PolyFlame

This issue of PolyFlame mainly arose from the multiplicity of centers supervising the PhD thesis in different countries. Also, pursuing the release of the last issue of PolyFlame (N° 25), we received the comments of Kathryn Rodgers from Boston University on two articles published in N° 25: « Could Flame Retardants in Furniture be Increasing the Fire Risk? » and « Flame Retardants and the Associated Toxicity »

Kathryn Rodgers' comments on "Fleming" and "Hirschler" articles published on PolyFlame N°25

Kathryn Rodgers

Boston University

One of the central questions that both Fleming and Hirschler approach in the September 2022 PolyFlame newsletter is what the effect flame retardants added to upholstered furniture (henceforth called furniture) have on fire outcomes. It is not possible to know the true causal effect of flame retardants in furniture and fire outcomes. In order to know that, we would need to compare outcomes from fires that started on flame retardant-treated furniture to their counterfactual: the same fire that started on flame retardant-free furniture.

Since flame retardants in furniture have been used to meet flammability standards, which have locality-specific enforcement, one might think it is possible to do an ecological study. However, in the U.S., we are not able to do an ecological comparison of outcomes from fires started on furniture with flame retardant treatment (say, from Town A) to outcomes in fires started on flame retardant-free furniture from, say, Town B. Before the U.S. adopted a national furniture flammability standard in 2021 [1], standard enforcement existed in some places like California. However, the addition of flame retardants to furniture was a default manufacturing process in the U.S., making selection of a "Town B" challenging if not impossible.

Instead, colleagues and I, including Fleming, modified our question to understand the effect of flame retardants added to furniture on outcomes from furniture fires ignited by different heat sources. This is an important question were designed to protect against different heat sources: one was designed to lengthen time to ignition from an open flame heat source (e.g. a match), and the other to lengthen time to ignition from a smoldering heat source (e.g. an unattended, lit cigarette).

In our analysis, we looked at 34,081 unconfined residential fires from the Massachusetts Fire Incident Reporting System from 2003-2016, a time in which furniture sold in the U.S. was nearly uniformly made to meet a flammability standard that targeted open flame heat sources. We excluded 114,748 confined fires because of a high degree of missing data. We compared fire outcomes (death, severe casualty, any casualty) by item first ignited and heat sources. We found that odds of death in fires that started on furniture and were ignited by smoking materials (e.g cigarettes) was significantly elevated (OR_{death} = 3.4; 95% CI = 1.3, 10.9) relative to furniture fires ignited by open flame heat sources [2]. Our analysis controlled for area of origin, equipment involved in ignition, human factors (e.g. asleep, disabled), season, fire year, and time of day. These factors may have independent relationships with both the occurrence of a fire and fire outcomes, thus confounding the true relationship between furniture fires and outcomes.

Société Chimique de France

Our findings suggested that furniture flammability standards designed to intervene on the initiating event of foam ignited by open flames were not appropriate fire safety measures in the time period of our study. A standard designed to slow fire spread from smoldering heat sources, such as a burningcigarette, would appear to address the relatively high fatality of furniture fires started by smoking materials. Indeed, as of 2021, the national flammability standard for furniture in the U.S. requires the upholstery cover material (or underlying liner) to not produce a flame, not burn more than two inches of fabric, or not smolder for more than 45 minutes after exposure to a smoldering cigarette [3]. This standard, called TB 117-2013, can be met without treating furniture filling with flame retardants.

As Fleming notes, while the rate of deaths from furniture fires and associated deaths has steadily decreased since 1980 in the U.S., the furniture fires that have occurred since 1980 have become deadlier. In fact, data from the U.S. National Fire Protection Agency (NFPA), show that the proportion of deaths from furniture fires started by smoking materials increased fourfold from 1980-2014, while the proportion of deaths from furniture fires started by open flame heat sources had a much smaller increase (Figure 1).

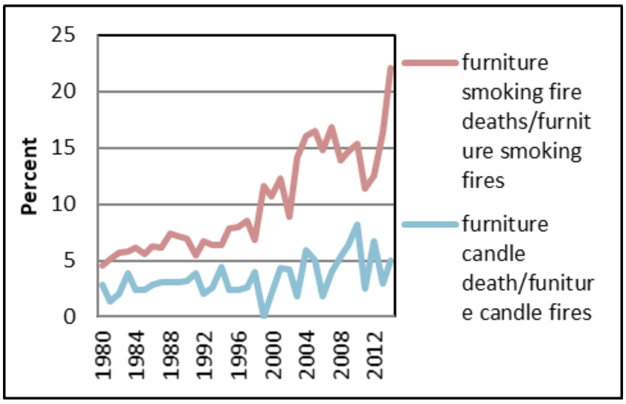

Figure 1. Percent of deaths per furniture fire started by smoking materials and open flames, 1980-2014 from National Fire Protection Agency

There are many factors that could have influenced the lethality of furniture fires ignited by smoking materials over this period. One such factor that cannot be ignored is smoke toxicity from flame retarded furniture. While Hirschler states that the smoke

Findings from our analysis indicate a furniture flammability standard that stops flame spread from smoking materials is more protective against fire fatalities. Though our study was limited to Massachusetts, national data from NFPA supports this finding. The enforcement of such a standard in the U.S. will hopefully reverse this trend of increasingly dangerous furniture fires started by smoldering materials.

Author: Kathryn Rodgers, MPH is a PhD student at Boston University School of Public Health

References:

[1] Standard for the Flammability of Upholstered Furniture, 86 Fed. Reg., 18440-18444 (April 9, 2021), 16 CFR 1640. <https://www.federalregister.gov/documents/2021/04/09/2021-06977/standard-for-the-flammability-of-upholstered-furniture>

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[4] Kim, Y.H., Warren, S.H., Kooter, I. et al. Chemistry, lung toxicity and mutagenicity of burn pit smoke-related particulate matter. Part Fibre Toxicol 18, 45 (2021). https://doi.org/10.1186/s12989-021-00435-w

Short description of PhD thesis under progress in Belgium, Germany, Hungary, Italy, United Kingdom, United States and France

Optimized vegetal wools for indoor comfort: coupling fire treatment with acoustic and hygrothermal performances

PhD student : Thomas Schatzmayr Welp Sa

Supervisors : Sandrine Marceau[a], Clément Piégay[b], Fouad Laoutid[c], Philippe Glé[b], Cesar Segovia[d], Emmanuel Gourdon[e]

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Funding: This work has received funding from MSCA-COFUND-CLEAR-Doc program

Bio-based materials, such as vegetal wools, contribute to the indoor comfort of buildings, by acoustic and hygrothermal properties. Differently from conventional building materials, these materials are hygroscopic and a heterogeneous. Their performances are related to their microstructure: fiber diameter distribution and composition, density… (Piégay et al. 2020, 2021).

Moreover, bio-based materials contain cellulose and hemicellulose and are poorly classified in terms of their reaction and resistance to fire because of their flammable and flamespreading characteristics (Lazko et al. 2013, Freivalde et al. 2014). Thus, it is necessary to apply a fireproof treatment to increase the material and its derivative products' safety.

Therefore, the main objectives of the thesis are to develop a fireproof treatment adapted for vegetal wools, to analyse its influence on the microstructure and porosity, and to understand how it affects the hygrothermal and acoustics of the vegetal wools. Modeling models will be developed to simulate the fire treatment impact on the acoustic and hygrothermal properties.

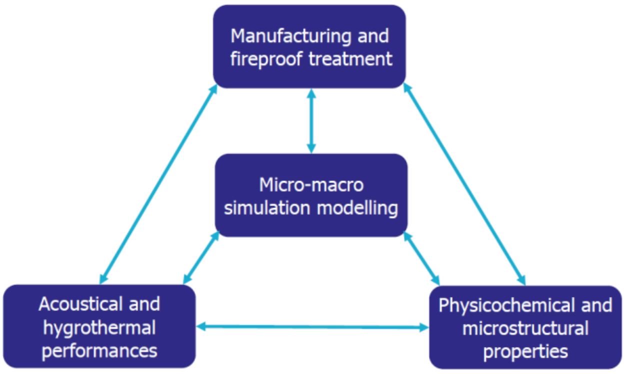

Figure 1: The project's structure.

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Lazko, J. et al. Polymer Degradation and Stability, 98 (5), 1043–1051

Piégay, C. et al., Journal of Sound and Vibration, 495, 115911

Residue Design: Revealing the Secrets of Intumescence

PhD student : Michael Morys

Supervisor : Prof. Dr. habil. Bernhard Schartel

Bundesanstalt für Materialforschung und -prüfung (BAM)

Description:

- Bench-scale fire resistance testing, particularly STT MuFu+ but also high temperature burner
- Intumescent coatings
- µ-computer tomography

Papers:

M. Morys, B. Illerhaus, H. Sturm, B. Schartel. Revealing the inner secrets of intumescence: Advanced standard time temperature oven (STT Mufu+) - µ-computed tomography approach. Fire Mater. 41, 927-939, 2017. Doi: 10.1002/fam.2426

M. Morys, B. Illerhaus, H. Sturm, B. Schartel. Variation of Intumescent Coatings Revealing Different Modes of Action for Good Protection Performance. Fire Technol 53, 1569–1587,

M. Morys, B. Illerhaus, H. Sturm, B. Schartel. Size is not all that matters: Comparing the fluence of different binders on the performance and morphology of intumescent coatings. J Fire Sci 35, 284-302, 2017. Doi: 10.1177/0734904117709479

M. Morys, D. Häßler, S. Krüger, B. Schartel, S. Hothan. Beyond the standard time-temperature curve: Assessment of intumescent coatings under standard and deviant temperature curves. Fire Safety J 112, 102951, 2020. Doi: 10.1016/j.firesaf.2020.102951

