principles of wasp papers into wood-plastic composites led to significant changes of their drip off-behavior during combustion.

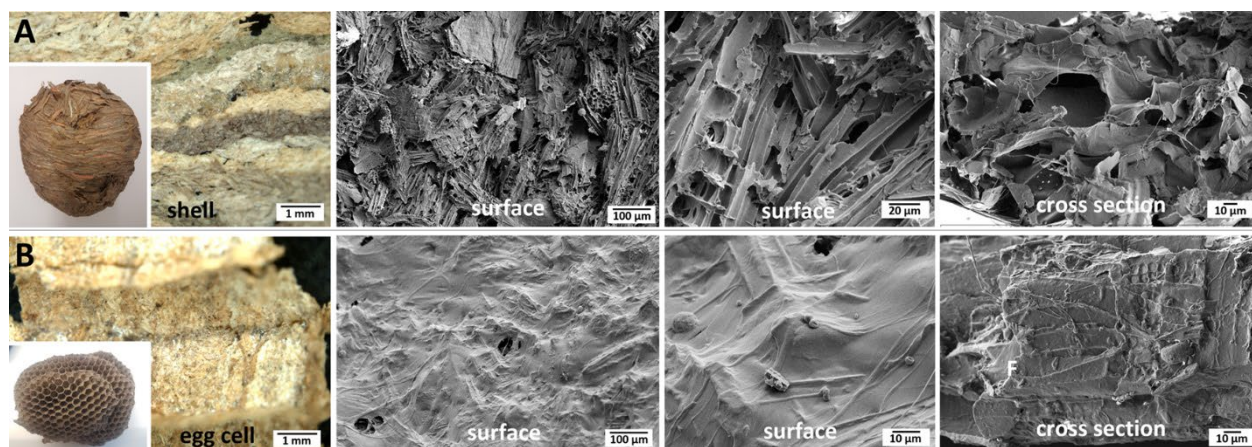


Fig. 1: Macro- (light microscopy) and microstructure (scanning electron microscopy) of (A) shell material and (B) egg cells from a *Vespula germanica* nest.

15.

Recent advances in designing fire barriers

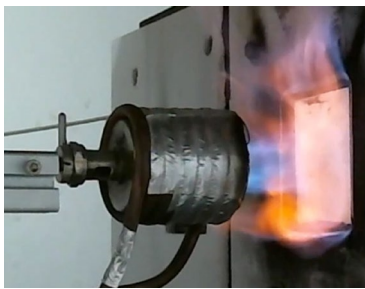
Serge Bourbigot^{1,2}, Johan Sarazin¹, Laura Geoffroy¹ and Gaëlle Fontaine¹

¹*Univ. Lille, CNRS, INRAE, Centrale Lille Institut, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France*

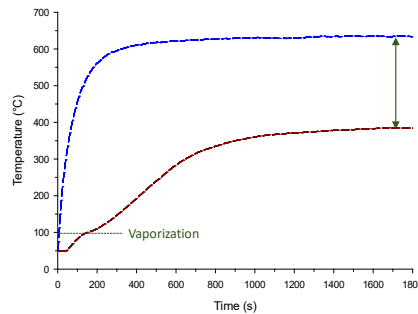
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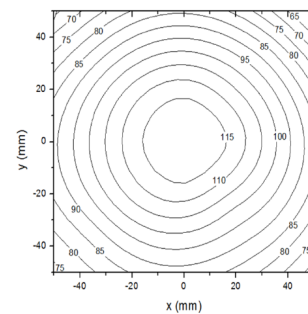
In case of fire, people must be protected by materials confining and stopping fire. It is the goal of this research to design materials and assembly of materials exhibiting low flammability, protecting substrates and limiting fire spread. An approach was to prepare foamed geopolymers (GPs) as fire barrier to protect a substrate. GP foam was coated on steel plate as a substrate and was evaluated using a burn-through test (Figure 1-(a)) delivering heat fluxes as high as 116 kW/m^2 (Figure 1-(c)). The temperature reached on the backside of the steel plate is much lower for the GP foam than that of the virgin steel (Figure 1-(b)). In the steady state, the temperature difference is about 250°C . Other fire barriers will be considered such as intumescent coating and multilayered materials (e.g. intumescent coating/aluminum foil). Examples will be shown in the talk in the conditions of jetfire and burn through testing respectively.



(a)



(b)



(c)

Figure 1: (a) Flame impinging GP foam during burn-through test, (b) comparison of the time/temperature curves of virgin steel plate (in blue) and steel coated by GP foam (in red) and (c) mapping of heat flux (in kW/m^2) at the surface of the plate

16.

