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PolyFlame est une newsletter à destination des chercheurs et des industriels du domaine du « comportement au feu des matériaux organiques ». Cette newsletter périodique est publiée via la Société Chimique de France (SCF).

A travers cette newsletter, vous découvrirez les nouveautés et les dernières avancées dans le domaine du comportement au feu en matière de recherche et développement, la synthèse et la production de nouveaux systèmes de retardateurs de flamme, les besoins industriels. Pour faire avancer la connaissance et l'expertise, une partie de cette newsletter est consacrée à l'écoute des chercheurs et des industriels reconnus dans ce domaine.

Bonne Lecture,

Biodegradable polyester thin films and coatings in the line of fire: The time of polyhydroxyalkanoate (PHA)?

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Summary

From sustainability standpoint, bio-based resins are of crucial importance nowadays rather than fossil-based resins, but the former has lower flame retardancy. Bio-based coatings are in their early stages; therefore, a long way must be gone to make them resistant against flame. Polylactic acid (PLA)-based biodegradable coatings have been in the core of attention, but one can rarely find reports on flame retardancy of bio-based thin films and coatings. Attention should also be paid to the fact that first-generation biodegradable polyesters, PLAs, are hooked on crop consumption. On the other hand, polyhydroxyalkanoates (PHAs) with more or less similar structure, but different physical properties arising from their lower glass transition temperature compared with PLAs, are known as the second-generation of bio-polyester. Overall, we highlight highlight here that PHAs might a better candidate for thin film manufacturing thanks to their synthesis by microorganism. Though mass production of PHAs is not cost-effective these days and their market just entered into the growth phase, we suggest study on flame retardancy of PHA-based resins, thin films, and coatings. This short communication deals with the current status and future ahead of PHA-based flame retardant thin films and coatings.

Keywords: Bio-based coating; Fire retardancy; Polyhydroxyalkanoate (PHA); sustainability

1-INTRODUCTION

Bio-based and biodegradable polymers such as chitosan [1], agarose [2], gelatin [3] and silk [4] have received a considerable attention in recent years, even more than what an optimistic could hope, due to ever increasing sustainable development. Environmental threats and resource limitations are the main issues accompanied by the use of fuel-based polymers [5-9]. Such debates have aligned the developed

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countries in the need of replacement of unsustainable routes in manufacturing advanced materials and systems as well as developing modern technologies to draw a green horizon of opportunities upon material design [10-13]. Synthesis of bio-based and biodegradable resins still experiences early stages of development; therefore, a long road should be paved to make bio-based resins directed toward global plastic market [14-19]. Research on naturally driven, bioengineered, and synthetic biopolymers gained from bacteria, conventional biotechnology, and biomass has undergone an accelerating trend just in between 1993 and 2012 by ca. 35-fold and 15-fold rise in the number of scientific papers and patents, respectively [20-22]. Synthesis of polylactic acid (PLA) as the first-generation biodegradable polyester opened hope tracks beyond commercialization of bio-resins for widespread uses [23]. PLA known as the most promising bio-resin comes from fermentation via conventional chemistry followed by polymerization of lactic acid [24]. Undesirably, however, a large volume of corn, the main food supply in developing countries, must be utilized in the synthesis of PLA, which remains big challenge over future ahead of PLA production [25, 26]. An elaborate analysis of patents unraveled that long-term research and development on PLA aligned it in the line of maturity, but its limited potential of commercialization was recognized for further PLA market progression [27].

Despite promising aspects of bio-resins for a sustainable future, they are highly flammable as well as they show poor mechanical properties; hence, they should be modified/reinforced with additives [28]. Pursuing instructions on the ban of usage of some halogenated flame retardants, substantial attempts were directed toward development of bio-based additives to meet low toxic product emission requirements [29-32]. Fire retardancy of bio-based resins filled with minerals, biofillers, biofibers, as well as bio-based composites composed of both bio-matrix and biofillers has been the focus of a wide variety of surveys over the past decade [33-38]. PLA-based flame retardant systems from metal oxide source were extensively studied, but the use of phosphorous-based and nanoclay flame retardant additives, alone or combinatorial, still remains in a long research road with a trace of hope in resolving poor mechanical properties of PLA composites[39].

The advent of polyhydroxyalkanoate (PHA) as second generation fully biodegradable polyester resin through synthesis from a wide range of microorganisms and bacteria has eliminated the need for fermentation of crops [40-42]. This biogenic resin has just entered the market, but rapidly experienced growth period [43]. PHA family resins are appropriate candidates for energy storage and intracellular carbon purposes. They can be classified into short-chain length (C3-C5) and medium-chain length (C6-C14) groups with poly(3-hydroxybutyrate) (PHB) as the first widespread resin [44, 45]. Thanks to their compatibility to blood and tissues and low permeability against H2O, CO, and O2, PHAs have been used in a wide variety of fields ranging from food packaging industry to tissue engineering (Figure 1) [46-49]. Nevertheless, high production cost and poor mechanical properties were recognized as major drawbacks that have limited large-scale application of PHA [50]. In this sense, modification of PHA by the aid of plasticizers, its blending with the second polymer, and its chemical modification with different functional groups/chains were examined [51, 52].