But also

Doi: 10.1016/j.polymdegradstab.2016.06.023 and 10.1002/bate.201600032

Dynamic population balance-controlled dripping in flammability tests

PhD student : Melissa Matzen

Supervisor : Prof. Dr. habil. Bernhard Schartel

Bundesanstalt für Materialforschung und -prüfung (BAM)

Description:

- Dripping investigation simulating vertical UL 94 conditions
- Explanation of melt flow and dripping based on investigating the population balance of the pyrolysis products
- Investigation of the impact of flame retardants on dripping
- Simulation of the dripping behaviour of a nonflaming dripping V-0 in the UL 94 using Particle Finite Element Method (PFEM)

Papers:

M. Matzen, B. Kandola, C. Huth, B. Schartel. Influence of Flame Retardants on the Melt Dripping Behaviour of Thermoplastic Polymers. Materials 8, 5621-5646, 2015 Doi:

M. Matzen, J. Marti, E. Oñate, S. Idelsohn, B. Schartel. Advanced Experiments and Particle Finite Element Modelling on Dripping V-0 Polypropylene. Conference Proceedings, Fire and Materials 2017, 15th International Conference, Interscience Communications, 2017, 57-62

No Smoke no Fire – the impact of SP on flame retardant polymers

PhD student : Sebastian M. Goller

Supervisor : Prof. Dr. habil. Bernhard Schartel - Bundesanstalt für Materialforschung und -prüfung (BAM)

Description:

The project is about smoke suppression in flame retardant polymers. The correlation between polymer matrix, smoke suppressant (SP), and flame retardants is of major importance to assess the fire and smoke properties. A key factor is the knowledge of their decomposition mechanism and burning behaviour. Therefore, TGA-FTIR experiments are conducted, and the materials are exposed to different fire scenarios like flammability test (UL 94, LOI), forced flaming conditions (cone calorimeter) and smouldering conditions (smoke density chamber). SEM images of the residues enable structure property relationships. The aim is to understand which mode of action is beneficial for good fire properties and less smoke emission. To characterize the impact of the SP on the smoke, particle analysis with an ELPI and gas analysis with FTIR are conducted in parallel to the optical density measurement. The evolved gases enable an estimation about the toxicity of the smoke and enable insights in the decomposition mechanism of the material.

Papers: The first two will be submitted until end of 2022

Transfer mechanisms between the flame-retardant polymer materials and the fibre-reinforced plastics: Flame Retardancy – Fire Resistance – Post-Fire Mechanics

PhD student : Maria Jauregui Rozo

Supervisor : Prof. Dr. habil. Bernhard Schartel - Bundesanstalt für Materialforschung und -prüfung (BAM)

Description:

In the last 20 years, important research and development of halogen-free synergistic flame retardants has been conducted for pure resin systems. However, it is not clear whether these flame retardants are also suitable for composite materials. When the reinforcing fibres from the composites are in direct contact with the decomposition products from the fire retardants, the mechanical and rheological properties, thermal conductivity, and heat capacity of the composite materials can change. The fibres strongly influence the composite materials' fire behaviour and flame retardancy. Therefore, it is imperative transfer mechanisms between fire retardants and fibre-reinforced plastics. The main goal of this research project is to investigate, describe and understand the two complex transfer mechanisms of flame-retardant polymer materials with fibre-reinforced polymer composites, namely char enhancement and flame inhibition. It is important to compare the reaction of flame retardants in the fibre composite material and the pure resin and their influence on the mechanical performance before, during, and after the fire event.

Prediction of wildfire propagation—Experimental and numerical investigation of fires in vegetation

PhD student : Hongyi Wu

Supervisor : Prof. Dr. habil. Bernhard Schartel - Bundesanstalt für Materialforschung und -prüfung (BAM)

Description:

- Wildfire simulation with wildland-urban interface Fire Dynamics Simulator (LES based CFD)
- Experiment-based kinetic parameter values and fuel properties
- Experiments under different scales (Laboratory, Pilot scales)
- Samples from different kinds of forests (Beech, Oak, Pine)
- Investigating the flow field with Schlieren Photograph technology

Papers:

Y. Y. Chan, C. Ma, F. Zhou, Y. Hu, B. Schartel. Flame retardant flexible polyurethane foams based on phosphorous soybean-oil polyol and expandable graphite. Polym Degrad Stabil 191, 109656, 2021. Doi: 10.1016/j.polymedegradstab.2021.109656.

Y. Y. Chan, C. Ma, F. Zhou, Y. Hu, B. Schartel. A liquid phosphorous flame retardant combined with expandable graphite or melamine in flexible polyurethane foams. Polym Advan Technol 33, 326-339, 2022. Doi: 10.1002/pat.5519.

Y. Y. Chan, B. Schartel. It takes two to tango: Synergistic expandable graphite – phosphorus flame retardant combinations in polyurethane foams. Polymers 14, 2562, 2022. Doi: 10.3390/polym14132562.

Y. Y. Chan, B. Schartel. It takes two to tango: Industrial benchmark PU-foams with expandable graphite/P-flame retardant combinations. In press KGK 2022

Y. Y. Chan, A. Korwitz, D. Pospiech, B. Schartel. Flame retardant combinations with expandable graphite/phosphorus/CuO/castor oil in flexible polyurethane foams. Submitted 2022

But also: Doi: 10.1016/j.polymdegradstab.2021.109557 and Doi: 10.1016/j.polymdegradstab.2020.109160

Biobased Flame Retardant Epoxy Resins and Composites

PhD student : Sandra F. Falkenhagen

Supervisor : Prof. Dr. habil. Bernhard Schartel - Bundesanstalt für Materialforschung und -prüfung (BAM)

Description:

Different promising bio-fillers were investigated as adjuvants in flame retarded kenaf reinforced bio-epoxy resin.

Fire Behaviour of Bonded Materials

PhD student : Vitus Hupp

Supervisor : Prof. Dr. habil. Bernhard Schartel

Bundesanstalt für Materialforschung und -prüfung (BAM)

Description:

In recent years, more and more mechanical fasteners were replaced by adhesives due to their advantages in handling, durability, and freedom in design. These glued materials boast very different fire properties than bulk materials and have certain advantages and risks that emerge from the adhesive gap. These special characteristics depend on the substrates, adhesives, and the fire scenarios, all of which are investigated in this PhD work. Especially pressure sensitive adhesive (PSA) tapes are used in construction, railway vehicle and automotive industry, where the fire properties of laminates are of great importance. Laminates of different tapes and substrates were manufactured and subsequently investigated in several fire scenarios. The results show that, in certain materials such as polycarbonate and wood, the adhesive gap can lead to additional fire hazards, which was expressed by a up to 18% higher FIGRA and additional peaks of heat release rate in the cone calorimeter. In contrast, the same tapes can improve the fire properties of bonded materials such as PMMA in the cone calorimeter significantly and reduce the MARHE by 30%. These results are transferred to the adhesive industry and help to develop new material combinations and avoid unnecessary testing expenses.

Graphene-Based Rubber Nanocomposites: New Perspectives for their Path to Industrial Applicability

PhD student : Bettina Strommer

Supervisor : Prof. Dr. habil. Bernhard Schartel

Bundesanstalt für Materialforschung und -prüfung (BAM)

Description:

Nanocomposites provide unique property profiles and open doors for new application fields. The combination of the strong, withstanding, and resistant nanoparticle graphene with the damping, sealing elastomer brings out the best of both worlds. Via a developed processing route of natural rubber latex premixing and further processing on conventionally industrial machines, nanocomposites at 2.6 wt.-% graphene concentration yielded an increase in Young's modulus of 157% and a reduced peak heat release rate in the cone calorimeter of 55%. By making use of the intrinsic flame retardancy of the elastomer, chlorosulfonated polyethylene in combination with ATH, the development of an elastomeric graphene nanocomposite was accomplished, reaching the one of the highest standards of flame retardancy requirements for transportation, namely a MARHE < 90 kW m^{-2}, at 1.8 wt.-% graphene concentration.

Papers:

B. Strommer, A. Battig, D. Frasca, D. Schulze, C. Huth, M. Böhning, B. Schartel. Multifunctional Property Improvements by Combining Graphene and Conventional Fillers in Chlorosulfonated Polyethylene Rubber Composites. ACS Appl Polym Mater 4, 1021−1034, 2022

B. Strommer, D. Schulze, B. Schartel, M. Böhning. Networking Skills: The Effect of Graphene on the Crosslinking of Natural Rubber Nanocomposites with Sulfur and Peroxide Systems. Polymers 14, 4363, 2022, doi: 10.3390/polym14204363

B. Strommer, A. Battig, D. Schulze, L. Agudo Jácome, B. Schartel, M. Böhning. Shape, Orientation, Interaction or Dispersion: Valorization of the Influence Factors in Natural Rubber Nanocomposites. submitted 2022

B. Strommer, D. Schulze, B. Schartel, M. Böhning. The Quantification of Anisotropy in Graphene / Natural Rubber Nanocomposites: Evaluation of the Aspect Ratio, Concentration and Crosslinking. Submitted 2022

Sustainable, flame retardant biocomposites based on industrial waste fibres

PhD student : Daniel Rockel

Supervisor : Prof. Dr. habil. Bernhard Schartel

Bundesanstalt für Materialforschung und -prüfung (BAM)

Description:

On the way towards a sustainable and circular economy, biopolymers and biocomposites have an important role as alternatives to conventional polymers from fossil fuels. This project focusses on biocomposites which are sustainable in their components. Thermoplastic starch, a common biopolymer, is used as a polymer matrix. The fibres to reinforce the composites derive from the waste of industrial leather production. These fibres do not need additional space to grow or energy to be harvested. We focus on halogen-free flame retardant, mainly ATH based synergistic mixtures.

Papers:

A. Battig, G. Sanchez-Olivares, D. Rockel, M. Maldonado-Santoyo, B. Schartel, Waste not, want not: the use of leather waste in flame retarded EVA, Mater Design 210, 110100, 2021. doi:10.1016/j.matdes.2021.110100.