Water-Based, Environmentally-Benign, Polyelectrolyte-Based Flame Retardant Treatments

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Flame retardants mitigate the threat of fire from inherently flammable materials responsible for sustaining a high standard of living. Although bulk flame retardants have proven effective for many years, there is now increased interest in the use of surface treatments to localize flame retardant chemistry at the exterior of a material, where combustion occurs. These water-based coatings preserve desirable bulk properties and minimize the amount of additive needed. The success of these treatments depends on the scalability, durability, and efficacy.

Our work in the fields of layer-by-layer (LbL) assembly and polyelectrolyte complexation has provided new water-based coating technologies for imparting effective flame retardancy to polymeric materials without using environmentally harmful chemistries [1][2]. These water-based coatings are very thin (typically < 500 nm thick) and conformal. The ability to place flame retardant chemistry exclusively at the surface prevents loss of beneficial bulk properties and reduces the amount of flame retardant required to achieve self-extinguishing behavior.

References

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Formulation of thin and thick FR sol-gel coatings

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Sol-gel coatings are used for a large variety of applications and have the potential to fulfil each and every expectation of the end user in terms of cost effectiveness, environmental friendliness and functional properties. In this work, thin and thick flame retardant (FR) sol-gel coatings were formulated and evaluated to fire protect foams, textiles and wood panels. The coatings developed are mainly based on a mix of silane monomers in an ethanol/water solution with diethylphosphite or eco-friendlier FR molecules.

Thin sol-gel coatings were deposited on foams and textiles and the resulting materials led to self-extinguishment when exposed to a flame. They also exhibited a very interesting intumescent phenomenon. Thick transparent sol-gel coatings were deposited on wood panels. The resulting materials were tested under mass loss cone test (50 kW/m^2), furnace test and under a mini Single Burning Item (SBI) test (Figure 1) set up in our lab.

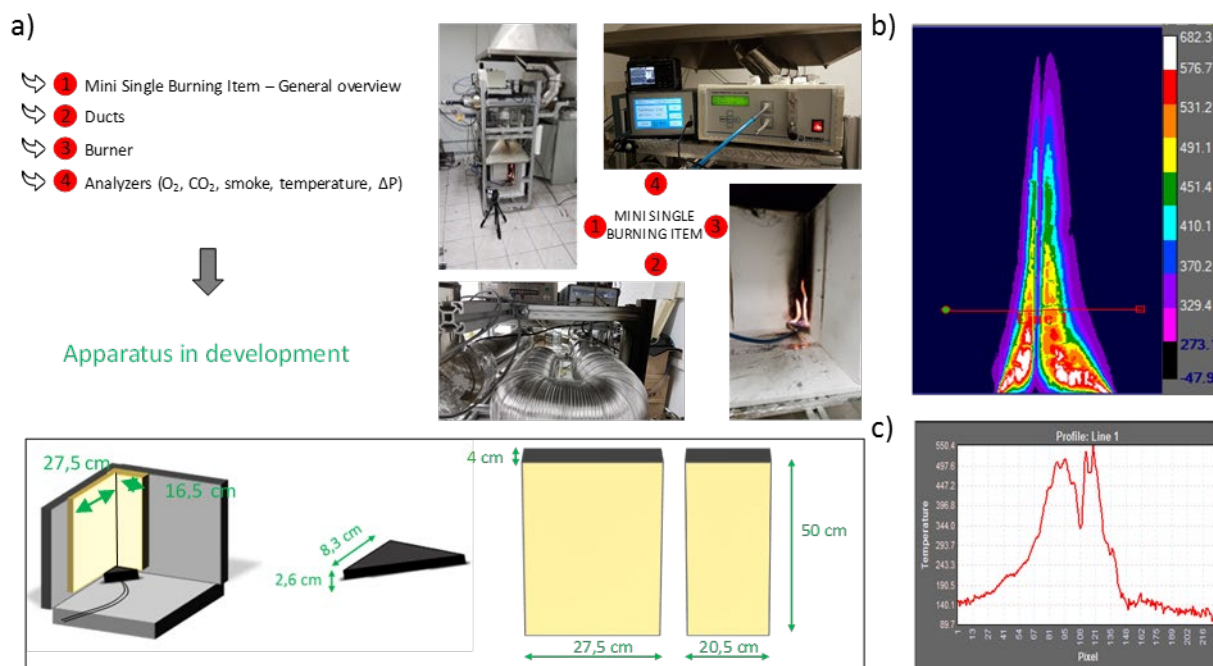


Figure 1 : Scheme of the Mini Single Burning Item (M-SBI) (a), infrared image of a burning sample (b) and the corresponding temperature profile (c)

18.