Towards Environmentally Friendly Flame Retardant Epoxy Coatings

PhD student : Amer Aljamal
Supervisor : Beáta Szolnoki

Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Budafoki út 8, H-1111 Budapest, Hungary

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Epoxy resins have been widely used since they offer many advantages in terms of mechanical and thermal properties provided by the cross-linked structure. Epoxy coatings are usually cured in place to produce a durable coating layer. Flame retardancy has become a requirement for epoxy resins in all applications. The new trends in coatings favour bio-based and waterborne compositions due to the increased legislative restrictions on the emission of organic solvents into the atmosphere.

In the present research, many flame-retardant systems are prepared based on the highly functional sorbitol glycidyl ether as an epoxy monomer. The solvent-borne SPE is cured with a cycloaliphatic amine hardener. Waterborne SPE is cured with a waterborne polyamine hardener to form a fully waterborne epoxy system. Phytic acid (PA) is also used as a reactive flame retardant (FR) due to its high P-content (28%), which can be beneficial for flame retardant properties. Phosphorus-containing compounds present a good alternative to halogen-containing FRs to reduce the flammability of epoxy resins. Some commercially available additive flame retardants are used to reach flame retardancy properties. Since fillers are important components in coatings due to functional and economic reasons, the flame-retardant effect of some commonly used fillers like titanium dioxide, talc, and kaolin FR system is also investigated.

phosphorus content. Besides the standard flammability tests like limiting oxygen index measurement (LOI), UL-94, and mass loss calorimetry (MLC) measurements, the MLC instrument is also used to measure the thermal transition within the char by measuring the back surface temperature of coated steel plates. Dynamic mechanical analysis (DMA) tests are done to investigate the damping ability of the cured epoxy samples. The solid-phase effect of FRs is determined by scanning electron microscopic (SEM) and attenuated total reflection-infrared spectrometry (ATR-IR) analysis of the residual char after cone calorimetry measurements. At the same time, pyrolytic degradation gaseous products are analysed by a coupled Laser Pyrolysis–Fourier Transform Infrared (LP-FTIR) to have a detailed complex view of the mode of action of the different systems.

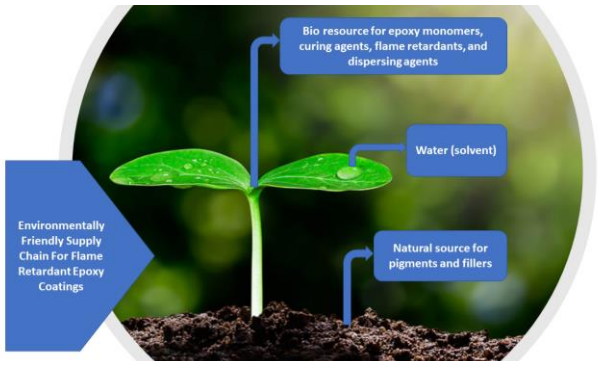


Figure 1. Environmentally friendly sources to prepare flame retardant epoxy coatings

Biobased flame retardants for poly(lactic acid)

PhD student : Kata Enikő Decsov

Supervisor: Katalin Bocz

*Budapest University of Technology and Economics, Department of Organic Chemistry and Technology, Budapest, Hungary, *decsov.kata@vbk.bme.hu*

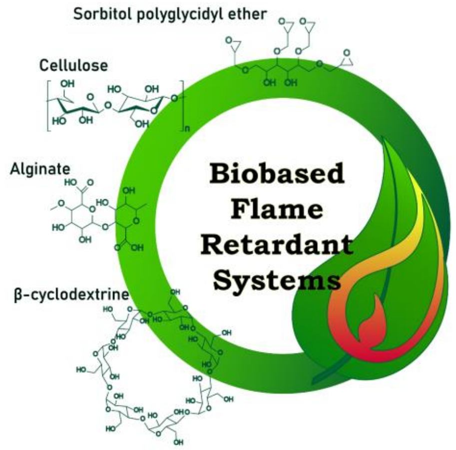
The overall goal of the research work is to provide environmentally benign flame retardancy solutions for poly(lactic acid) (PLA), the most promising biopolymer for technical applications. Novel flame retardancy approaches are explored by newly synthesised compounds, by chemical

such as surface treatment and encapsulation - of existing flame retardants, by utilising synergistic interactions and by using special carriers - such as fillers, nanoparticles or molecular complexes - for the active ingredients, respectively.

During the 4-year research period, the potential of various carbonising agents of renewable origin - such as cellulose, cyclodextrins, alginates, and bioresins - are comprehensively investigated in different intumescent flame retardant formulations. Composition-structure-property relationships are evaluated using morphological, spectroscopic, thermal, flammability and mechanical analyses.

It has been found that the formation, swelling ability, structure and mechanical resistance of a fire-protecting char can be noticeably affected by the length of cellulosic fibres, thus it can determine the efficiency of the flame retardant system [1]. It has been also demonstrated that natural fibre reinforced composites - when flame retarded with a combined approach, i.e., balanced distribution of phosphorus-containing additives between the matrix and reinforcing phases - gain improved mechanical performance and fire retardancy at the same time [2].

A new process of microencapsulating the widely used ammonium polyphosphate (APP) flame retardant with sorbitol-based bioepoxy resin has been developed. The bioresin shell effectively promotes the charring of the APP-loaded PLA composites besides providing water resistance to the flame retarded biocomposite [3].



The flame retardant effectiveness of a cyclodextrin-type increase when used in a microfibrous form—produced by electrospinning method [4]. The flame retardant performance of the electrospun cyclodextrin microfibres could be further enhanced by reactive surface modification with a phosphorous silane compound [5]. Furthermore, outstanding flame retardant efficiency has been observed for a newly synthesised phosphorous-silane-modified alginate compound.

1. The effect of cellulose fibre length(...), poster pres.;3rd ECOFRAM Conf, Alés, France (2022.05.17-18.)

2. Express Polym Lett 2020; 14:606–618.

3. Molecules 2019 24:4123.

4. Polym Degrad Stab 2021; 191:109655.

5. Polym Degrad Stab 2022; 200:109938.

Different ways to improve the flame retardant effect of APP

PhD student : Thuy Tien Nguyen Thanh
Supervisor: Beáta Szolnoki

Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Budafoki út 8, H-1111 Budapest, Hungary

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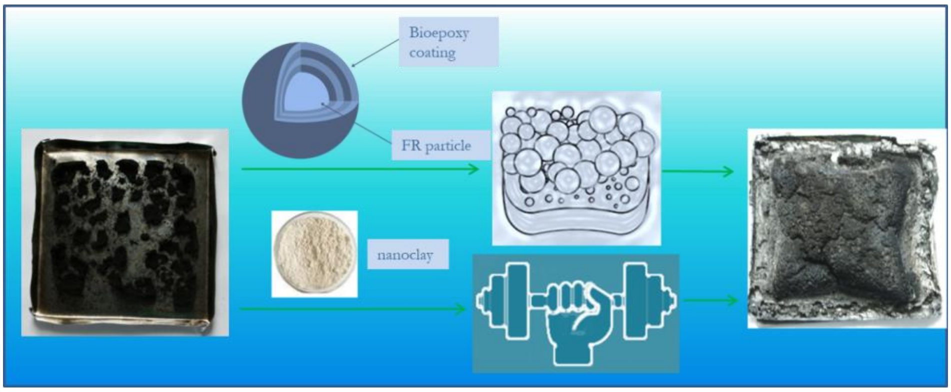
Nowadays, the escape time during a building fire significantly reduced to couple of minutes while decades ago the average time was 17 minutes to get to safety. The intumescent flame retardant (IFR) system through the formation of protective charred layer on the polymer is considered a promising solution to decrease the emission of volatile toxic waste products and reducing the flammability of the materials.

In our course of work, the focus is on the flame retardancy of different, conventional (such as polypropylene) and biobased (like polylactic acid or poly butylene succinate) thermoplastics with ammonium-polyphosphate (APP), a commonly applied IFR, and finding ways to enhance its flame retardant properties. For this purpose, the charring ability is modified, and also the possibilities of char strengthening are under investigations. Through microencapsulation of APP with bioepoxy resins, the charring ability of the IFR system can by significantly improved in an environmentally friendly way, compared to the application of these components with no additional formulation. The protective ability of the formed charred layer depends much on its foam structure which can be strengthened with clay minerals of natural origin by having an improved coherent porous cellular network. Recent research targets the creation of an IFR system through combining different phosphorous-based flame retardants, to take the best advantages of their flame retardant mechanism.



Development of flame retardant coatings for fibre reinforced polymer composites

PhD student : Zsófia Kovács

Supervisor : Andrea Toldy

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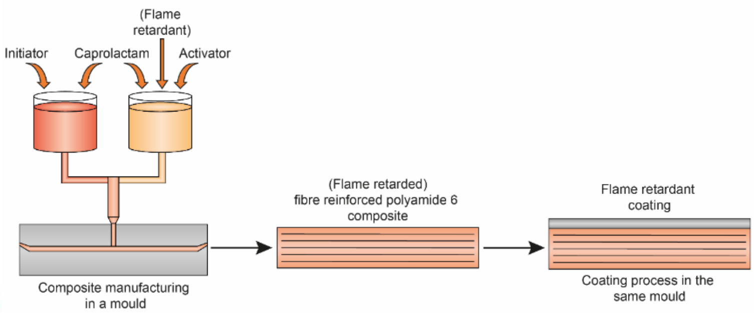
kovacszs@pt.bme.hu

The flammability of polymers hinders the broader uptake of polymer engineering solutions in many areas. Increasingly stringent safety requirements make it necessary to effectively decrease the flammability of polymer systems while maintaining or possibly improving their mechanical and other properties. In addition to using flame retardants in a matrix, a particularly effective flame retardant method is to apply the flame retardant-containing polymer as a coating to the outer surface of the composite. The use of coatings prevents the flame retardants from altering the properties of the composite, prevents the solid additives from being filtered out by the reinforcing materials, and avoids delamination caused by intumescent flame retardants.

Due to short cycle times and easy recycling, thermoplastic matrix composites are becoming increasingly important in many technical fields, particularly in the automotive industry. Polyamide 6 (PA6) is one of the most commonly used matrix composites. PA6 can be produced from ε-caprolactam monomer by anionic ring-opening polymerisation in the presence of an activator and initiator. One of the most promising methods for their production is thermoplastic resin transfer moulding (T-RTM) technology based on in-situ polymerisation, where the polymerisation of the monomer impregnated in the reinforcing materials takes place in the mould.

The aim of my thesis is to develop a flame retarded PA6 system by ring-opening polymerisation of ε-caprolactam, which can be used as a coating for long fibre reinforced PA6 composites produced by T-RTM. In-mould coating is used to create the coating during composite production. By using combinations of flame retardants with different mechanisms, more effective flame retardancy can be achieved, thus, my research also investigates the synergism of different flame retardants. My objectives also include the developement of self-



EVA-based compounds containing different types of Biochar: novel fire retardant systems

PhD student : Samuele Matta

Supervisors : Pr. Giulio Malucelli and Alberto Frache

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In recent years, the use of bio-sourced and environmentally friendly products has been exploited for the design of effective and 'green' alternatives to common flame retardants. Among them, biochar (BC), which is a solid product obtained from the thermo-chemical conversion of biomasses in an oxygen-limited environment, is attracting great interest as a low-cost carbon source for flame retardant applications. The purpose of this Ph.D. work was to investigate the behavior of different types of BC, obtained by pyrolysis of biomass/waste (i.e., softwoods, rapeseed, rice husk, Tetra Pak®, kraft lignin). The so-obtained BC particles were incorporated as flame retardants into Ethylene Vinyl Acetate (EVA) using a co-rotating twin-screw extruder, at different loadings, ranging from 15 to 40 wt.%. Thermo-compression and injection molding processes were utilized for preparing the specimens for the characterization tests (i.e., SEM, DSC, TGA, forced-combustion and tensile tests). SEM observations performed on EVA/BC compounds showed a good distribution of the particles within the polymer matrix. Their size was substantially micrometric, though some bigger aggregates (not exceeding 100 microns) were clearly visible. These findings indicate that the experimental conditions adopted for compounding were suitable for obtaining a homogeneous dispersion of the fillers, regardless of their type and loadings. DSC analyses revealed that the presence of BC didn't affect the melting temperature and the crystallization (about 85 and 65°C, respectively), while the degree of crystallinity was slightly reduced with respect to the unfilled polymer. Because of the barrier effect on oxygen diffusion provided by BC particles, the thermal and thermo-oxidative stability of the compounds showed an increase in the characteristic temperatures, i.e., Tonset and Tmax, compared to unfilled EVA, and of the residues at the end of the tests. Figure 1 shows the typical HRR vs. time curves of the compounds containing the different biochars at 40 wt.% loading: a significant decrease in the peak of heat release rate is observed; this effect is more pronounced when the filler loading increases. Finally, the incorporation of BC negatively affected the ductility of EVA, making the compounds, at the same time, stiffer.

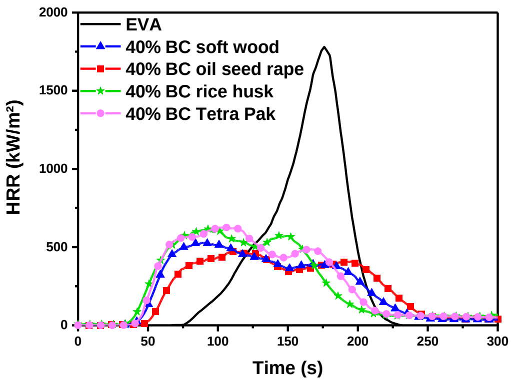


Figure 1. Heat Release Rate (HRR) vs. time curves for EVA and its composites filled with 40 wt.% of different types of biochar.

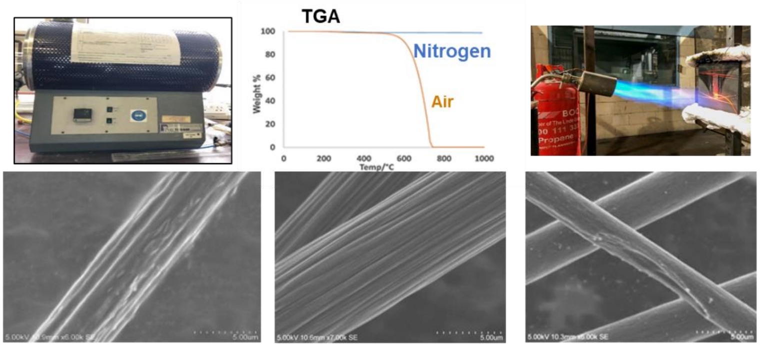
Designing carbon fibre-reinforced composites with improved structural retention on exposure to heat/fire

PhD student : Francesca McKenzie

Supervisors : Pr. Baljinder Kandola, Pr A R Horrocks, Pr John R Ebdon

Fire Materials Research Group - Institute for Materials Research and Innovation - University of Bolton, Bolton, UK

Carbon fibre is a highly versatile material often used in carbon fibre-reinforced composites (CFRCs) for aerospace and automotive industries. CFRCs, while are relatively heat resistant up to 300°C (depending on the resin type), at higher temperatures the resin starts decomposing. On autoignition or exposure to fire, the resin burns, leaving behind carbon fibres. Carbon fibres being electrically conductive, may pose a hazard to the surroundings. Moreover, carbon fibres in fire defibrillate into small porous fibrils, which are hazardous to human health. The purpose of this PhD is to (i) investigate the damage caused by high temperature, radiant heat and flames on carbon fibres, and (ii) develop CFRCs which either do not ignite, or if they ignite maintain their structural coherence. The approaches taken for the latter include adding flame retardants and nano-additives to the resin matrix to form protective residue and char barriers on the carbon fibres, the use of high temperature resistant hybrid layers to shield the underlying carbon fibres and applying chemical coatings to the individual carbon fibres prior to making the CFRCs.



Exposed to 650°C for 30 min | **Carbon fibre** | **Exposed to jet fire for 5 min**

Mechanistic study of carbonisation of lignin for value-added materials applications

PhD student : Annan Xiang

Supervisors : Pr Baljinder Kandola, Pr A R Horrocks, Pr John R Ebdon

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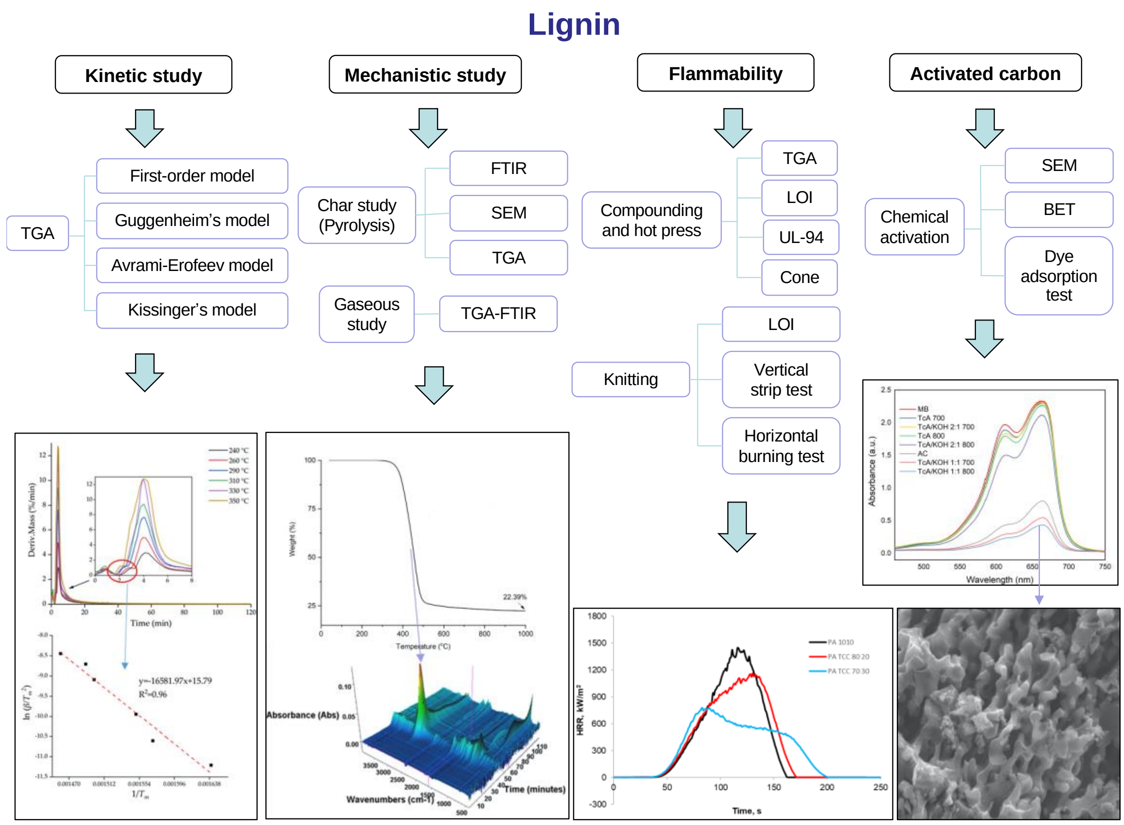
Lignin is the second most abundant renewable resource material in the world, with high char-forming ability because of its aromatic moiety. Owing to the charring tendency of lignin, it can be used as a (i) flame retardant additive in polymers either on its own or in combination with other flame retardant additives, (ii) precursor for carbon fibres and (iii) precursor to generate activated carbon. The purpose of this PhD is to explore effectiveness of different lignin types in these three areas. The pyrolysis kinetics of different lignins have been understanding of the pyrolysis processes of different lignin types under different heating conditions. Based on this understanding, the thermal stabilisation and carbonisation processes of the lignin derived fibres could be appropriately modified to prepare carbon fibres of good quality. Using an appropriate lignin type, activated carbon with adsorption properties equivalent to a commercal activated carbon could also be developed. Different ongoing activities are summarised



Designing high-performance flexible thermal barrier films or fibrous membranes for polymeric materials.