Surface functionalization Strategies for Fire Retardant

Nylon, Cotton and Nyco

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A 50/50 blend of nylon and cotton (Nyco) is widely used by the US Armed forces for Army Combat Uniforms (ACU) due to its excellent combination of mechanical properties, comfort, and low cost. Despite these excellent properties Nyco is inherently flammable. The burning behavior is also unique due to the combination of a natural fiber (cotton) and a thermoplastic polymer (nylon) in the fiber blend which gives rise to the scaffolding effect. To address the flammability of Nyco fabric, several approaches have been developed for Nylon and cotton fabrics separately to impart flame retardancy. For Nylon fabric, polyphenols have been explored as char forming flame retardant. Polyphenols such as tannic acid can be coated onto the surface of the fabrics via acid dyeing techniques. The attachment of tannic acid on nylon helps improve the thermal stability and impart flame retardancy. Cellulosic fabrics on the other hand require phosphorus based flame retardant compounds for self-extinguishing characteristics. Various chemistries and processes were developed to covalently functionalize phosphorus based compounds on to cotton fabric. These compounds help in catalyzing the carbonization of cellulose, increasing the char formation, and giving rise to self-extinguishing fabrics with a char length of less than 4 inches in standard vertical flame tests. For Nyco fabrics, the combination of polyphenols along with a phosphorous containing compounds can impart FR characteristics. A systematic approach to functionalizing Nylon, Cotton and Nyco will be presented, and lessons learnt will be discussed. Detailed spectroscopic and thermal characterization of nylon, cotton and Nyco fabric as well as assessment of launder durability will also be presented.

19.

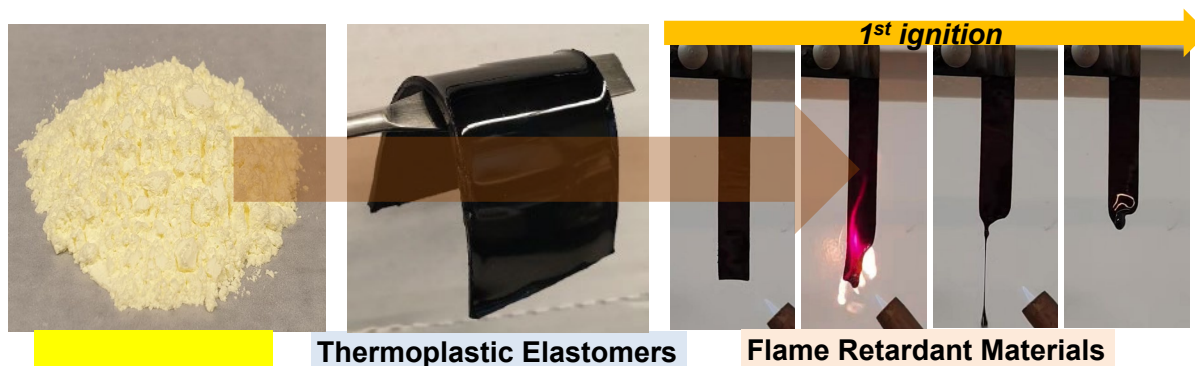
Polymers Derived From Elemental Sulfur with Enhanced Thermomechanical and Flame Retardant Properties

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The production of elemental sulfur (S_8) from petroleum refining has created a technological opportunity to increase the valorization of elemental sulfur by the creation of high performance sulfur based plastics with improved thermomechanical properties, elasticity and flame retardancy. We will discuss our recent efforts on the preparation segmented multi-block polyurethanes (SPUs) and thermoplastic elastomers derived from S_8 that incorporate an appreciable amount of sulfur into the final target material. These sulfur based polyurethanes were readily solution processed into large area free standing films where both the tensile strength and elasticity of these materials were controlled by variation of the sulfur polyol composition. SPUs with both high tensile strength (13-23 MPa) and ductility (348% strain at break) were prepared, along with SPU thermoplastic elastomers (578% strain at break) which are comparable values to classical thermoplastic polyurethanes (TPUs). The incorporation of sulfur into these polyurethanes, we observe enhanced flame retardancy in comparison to classical TPUs, which points to the opportunity to impart new properties to polymeric materials as a consequence of using elemental sulfur.



20.

Sulfenamides, sulfinamides and sulfonamides as flame retardants – similarities and differences in the mechanism of action

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Several sulfur-nitrogen compounds have proven their potential as flame retardants for polymeric materials.¹⁻³ In the current work we have investigated the flame retardant activity of three different sulfur-nitrogen derivatives: 1) sulfenamides, 2) sulfinamides and 3) sulfonamides. The flame retardant mechanism and efficacy were investigated by performing standard fire tests such as DIN4102 and LOI tests in combination with thermal analysis (TGA/DSC) and chemical analysis of the decomposition products of the neat sulfur-nitrogen compounds. Despite the structural similarities some differences in efficacy and mode of action for these compounds were observed for flame retardancy of polypropylene. Here we present our preliminary findings on the activity differences of these 3 groups of sulfur-nitrogen compounds with respect to flame retardant efficacy in polypropylene films.