PhD student : Selvan Thamizhirai

Supervisors : Pr. Baljinder Kandola, Pr A R Horrocks, Pr John R Ebdon

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Carbon Fibre Reinforced Polymeric Composites (CFRP)s, particularly those comprising epoxy resin are commonly used in aerospace, owing to their significant weight saving over metallic structures. However, under extreme temperature and pressure, resin in CFRPs may soften and thermally decompose and lead to ignition. Surface coatings, chemical or ceramic thermal barrier coatings (TBC)s can be used to mitigate this risk. The purpose of this project is to design low-cost, flexible thin films and fibrous membranes with thermal barrier properties, that can be applied to CFRC substrates either as a part of the or on the developed product by simple after-processing. The

approaches being undertaken include (i) application of ceramizing nanomaterials on fibrous veils from fibres of low thermal conductivity, (ii) further modification of thin films from inherently flame retardant polymers wih ceramizing materials and (iii) developing aerogel based treatments. Aerogels can act as excellent thermal barriers, but at ≥ 800oC become brittle and lose physical and thermal barrier properties, and hence need to be modified to give thermal stability over a prolonged period of time.

Sensing in carbon fibre composites for early detection of fire

PhD student : Lewis Roberts

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Owing to the nature of composites and with regards to increasing the operating temperature of them, most research is focused towards the fire retardancy of the matrix. This work intends to contribute towards research focused on preventing fire damage to the composite by detecting the precurser conditions to ignition during elevated temperatures, and ultimately providing a warning of any potential fires. With this aim, in the first instance, a number of representative epoxy resins are being studied by thermogravimetry coupled with Fourier transform infrared analysis (TGA-FTIR) and pyrolysis-gas chromatography mass spectrometry (Py-GCMS) for product produced at different tempertures. The identification and quantification of evolved gases will allow prediction of the time-to-ignition of the composite. The next step is to introduce sensors within and/or on the surface of the resin matrix of carbon/glass fibre-reinforced polymer composites so as to enable the identification of resin degradation and/or gases generated by chemical degradation on exposure to high temperatures. The sensors will also be able to detect chemical and physical changes within the resin as it decomposes, from which likely thermal and mechanical damage in composites in-service can be predicted.

Novel inorganic environmentally sustainable flame retardant and thermal barrier compositions

PhD student : Fawad Khan

Supervisors : Pr Baljinder Kandola, Pr A R Horrocks, Pr John R Ebdon

Fire Materials Research Group - Institute for Materials Research and Innovation - University of Bolton, Bolton, UK

Certain inorganic elements, owing to their low atomization enthalpies and ionization potentials, are widely used in sensors, electronics, optics and biomedical applications. Majority of these have low thermal conductivities, hence offer excellent thermal insulation and barrier effects. For example, yttria-stabilized zirconia thin coating of ~250 µm can reduce the metal surface temperature by 170 °C. The purpose of this PhD is to novel inorganic compounds and investigate their flame retardant efficiency in a number of polymers either on their own or in combination with other flame retardants, (ii) develop simple, novel and industrially viable methods for applying thermal barrier coatings comprising these novel compounds on to textile/polymeric substrates and (iii) elucidate their mechanisms of flame retardant/smoke suppression actions.

Synergistic Effect of Phosphorus and Nitrogen Containing Groups in Fire Retardancy of Polystyrene

PhD student : Aloshy Baby

Supervisors : Svetlana Tretsiakova-McNally, Jianping Zhang, Seng-Kwan Choi

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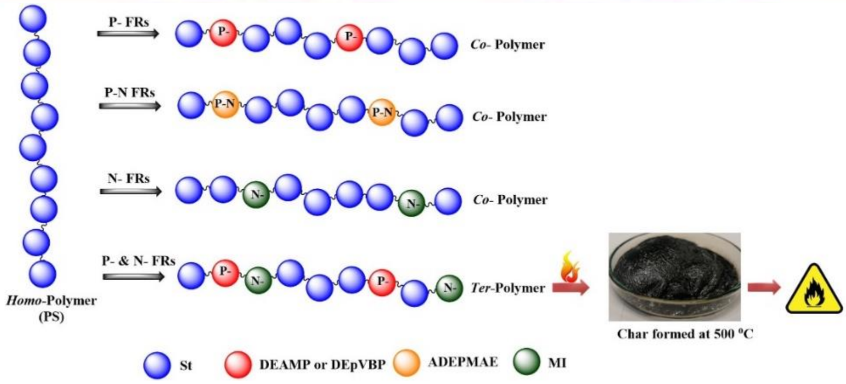
The primary strategies to improve the fire retardance of commercially important styrene-based polymers are largely reliant on halogenated fire retardants (FRs). Currently, these compounds are considered to be hazardous to public health and environment. As a result, many halogen-based FRs have been withdrawn, especially, from their use in products that form construction elements in built environments [1]. Thus, it is necessary to develop efficient fire-retardant systems for mitigating their hazardous impact in fire scenarios. Among the proposed FR solutions, the compounds containing P atoms can be very powerful in inhibiting the ignition, and often supress the combustion of polymeric materials effectively. Through this



study we focus on the chemical incorporation of various P- and/or N- containing unsaturated compounds into polystyrene (PS) via co- and ter- polymerisations and characterisations of the modified materials with regards to their thermal degradation and combustion attributes. The primary aim of this study to find the effective combination of P- and N- containing compounds that can trigger P-N synergism, thus enhancing fire retardance of PS. The compounds such as diethyl(acryloyloxymethyl)phosphonate (DEAMP), diethyl-p-vinylbenzyl phosphonate (DEpVBP), acrylic acid-2-(diethoxyphosphorylamino)ethyl ester (ADEMPAE), maleimide (MI), acrylamide (AM) and N,N-dimethyl acrylamide (DMA) had been used for the modification of PS [2]. The fire performance of unmodified PS and modified PS was determined using a Theyinclude 'bomb' calorimetry, thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier Transform Infrared (FT-IR) spectroscopy, Nuclear Magnetic Spectroscopy (NMR) Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS).

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An evaluation of bench scale experimental methods for the purpose of producing scalable fire properties from under-ventilated compartments

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Supervisors : Jianping Zhang, Svetlana Tretsiakova-McNally

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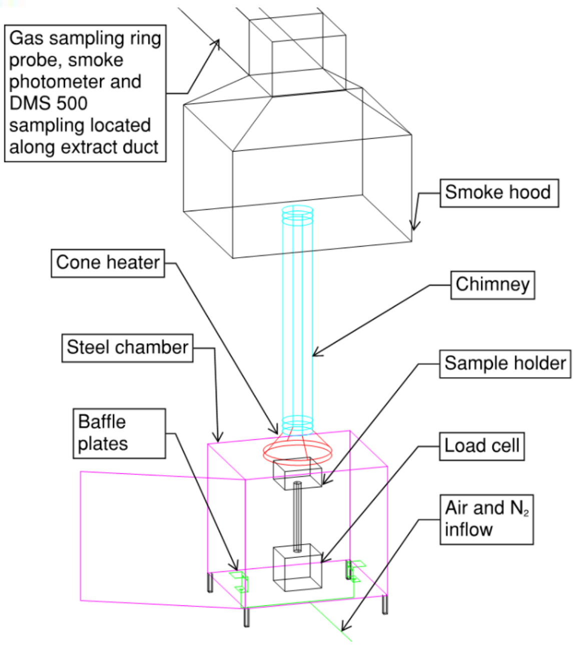
One of the key challenges in applying the findings of fire science research to real world applications in the built environment is the issue of scalability. An observed effect using bench scale laboratory equipment may not necessarily perform the same as a full scale enclosure fire. This is further complicated by the effect of under-ventilated conditions on material burning behaviour. Under-ventilation is a common and dangerous stage of fire development within the enclosure of a room, but these conditions are hard to replicate in small scale equipment where oxygen is freely available from the laboratory surroundings. Equipment allowing the control of oxygen concentration offer a solution to this and allows for the creation of a controlled, hypoxic environment. However, the mode in which oxygen vitiation occurs within the ambient environment significantly differs between hypoxic and under-ventilated cases. General research into hypoxic conditions is extremely limited and there is even less research remarking upon its comparison with under-ventilated conditions.

This research investigates fire dynamics and material behaviour in hypoxic conditions, created by lowering the volume percent of oxygen in air, and how it compares to material behaviour in ambient and under-ventilated conditions. The work intends to explore whether hypoxic and under-ventilated environments



induce similar material burning behaviours; specifically, whether the material deformations, product yields, and heat release rates are comparable.

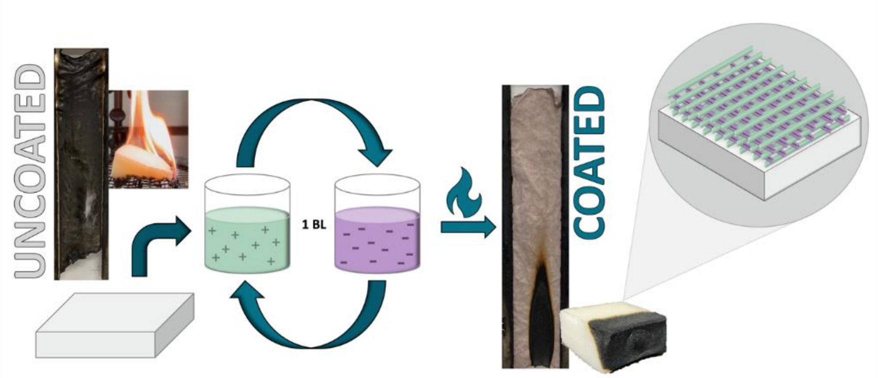
Using different experimental methods commonly used in the field of fire science (cone calorimeter, controlled atmosphere cone calorimeter, fire propagation apparatus) this research will determine optimal methods for the collection of bench scale data as well as highlight limitations of current methods. The creation of bench scale data that is upwardly scalable is of great value in providing full realisation of the risks of under-ventilated conditions. Research outcomes could assist academics in using hypoxic/under-ventilated test data more appropriately by highlighting data variability between

Layer-by-Layer Assembly of Environmentally Benign Flame Retardant Nanocoatings

PhD student : Natalie Vest

Supervisor : Jaime Grunlan - Texas A&M University

Increased frequency in fires, both manmade and naturally caused, have resulted in billions of dollars in damage and thousands of fire-related deaths worldwide. High flammability textile and construction materials create an increased risk of fire propagation and injuries due to release of toxic fumes and potential to melt drip. In the past two decades, development of environmentally-benign flame retardants, as an alternative to harmful halogenated surface treatments, has been accelerated due to increased fire damage worldwide. Layer-by-layer assembly allows for the attainment of tunable properties, such as flame retardancy, with ambient processing on diverse substrates, through the deposition of oppositely charged polymers, nanoparticles, and small molecules. Furthermore, technique can be customized to achieve intumescent flame retardant behavior through the incorporation of a carbon source, blowing agent, and acid source to create a thermally insulating barrier. With the additional integration of bio-sourced components, effective layer-by-layer assembled thin films can be sustainably created to reduce flammability of materials. This dissertation showcases the potential of intumescent layer-by-layer thin films to render highly flammable materials (e.g. polyurethane foam and cellulosic/synthetic blended textiles) flame retardant and potentially reduce fire-related injuries. There is also a focus on the efficacy of renewable molecules to reduce flame propagation.



Flame retardancy via reactive extrusion

PhD student : Léa Gratier

Supervisors : Henri Vahabi[a], Marianne Cochez[a], Jean-Marie Raquez[b], Fouad Laoutid[b,c]

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Polyurethanes is a wide family of different materials which are used in various field of applications, like construction, insulation, automotive, electronic and spatial conception (1). The material of interest in this PhD study is thermoplastic polyurethane (TPU). This type of polyurethane contains polyurethane bonds and it is composed like a block copolymer, with an alternance of hard segments and soft segments, which allows it to be flexible (2).

The traditional route of synthesis for these materials includes some solvents and take a lot of time; moreover, it uses some hazardous precursors, as isocyanate. The impact of the synthesis in terms of costs and ecology is huge and it's needed to be reduced. There is also a need to enhance the fire retardancy of this polymer; as it is oil-based, it is very flammable and can be very dangerous due to it presence on many materials.

reactive extrusion process. This type of synthesis doesn't include a solvant to be carry out and is very fast. The principle is simple: precursors for TPU are introduced into the extruder as pellets. Precursors for the flamme retardant are introduced as pellets immediatly after the TPU in the extruder. The system of corotative twin screw allows mixing the pellets, the temperature allows melting them and the rotation carries them to the end of the extruder, where material could take different shapes (film or tubes).

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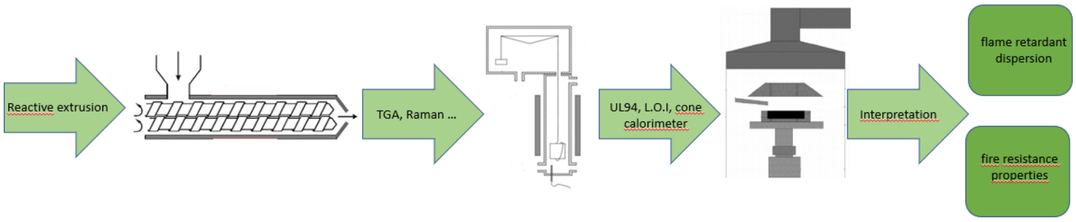

Figure 1 : Project's structure

Ageing of flame retardant polymer blends

PhD student : Maël Kervran

Supervisors : Henri Vahabi, Christelle Vagner,

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Over the last decade, bio-based and biodegradable polymers have attracted much attention due to the increasing interest to the development of sustainable materials. Polylactic acid (PLA) is known as the most promising among them but recently, polyhydroxyalkanoates (PHAs) a family of bio-polyesters produced by bacterial fermentation gained in interest [1].

However, some of their properties are too weak to replace petroleum-based polymers. One solution may consist to blend these polymers to improve their properties. To promote the development of industrial development of these materials the use of additives is necessary. Indeed, the low thermal stability and the high flammability are the main drawbacks of these materials. It is possible to improve their fire behavior, in particular using suitable flame retardants. However, it can change significantly after ageing, endangering property and people in the event of fire. Until today, the standards require the evaluation of the reaction of the material to fire just after the manufacture and exceptionally after ageing representative of the real conditions of use. The evolution of the characteristics of flame-retardant polymers over time is currently little-known and only a few studies have been carried out on this subject [2, 3].

The main objective of this work is to improve the fire properties of a PLA/PHB matrix using mainly bio-sourced flame retardant systems. The properties of polylactic acid (PLA)/ polyhydroxybutyrate (PHB) blends according to the composition was studied in order to select the composition with the best properties. For the first time, the flame retardancy of PLA/PHB blend is studied and new bio-based flame retardant systems were introduced into a PLA/PHB matrix in order to improve the fire behaviour of the blend. As PLA and PHB are not miscible, the morphology of the neat blends and of blends containing flame retardants is controlled. The evolution of the material and particularly of the fire properties during the ageing of the sample will be studied.

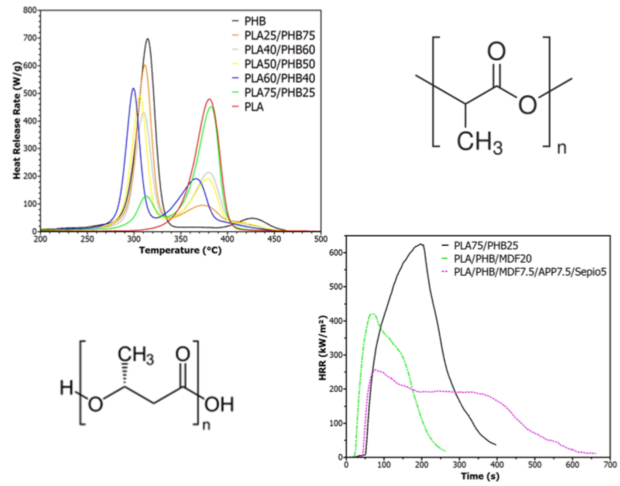

Figure 1: PCFC curves of PLA/PHB blends, cone calorimeter curves of flame retardant formulations and chemical formulas of PLA and PHB

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Influence of prescribed burning on litter quality, decomposition and community structure of organisms in Pinus laricio forest

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In the Mediterranean region, climate change is altering the dynamic of fire events. In Corsica, the presence of endemic species sensitive to forest fires, such as Pinus laricio, encourages managers to develop fire risk reduction methods. Prescribed burning seems to be the most appropriate, as it is easy to set up, even in areas that are difficult to access. It also allows to reintroduce fire in ecosystems adapted to this kind of events.

The objective of this thesis is to evaluate the impact of prescribed burns on the soil, by studying the arthropod community present, the plant biodiversity, the chemical and soil, the rate of litter fall and decomposition, and to evaluate the effectiveness of prescribed burns carried out under different conditions.

Field experiments were conducted in a pure stand of Pinus laricio, Zonza (Corse-du-Sud): two prescribed burns were performed, one in a mecanically pruned plot with elimination of the weakest trees, the other without pruning in november 2020.

On the first plot, mechanical treatment resulted in a lower population density, but a high fuel load on the soil with the presence of branches and trunks. In contrast, the untreated plot had a higher population density and a lower fuel load.

On each plot, several experiments were carried out before and after the prescribed bruning: pitfall traps were set up for a week, and humus and soil samples were taken each season. Botanical monitoring was conducted in the spring, litter traps were used to collect needles and litter bags were filled with needles and placed on the soil.

Modifications of the arthropod communities of the soil, were followed during 22 months, and related to nutrient composition of humus, needle litter fall and decomposition, and botanical monitoring to better understand the links between the different soil parameters. Taking an interest in the resilience of the environment after the various disturbances induced by man will allow the development of forest management guidelines to limit the ecological impacts of human intervention.

Figure 1: Prescribed burning in a (a) without treatment forest and in (b) a pruned forest

Virgin cork extracts (Quercus suber L.): characterization and integration in fire-retardant intumescent formulations.

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Supervisors : Toussaint Barboni, Paul-Antoine Santoni

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In the last few years, fire induced disasters have shown the necessity to aim for a better control of fire hazard which includes further protective measures to prevent these types of risks. In the case of wildland-urban interfaces, wood structure elements may act as spread vectors to the housings leading to security issues. One of our best ways to address these issues is to fireproof materials used as furniture or construction. In a context of on-going increasing risk, it became a leading problematic in terms of fire-safety concerns.

Fire retardants are classified following their thermal behavior and action mechanisms. Among these, intumescent coatings constitute an innovative way to protect substratum using a synergistic effect leading to the formation of a carbon-rich protective layer. This effect is based on the polymerization of a carbon source with an acid source when exposed to heat flux. The aim of this study is to define and measure the thermal abilities of a newly formulated intumescent mixture at bench-scale by using cone-calorimeter and thermogravimetric analysis. This formulation contains natural extracts obtained by pressure assisted method using “green” solvents (ethanol, water and mixtures of both). Measurements of total polyphenol content (TPC) and antioxidant capacity (ORAC) were conducted and indicated high polyphenols and tannins concentration, both showing good capabilities as carbon source. More precise chemical characterizations of these extracts were carried out by HPLC-PDA/MS analysis to identify and quantify main phenolic acids and tannins.