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2. Teija Tirri, Melanie Aubert, Humayun Aziz, Yury Brusentsev, Weronika Pawelec, Carl-Eric Wilén, Sulfenamides in synergistic combination with halogen free flame retardants in polypropylene, *Polymer Degradation and Stability*, Volume 164, June 2019, 75.
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21.

Effect of crosslinkers on charring efficiency of lignin-polyamide precursors for the production of carbon fibers

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There is a continuous increase in the demand for carbon fibres in the global market despite their high costs of manufacturing, which is mainly associated with those derived from precursor polyacrylonitrile fibres. This route is partly the reason that carbon fibres are expensive and involve a large carbon foot print in their manufacture. Lignin, a biobased polymer, owing to its high carbon content (> 60%), excellent char-forming ability and a potential to be spun into fibres, offers itself as a possible alternative precursor. There are however multiple technical challenges to produce lignin precursor fibers, the main ones being compounding/spinning the more processable, lower molecular weight lignins and long thermal processing times required for carbonisation. In order to address the first challenge, the lignin can be blended with a wide range of thermoplastic polymers and the resulting blends melt spun into fibers. Another challenge is to increase the char yield of the lignin-based precursors for carbon fiber production. To date, the lignin based systems have shown considerably lower char yields than commercial tar pitch char yields under a nitrogen atmosphere, which is further reduced when lignin is blended with other polymers. This can be addressed by adding crosslinkers and char promoters in the blends, which however can affect the processability of the blends.

In our recent research we have successfully blended a hydroxypropyl modified organosolv lignin with a bio-based polyamide, PA 1010, and extruded into fibres. This study aims to explore the enhancement in charring efficiency of the blends by using a number of crosslinkers and char promoters either as additives prior to melt spinning fibres or as surface treatments of the extruded fibres. The charring efficiency of the blends has been investigated by thermal analytical techniques (e.g. TGA, DSC, DMA) at various stages of heat treatments used for thermal stabilisation and carbonisation of the fibres. The flammability of blended polymers has been studied by UL-94 test, where V-2 rating could be achieved for blends containing 20 – 40 wt% lignin compared to ‘no-rating’ for the polyamide. The effect of crosslinkers on the flammability of the extruder fibres is being investigated and will be presented in the conference.

Acknowledgements: This work is part of the project funded from the BioBased Industries Joint Undertaking under the European Union’s Horizon 2020 research and innovation programme under grant agreement No 720707rs.

Modeling of Flame Spread On Charring, Non-charring, and Flame Retardant Polymers In UL-94V

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The UL-94V test is widely used to assess the flammability of polymers in a vertical configuration; accurate modeling of it could facilitate the development of polymers safer from fire. In this work, flame spread in slightly modified UL-94V tests was tracked and modeled on several polymers including poly(methyl methacrylate) (PMMA), poly(ether ether ketone) (PEEK), and glass-fiber reinforced polyamide 6,6 (PA66/GF) with and without flame retardant red phosphorous (RP). The model, implemented via a numerical pyrolysis solver, ThermaKin, couples previously developed and validated pyrolysis models with submodels representing the burner and polymer flames. A few model predictions compared with experimental data are shown in Fig. 1. Model agreement is good apart from the model's inability to predict the extinction of the PA66/GF/RP9 flame due to gas-phase effects which were not included.