Extracts were then selected following tests carried out with a thermogravimetric analyzer based on char residue at 900°C and temperature of maximal decomposition under nitrogen flow. Different ternary formulations shaped into pellets were tested with a cone calorimeter at 50 kW.m-2 irradiance without forced ignition. Physical properties measurements were conducted including expansion coefficient of char layer and solid FTIR analysis. Samples showing the best results will be included in intumescent paint formulations.

These paints will rely on a well-known formulation based on VA-VeoVa chemistry in which ternary mixtures will be added at different levels and finally applied onto pine plates. Intumescent coatings will then be tested and compared to selected commercial products using cone-calorimeter to benchmark their thermal abilities and fire behavior (figure 1). Samples showing the best results might be used at WUI to provide better fire protection for dwellings.

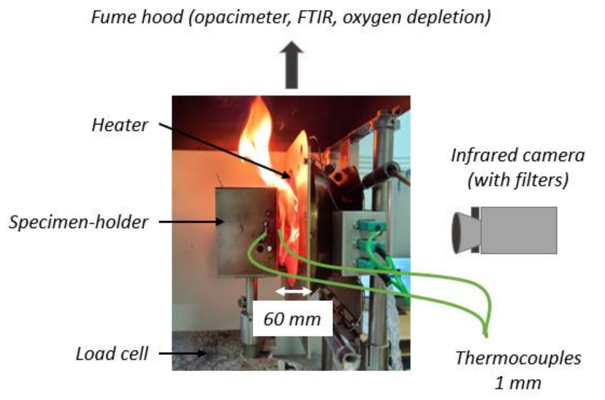

Figure 1: experimental setup to evaluate intumescent paint efficiency

Study of the vulnerability of the envelope of a construction subject to an outdoor fire

PhD student : Camille Luciani

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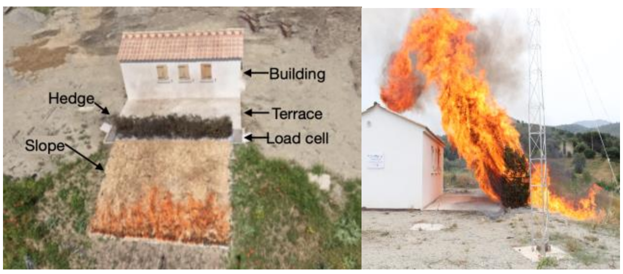
Due to climate change and the expansion of rural areas, the severity and frequency of large fires has increased dramatically around the world. Some of them have impacted the built environment sometimes resulting in fatalities. The objective of this thesis is to characterize the vulnerability of a construction subjected to a fire arriving in a Wild Urban Interface (WUI). In particular, this work is interested in the influence of the landscaping arrangement of ornamental plants around the constructions on the impact of fire, at the level of joinery and cladding. To carry out this research, an experimental and numerical approach is carried out.

The experimental study is based on multi-scale works. At laboratory scale, tests are carried out under a cone calorimeter and a Large Scale Heat Release calorimeter in order to determine the influence of moisture content and species on the fire behavior of ornamental plants. On the field scale, experiments are performed on the EXPLORII platform in order to see the impact of a vegetation fire (shrub and hedge) on a construction comprising different types of joinery (wood, aluminum and PVC) with or without shutter and different types of wood cladding (Figure 1).

The numerical part is carried out with Fire Dynamic Simulation and aims to complete the experiments by determining the influence of interface properties (position of plants, slope, etc.) and ambient conditions (temperature, humidity, wind, etc.) on the impact of fire on a building. These numerical simulations coupled with experimental data will make it possible to give recommendations on the materials to be favored and on the arrangement of plants around dwellings to reduce their vulnerability.



(a) (b)

Figure 1 : (a) EXPLORII plateform ; (b) Experiment of a hedge burning near a house

Characterization of smoke from the burning of forest fuels

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Supervisors : Toussaint Barboni, Paul-Antoine Santoni

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Vegetation fires produce many primary pollutants that enter through the respiratory tract to lodge in the various target organs (eyes, nose, throat, lungs, heart, blood, brain, reproductive system) of the human body causing short-term and/or chronic effects on individuals. Our knowledge of the aerosol composition of smoke emitted by vegetation fires is currently still limited. Thus, understanding the health impact of forest fires related to particulate or gaseous effluents remains a challenge due to the many chemical substances identified in the composition of smoke. Suspended particles emitted during forest fires can be considered at least as toxic as those resulting from human and industrial activities.

The first approach of this thesis is the aerosols characterization and chemical species at the following scales: at the laboratory scale (using oxygen consumption calorimeters; Figure 1), at full scale on the EXPLORII platform (experimentation of pollutants at the forest/habitat interface) with model vegetation and in an operational framework (controlled burning and fires). Smoke capture devices will be deployed at these scales, paying particular attention to devices for measuring fine and ultrafine particles (PM2.5 and PM1). The second scientific objective is to determine to what extent the nature and the dose of smoke from forest fires harm the health of the personnel involved. For this, direct and indirect measurement methods will be implemented. Samples of biofluids and exhaled air will be taken. Other measurements will concern the composition of the atmosphere in order to assess the working conditions in relation to the exposure limit values or the toxic potential of the smoke. After having determined the source terms (emission factors), numerical simulations, initially at the laboratory level, will make it possible to predict the dispersion of smoke and to determine the concentration of chemical compounds in space. Once the model has been calibrated, the simulations will be deployed on the largest scale in order to define the potential impact of the smoke on the responders and the population close to the fire. This proposed modeling approach aims to develop a detailed model to predict the composition of smoke emitted during a wildfire and predict their toxic effects on individuals. The simulations will be carried out on WFDS, within the framework of massively parallel calculations thanks to the computing resources of our Unit. The final objective of this thesis is to lead to the smoke characterization by improving in particular the knowledge on particles in suspension, at the level of their composition but also of their granulometry, and to a better consideration of the expectations of the population and decision-makers in preventing the risks of toxicity linked to smoke from forest fires.

Figure 1. Experiment at laboratory scale of burning shrub

Fire behavior of lightweight biobased concretes

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Supervisors : Laurent Ferry, Rodolphe Sonnier, Laurent Aprin, Arnaud Regazzi

Institut Mines-Télécom (IMT) - Mines Alès, Alès, France

Funding: Thèse BIOFEU

Nowadays, the construction field is still a big producer of carbon dioxide, responsible for a quarter of the total emissions of greenhouse gases. In order to minimize this problem, the utilization of biobased concretes, that is, (plant-based) bioresources mixed with a binder (gypsum, lime or earth), can be an innovative solution. The lightweight biobased concretes have remarkable thermal insulation and water regulation capacities. On the other hand, higher-density biobased concretes can act as a protective barrier applied to other The bioresources utilized correspond to local productions, contributing to stimulate the territories in which the biobased concretes are used. In the region of Occitanie, France, hemp, wheat straw, straw or rice husk are among the resources most used to produce the concretes. However, in order to be applied, the fire behavior of these concretes must be evaluated through Euroclass tests. At this time, due to a great diversity (different formulations, compositions, binders, bioresources), each biobased concrete is considered as a different material, which makes its evaluation more complicated. Therefore, the main goal of this work is to evaluate the effect of each source of variability on the behavior of the concretes in case of a fire and then to be able to handle these materials by family, thus optimizing the number of standardized tests to be carried out to officially demonstrate their performance, which can be understood from the study of three phenomena: flammability, fire resistance (including erosion during fire) and smoldering.

Different kinds of biobased concretes after cone calorimeter tests

Functionalisation of natural fibers using ionizing radiations

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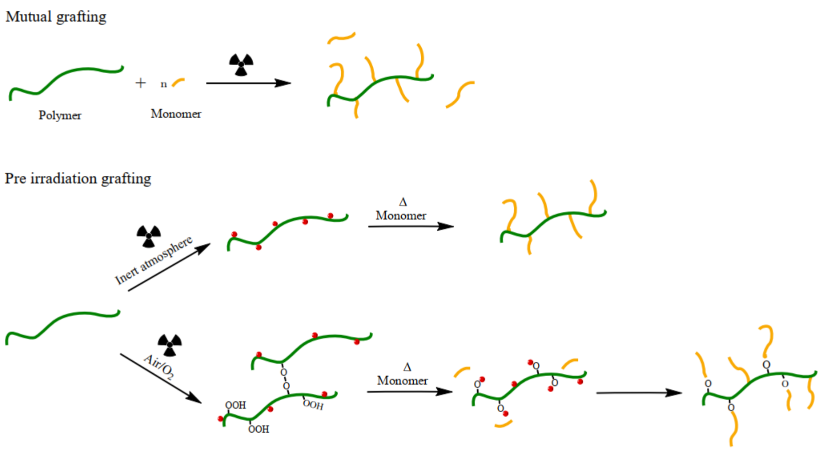
Supervisors : Rodolphe Sonnier, Belkacem Otazaghine

Institut Mines-Télécom (IMT) - Mines Alès, Alès, France

Funding: Thèse SABRES

Given their advantages, composite materials are gaining importance in many fields (construction, automotive, aeronautics, etc.). The current context, however, requests to limit the environmental impact of such composites so that efforts are made to replace conventional reinforcement materials (fiberglass, carbon fibers) by alternatives whose Carbon footprint would be lesser. In this respect, plant fibers such as flax or miscanthus seem to be relevant candidates. Combining lightness, low cost, and specific mechanical properties competitive with synthetic fibers, they nevertheless have some drawbacks such as their incompatibility with polyolefin matrices, their sensitivity to humidity, and their flammability. Plenty of chemical and physical techniques have these problems. Among them, radiation-induced grafting emerges as a promising functionalization route due to key advantages such as its adaptability and reliability. This method, based on the use of ionizing radiation, makes possible to create free radicals on plant fibers, allowing the graft-copolymerization of functionalized molecules onto them. Part of this work, therefore, consists in using this technique to graft methacrylatedmolecules containing phosphorus functions to improve the fire behavior of plant fibers. Optimization of the grafting yield needs to control the main parameters influencing these methods. Comparisons between two methods (mutual and pre irradiation grafting), and between irradiation technologies (gamma and e-beam) will be also carried out.