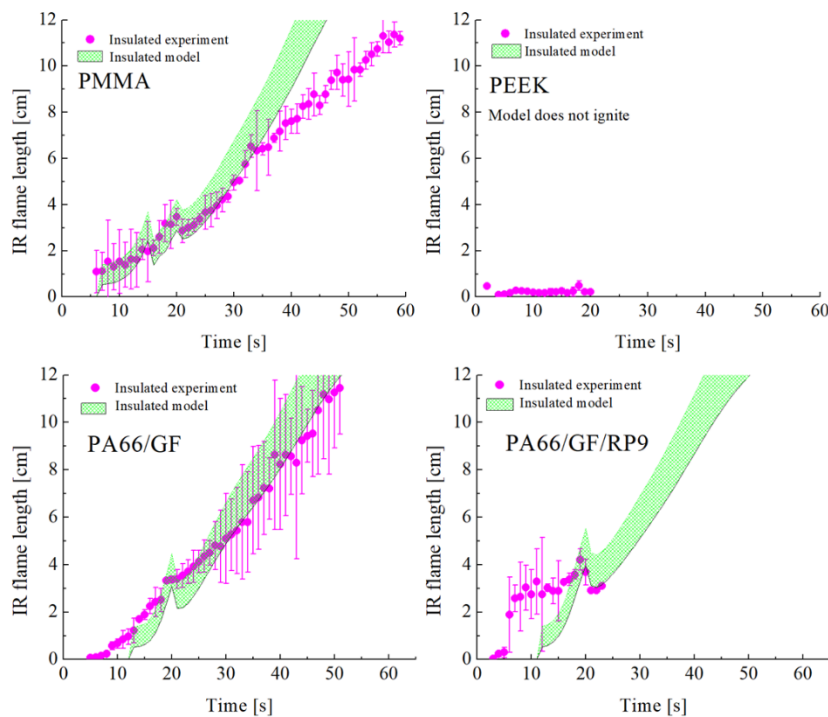


FIGURE 1. Comparison of experimental flame length data and model predictions. The shaded area accounts for the uncertainty in scaling the simulated results.

23.

Water-based processes exploiting high aspect ratio nanoparticles for the development of flame retardant flexible Polyurethane Foams

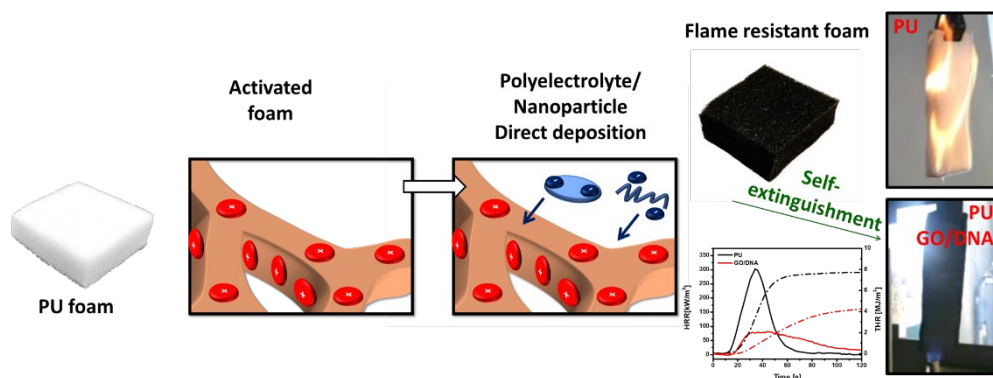
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Recent societal concerns associated to the safety of conventionally used flame retardant additives resulted in the need to find new, sustainable and high performing solutions to reduce the fire threat of common polymers. In this contribution, waterborne self-assembled coatings comprising 2D nanoparticles are employed as promising route to improve the fire safety of flexible polyurethane foams (PU). Different 2D nanoparticles (graphite oxide, montmorillonite clay MMT, kaolinite KA) have been selected and combined with natural polyelectrolytes (alginates, chitosan, deoxyribonucleic acids).¹ Polyelectrolyte/nanoparticle complexation, forced self-assembly or in-situ assembly are employed to deposit nanostructured coatings characterized by high flame retardant efficiency. Few deposition steps (one or two) were found sufficient to produce PU characterized by self-extinguishing behaviour and low heat and smoke release, evaluated by flammability and cone calorimetry test, respectively. The achieved results make it possible for the development of industrially viable approaches where the efficiency of the process and the flame retardant results are maximised.



¹ L. Maddalena, F. Carosio, A. Fina, *Advanced Materials and interfaces*, 8, 21, 2101083, 2021

Acknowledgment: The financial support from Italian Ministry of University (MUR) call PRIN 2017 with the project 2017LEPH3M “PANACEA” is acknowledged.

24.

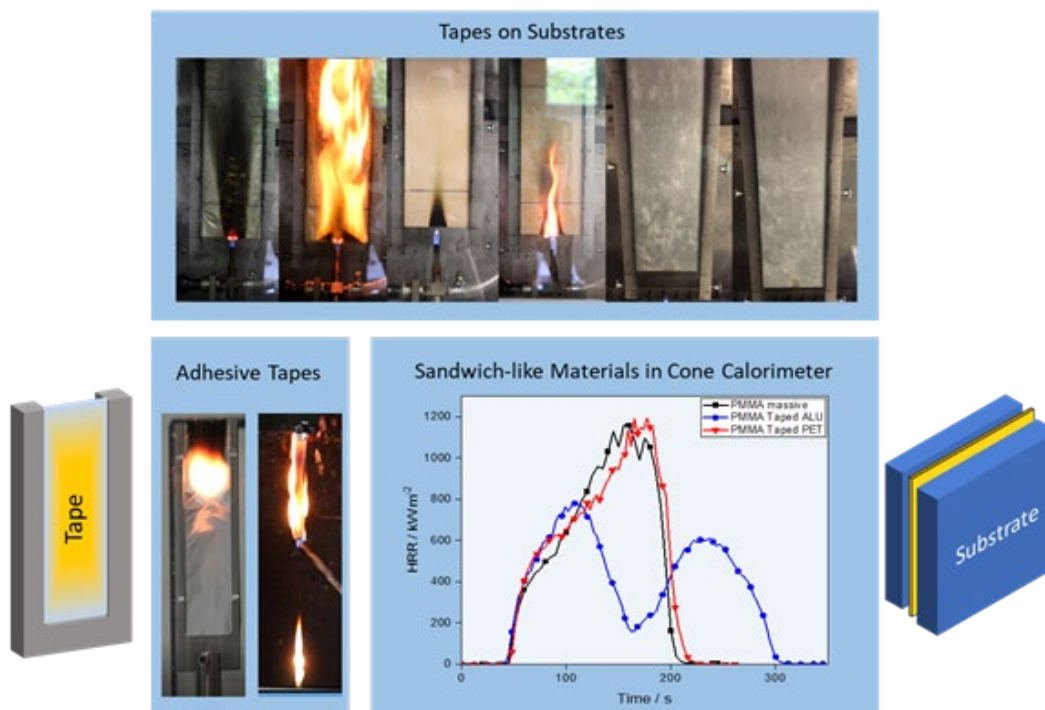
Adhesive tapes in bonded materials - fire risk or protective layer?

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In the recent years, more and more products in construction and automotive industry are bonded by adhesive tapes instead of mechanical fasteners but there is no sufficient understanding of how these bonded, layered materials behave in fires. Our research project gives an insight of how adhesives and substrates interact with each other in different fire scenarios and how flame retardants function in pressure sensitive adhesive (PSA) tapes. A systematic investigation on the burning behavior of PSA tapes as free-standing films, as top layers on different substrates and as sandwich-like adhesive joints was performed. The burning behavior of free-standing PSA tapes and those used as a coating was significantly improved by using phosphorus-based flame retardants. Furthermore, it was shown that, depending on tape structure and substrate, the PSA tape can lower the fire risk by acting as an intermediate protection layer in bonded materials.



25.

Halogen-free syntheses of phosphoric esters based on phosphorus pentoxide

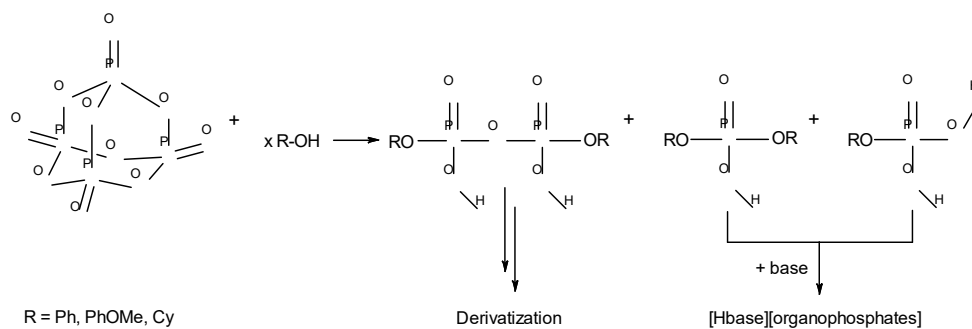
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The development of halogen-free phosphorus-based compounds is an omnipresent strategy to achieve the goal of an environmentally friendly flame retardancy in thermoplastics. Although numerous and efficient examples are broadly utilized, the syntheses of those flame retardants (FRs) frequently include halogenated intermediates and starting materials, which are hazardous and in form of contaminants corrosive to modern electronic devices.^[1] Flame retardants like melamine polyphosphate or red phosphorus, which renounce halogenated compounds in their production, lack derivatization ability for the development of tailor-made FRs.

Phosphorus pentoxide represents a halogen-free, albeit due to its insolubility and multi-center reactivity challenging, starting material for the synthesis of phosphate esters (Scheme 1).



Scheme 1: Alcoholysis of phosphorus pentoxide.

However, in dependence on the reaction conditions the alcoholysis of phosphorus pentoxide results in the formation of mono- and diesters of phosphoric acid as well as pyrophosphates.^[2] Subsequent to separation, the derivatization and reaction with bases enables a convenient and entirely halogen-free synthesis of potential FRs.

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26.

Mechanistic aspects of flame retarded polybutylene succinate

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Among the biobased polymers polybutylene succinate (PBS) is an attractive one. It can replace petrochemical polymers for different applications, indeed, it has a good processability, a controlled biodegradability and quite good thermal and mechanical properties. Unfortunately, its high flammability reduces its application in various field where flame retardancy is needed. Therefore, a lot of efforts are made to improve the reaction to fire of PBS [1]. As an example, PBS can be flame retarded by an intumescence approach using ethylenediamine phosphate (EDAP) and synergists (Figure 1) [2]. In this talk, the different approaches developed to reduce flammability of PBS will be presented and a focus will be made on the mechanistic aspects.