Radiation-induced grafting pathways

Synthesis of phosphorus biosourced flame retardant additives for the development of new polymers for wood paint with low environmental impact

PhD student : Maxinne Denis [a,b]

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Funding: Thèse CIFRE Lixol

Alkyd resins have been used as binders in paint or varnish formulations since the 1930s'. However, as all polymers, alkyd resins are flammable and their uses as coatings require the addition of flame-retardants. The most used in the field of coatings are mineral fillers that have the disadvantage of damage the mechanical properties, and halogenated compounds. The tightening of regulations limiting the use of toxic molecules for human health and the environment require finding new alternatives. Wishful to be part of a sustainable development approach, the company Lixol wanted, through this work, to develop a new range of flame-retardant alkyd resins for wood-applications. New phosphorus-based flame-retardants have been synthesized from biobased molecules, then introduced as monomers during the polycondensation of alkyd resins. The development of flame-retardant hybrid alkyd resins has made it possible to achieve coatings with excellent performances (drying time, adhesion and gloss). The incorporation of phosphorylated cardanol as reactive diluent provides flame retardant properties while reducing the level of volatile compounds. New hybrid alkyd resins have also been synthetized with the introduction of different phosphorus oligomers (based on siloxane or polyhydroxyurethane) to improve film properties such as drying time, gloss, hardness or alkali resistance while providing excellent flame retardant properties. All the alkyd resins have been tested as a coating on wood support for cone calorimeter analysis. The results have demonstrated excellent performance with the introduction between 1 and 3 wt% of phosphorus. Finally, paint formulations were made in order to highlight the flame retardant performance of a ready-to-use final product.

a b

Wood coating with alkyd resin a) before combustion and b) after combustion

Durability of flame-retarded polymer, 3D printable for railway industry

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Additive manufacturing is a process in huge expansion since 20th century thanks to its many benefits: save materials, save money, freedom for designing objects. Railway industry is particularly interested in using it for economic and ecological reasons. Indeed, 3D printing technology should avoid mass stockage of obsolete parts in huge hangars and permit faster maintenance. However, in railway industry, materials used need to comply with very strict fire/smokes requirements including the stringent EN 45545 standard. Unfortunately, 3D printed materials do not meet these requirements or are too expensive.

The aim of this project is to develop a new 3D printable material meeting with challenging fire/smokes criteria and durable. A material combining a polymeric matrix and flame-retardant fillers acting both in gas or condensed phases is developing. Thermomoulded or 3D printed parts will be thermo-oxidated to simulate ageing of the material. Compared to other works, this study will allow to explore several point in the same time: (i) to understand the impact of ageing on physico-chemical, mechanical and fire properties[1], (ii) to examine the influence between flame-retardant fillers and their effect on the durability[2], (iii) to predict the end of life. This multidisciplinary project, combining several skills such as additive manufacturing technology, flame retardancy, thermo-oxidative ageing and mechanical performances, opens several routes to explore and understand in a new way the durability of fire retarded polymeric materials.

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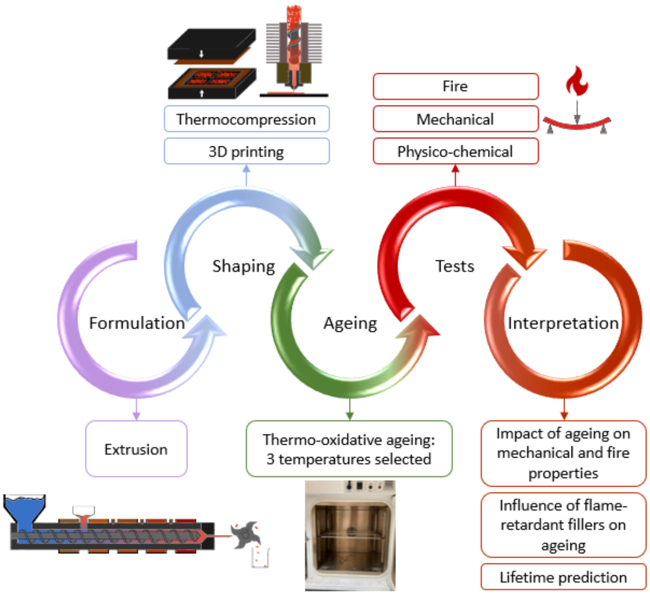

Figure 1: The project's structure.

Development of new fire-resistant formulations for optical cable sheaths based on the use of low melting glass

PhD student : Diana Amin Alsayed

Supervisors : Laurent Ferry, Belkacem Otazaghine, Rodolphe Sonnier

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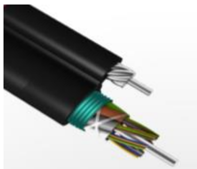
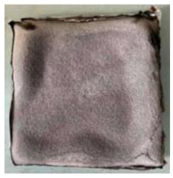
Funding : Thèse Cifre Corning - CETC

Due to the rise of numerical exchanges, the market of optical cables is continuously growing. In order to increase the quantity and quality of the transported data, cables have undergone strong changes in their structure (miniaturization of fibres, densification of cables) and their functional properties (flexibility, density…). Meanwhile, cables are products that exhibit fire hazard because of the intrinsic flammability of polymeric materials present in their composition. Hence, European regulation imposes the fire hazard to be assessed according to standard tests and the corresponding rating must be marked on the cable. In the framework, the cable industry is seeking to develop new fireproof solutions with low environmental and health impact enabling to obtain a good fire resistance while responding to the new issues of numerical exchanges.

This PhD thesis aims at developing new fireproof solutions for optical cable jackets based on the use of low melting glasses with the objective to generate an intumescent mineral layer during combustion. In order to reach this objective, three scientific obstacles should be overcome during this study:

- ✓ Developing new low melting glasses that can be used in flame retardant systems for cable jacket
- ✓ Developing innovating surface treatments for mineral fillers enabling to tune their functional properties
- ✓ Optimizing the jacket formulation in order to get the best performances.





Covalent grafting of phosphorus and fluorinated monomers onto flax fabrics by pre-irradiation process

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In recent years, researchers and manufacturers have focused on the use of natural fibers (cotton, hemp, jute, flax …) due to their various advantages such as their renewable character, biodegradability, good availability, low cost, low density and good mechanical properties. Natural fibers are therefore widely used in several industrial sectors such as building materials, paper industry, bio-composites and textiles. However, these fibers present several drawbacks such as their hydrophilicity or oleophilicity and their flammability which can limit or prevent their use for certain industrial applications. Most textile materials in our daily lives are highly flammable, with a rapid spread of flames that can cause very dangerous fires and lead to significant human and material losses. Therefore, a protection of materials based on these fibers against fire is necessary. In addition, water and dirt repellent fabrics are two properties that are very much in demand in the textile sector.

In this work, the grafting of polymer chains induced by radiation (pre-irradiation process) has been considered as the method of modification of flax fibers. The aim is to allow the grafting of different types of polymers (phosphorus and fluorinated) in to give new surface properties to these fibres: flame retardant and/or omniphobic. The method used consists in a first step to irradiate the fibers alone in the presence of oxygen to generate free radicals and peroxide radicals and then in a second step to introduce them in contact with the molecules to be grafted under thermal conditions to activate the peroxide radicals.

Pre-irradiation grafting of phosphorus flame retardant resulted in flame resistant fabrics. Furthermore, it was revealed that the thermal stability and flammability of treated flax fibers were mainly controlled by the phosphorus content and the highest phosphorus content obtained was 7 wt% for a dose of 100 kGy. The one-step grafting of phosphorus and fluorinated molecules was also developed in this project to obtain flame retardant and omniphobic flax fabrics. Currently, promising results have been achieved and a protocol has been adapted to graft several molecules in one step by controlling the reaction parameters such as the dose of irradiation, the concentrations of monomers, the nature of the solvent used, the time and the temperature of reaction.

Valuable extractives issued from Gabonese tropical wood species as flame retardants for biocomposites application

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The legislation on the ban of the export logs became into effective in 2010 in Gabon, has led to an increase of wood industry which was also accompanied by the emergence of a new source of pollution due to the waste and by-products of the wood industry. This represents very high volumes that wood companies have many difficulties to eliminate. In 2019, the processing of more than 2.9 million m3 of logs led to the production of nearly 1.8 million m3 of these related products, only from the first transformation. To deal with this statement, some companies have set up facilities to use some of this waste as wood energy. However, this represents only a small part of the produced waste, and in any case, these recovery facilities are not set up in all companies.

In this context, the valorization of this residual biomass as reinforcing fillers in biocomposite materials appears as a promising solution to manage this issue while providing a higher value. During the last decades, the development of eco-materials from biomass has undergone a real growth. These materials have performances equivalent to those of current conventional materials, and this in all sectors of activity transport, leisure, packaging...), while minimizing their impact on the environment.

For polymer-based composites, the presence of additives is often necessary to enable the composites to achieve the targeted properties, both for processing and serviceability. Among, the different classes of additives, flame retardants (FRs) represent the largest market in terms of volume and revenue. Indeed, fire safety issues in many industries, combined with constantly changing standards, are forcing materials to adapt. Recent studies have focused on bio-based FR alternatives such as phenolic compounds like lignin and tannins, which also have good antioxidant properties. Most species contain these aromatic biomolecules with, for a certain number of them, an efficient defense strategy to fight against environmental stresses. In this PhD study, we will focus on the chemical responses that Gabonese species have developed to fight against abiotic environmental stresses such as fire resistance strategies, and biotic ones with durability strategies against fungi and termites as recently demonstrated for Aucoumea klaineana and Dacryodes edulis through a

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