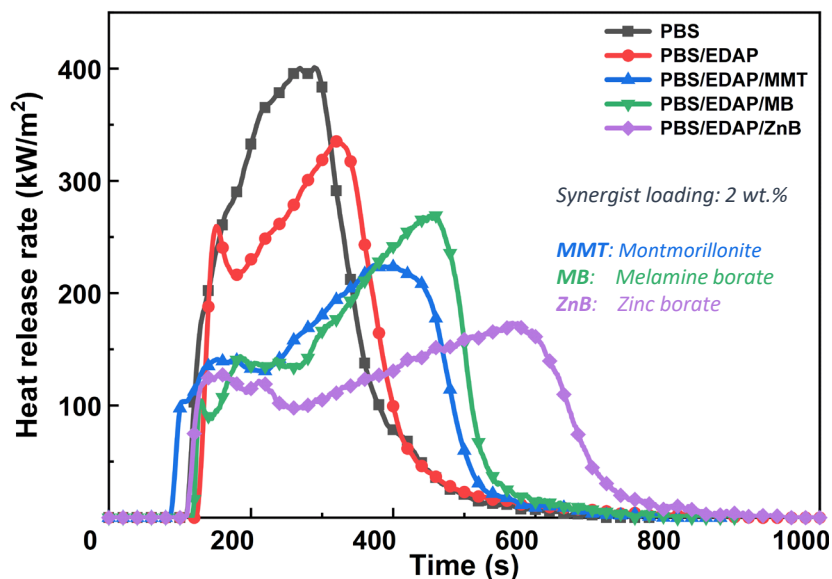


Figure 2: Flame retardancy of intumescent PBS evaluated by Mass Loss Cone

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27.

Polyelectrolyte Composites for Flame Retardant Additive Manufacturing

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Additive manufacturing, also called 3D printing, is a rapidly maturing technology that has found widespread use for prototyping parts and recently for mass-produced 3D printed items. Filament-based additive manufacturing is the most widespread form of 3D printing, forming objects by the extrusion of molten thermoplastics. The inherent flammability of these thermoplastics limits the applications of additively manufactured parts and is a barrier to the commercial viability of 3D printing for mass production. Polyelectrolyte coatings have risen to prominence in recent years as effective flame retardant treatments for a wide variety of materials, but are impractical for use in 3D printing filaments. However, polyelectrolyte complexes (PECs) are effective flame retardants for thermoplastics when mixed as bulk additives. Incorporation of bulk PECs preserves the printability of polylactic acid and polyamide while simultaneously yielding flame retardant filaments and parts. Reduction of part flammability without altering processing presents an opportunity for a scalable and cost-effective method to improve the safety of 3D printers and 3D printed parts.

28.

Lignin-based multilayer nanocoating for flame retardant cotton fabric

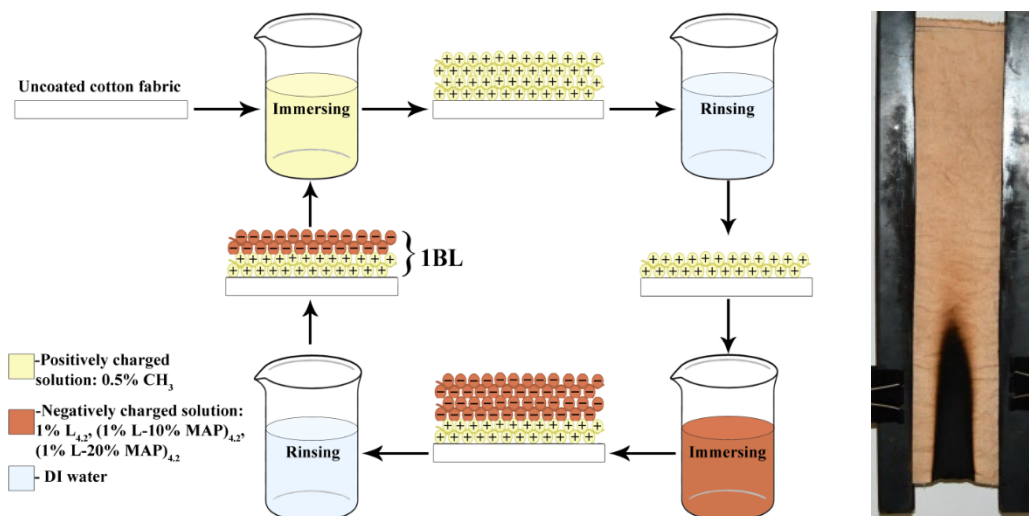
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Layer-by-layer (LbL) assembly is a simple, inexpensive, and highly tailorable water-based technique, performed by alternate exposure of a substrate to oppositely-charged solutions or suspensions at room temperature, giving rise to a multilayer nano-film. It is one of the techniques for textile finishing that uses polyelectrolytes, nanoparticles, and bio-macromolecules, possible to design an unlimited combination of assemblies with impressive functionality. Here we are producing lignin-based multilayered nanocoating composed of magnesium lignosulfonate (L), chitosan (CH), and monoammonium phosphate (MAP) that give self-extinguishing cotton fabric with less than 5 bilayers. 5 BL of CH₃/(L-20% MAP)_{4,2} imparted exceptional flame retardancy with only 15.5 wt% weight gain. This sample has 35 vol% LOI, 30.9 wt% residue at 600°C, and a 67.2 % reduction in heat release rate. In this intumescent system, lignin and chitosan are char-forming, while monoammonium phosphate, with its decomposing components ammonia and phosphoric acid, acts as a blowing agent and acid source.



29.

Iron Additives as Alternatives to Antimony Oxide in Flame -retardant Formulations

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Antimony oxide has long been used as an adjuvant in organohalogen flame-retardant formulations. Antimony oxide is neither a flame retardant nor a synergist. In the degrading polymer/flame retardant matrix it is converted to volatile antimony trihalide and oxyhalides which escape to the gas phase where they effectively scavenge combustion propagating radicals. Thus, the antimony halides and hydrogen halide from the decomposing flame retardant act in parallel to suppress combustion. Antimony oxide has been used in a similar way in halogenated polymers, in particular, plasticized poly(vinyl chloride) [PVC]. Unformulated PVC is effectively noncombustible (LOI 45). However, to be processed, it must be strongly plasticized. The presence of plasticizer often imparts two negative characteristics, toxicity and flammability. To combat flammability, antimony oxide is often added during processing. PVC degrades by thermally-induced dehydrochlorination. In the degrading polymer containing antimony oxide volatile antimony chlorides are formed which suppress gas-phase combustion. With the increasing awareness of the toxicity of antimony oxide [*Int. J. Environ. Res. Public Health*, **2019**, 19, 4474] alternatives have been sought [*Int. J. Mater. Res. Sci. Tech.*, **2020**, 1(1), 15-20]. Commercial replacements for antimony oxide are now available for use in some applications [R. J. Marshall Company]. However, the search for a general replacement continues. Iron compounds are widely available and low in cost. PVC formulations containing various iron compounds at 2 and 10 parts-per-hundred have been generated. The thermal degradation and flammability of these materials have been evaluated utilizing thermogravimetry (TGA) and limiting oxygen index (LOI).

30.

Polybenzoxazines: Development of Very High Performance Noncombustible Polymers without the Need of Flame Retarding Additives.

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Polymers are often used with flame retarding additives. Traditionally used flame retardants are often toxic, lead to toxic byproducts or cause adverse effects by the addition of secondary materials. More recently, natural renewable additives or green methodologies are attracting strong attention. As part of this environmentally benign approach, development of intrinsically noncombustible polymers offers non-toxic products and the ability to sustain the originally developed polymer properties. Polybenzoxazine is the newest rare class of polymers that has been commercialized. Polybenzoxazines offer extremely high molecular design flexibility, can be synthesized from readily available commercial raw materials, polymerize with near-zero shrinkage, and exhibit excellent mechanical, thermal and electrical properties. Being able to synthesize a fire-smart structure is one of the advantageous consequences of this excellent molecular design flexibility. In this lecture, we will introduce fire smart polymers that can exhibit T_g greater than 350°C, a constant G' property in a very wide temperature range (R.T.-400°C) with heat release capacity less than 100 J/g.K (noncombustible).

Cancel

Formulation of Flexible Polyurethane Foams with Significantly Reduced Flammability

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This study focused on the development of a family of highly flame retardant, environmentally friendly, flexible polyurethane foams. FR package is non-halogen, bound-in, meaning it is non-migrating, of low VOC, resolving key issues for stakeholders. Goal was to exceed fire retardancy of BX265 NASA SOFI rigid foam (354 Peak Heat Release Rate by Cone Calorimeter at 50kW/m² external flux, 1-inch thickness). Foams achieved down to 140 PHRR (40% of SOFI)(92% reduction in PHRR versus 1670 for base foam). Foams meet Cal133, BS5852, and FAA Oil Burner Test standards for seating; 16CFR1633, Cal129, and NFPA 267 (Navy Modification) standards for mattresses. Some foams meet US Air Force dynamic cushioning test for packaging. Foams made to any needed static stress performance, useful for energy absorption foams for automotive or aerospace. Some foams show 25% improvement in cryogenic insulating performance. Foams under 3.0 pcf available, foams in five applications are highlighted.