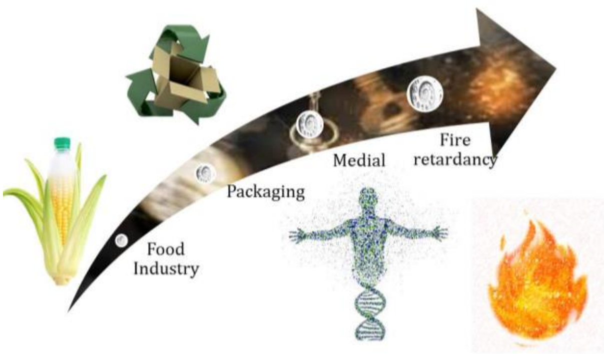

Figure 1 : Developments in application of biodegradable polyesters, PHA in the line of fire.

Bio-based thin films and coatings have opened new era of research for widespread uses. Fu et al. synthesized and fully characterized bio-based waterborne polyurethane dispersions starting from castor oil by the use of chain extender, and obtained good thermal and hydrophobic properties[53]. Turkenburg et al. developed highly thermos-reversible self-healing coatings by incorporation of high amounts of bio-based precursors and reported acceptable abrasive wear and solvent resistance together with mechanical properties [54]. There have also been some attempts to synthesis of bio-based UV-curable resins for applications in waterborne coatings [55-58] in the quest of adhesion, flexibility, mechanical and anti-corrosion properties. Biodegradable coatings based on waterborne polyester [59, 60] as well as vegetable oil-derived nanocomposite coatings were also investigated [60]. The open literature suggests that bio-based polyurethane resins were quite often the subject of studies in this field [60, 61].

There are several reports on PLA-based coatings. Active PLA films used in packaging containing bergamot, rosemary, lemongrass or clove essential oils were developed by Qin et al., where acceptable antimicrobial and mechanical properties were obtained [62]. Elsewhere addition of equivalent weight of acrylic polyol and PLA ended in packaging films resistant against humidity and the cured films revealed good hydrolytic degradation resistance in humid media [63]. Durable hydrophobic PLA coatings obtained from pulsed plasma polymerization [64], fast-formed microporous PLA coatings [65], nanostructured composite coatings based on PLA and amorphous magnesium phosphate with anti-corrosion and bioactivity characters [66], and PLA-based nanocomposite coatings from electron beam with substantial antibacterial features [67] were also subjects of research. There were also some works on the use of blends of PLA or PHB with other polymers, e.g. thin films and bio-coatings based on PHB and cellulose showing improved tensile properties [68]. Biodegradable smooth coatings based on polycarbonate and PLA [69] were among limited reports on the use of second-generation PHA coatings. It is worthy of note that the blend of PHA and PLA lacks miscibility; hence, chain extenders make possible formation of compatible bio-based coatings with acceptable thermal and mechanical properties thanks to intensified intermolecular entanglements [70, 71].

The quantity of research on flame retardancy of PLA thin films and coatings containing flame retardant additives is indeed limited. Solution casting PLA films containing phosphorous flame retardant were examined for thermal stability and flame retardancy performance in terms of the limiting oxygen index (LOI), UL-94, and themogravimetric analysis (TGA) [72]. There are some works on the individual or combined use of conventional flame retardants with nanoparticles in PLA thin films. Shi et al. used nanoparticles of metal-organic framework (MOF) in PLA solution film casting having thickness of ca. 140 µm for electronic devices [73]. The LOI value for neat PLA film was ca. 20%, which was indeed low. The neat sample failed in UL-94 test and continued to burning for about 21 s, implying high flammability of PLA. The surprising point wat that by incorporation of just 0.2 wt.% of MOF into PLA films the LOI value increased to 23.5%, and nanocomposite sample burned in a very shorter time of ca. 16 s. Increase of MOF content to 1 and 3 wt.% in the PLA film caused rise in LOI to 24.5 and 26.0%, respectively. In the same direction, burning times were decreased to 4.3 and 2.9 s. Film-stacking method was also used to obtain PLA films containing 10:1 ratio of polyphosphorous: montmorillonite (MMT), where self-extinguishing PLA films were achieved at 16 wt.% flame retardant content [74]. Having met V-0 rating UL-94 as well as up to 50% decrease in the value of peak of Heat Release Rate (pHRR) in cone calorimetry measurements and the Total Heat Release (THR) were signatures of a superior fire retardancy performance. The combined use of a phosphinic acid-contained precursor and layered double hydroxide (LDH) [75] and a hybrid containing di(phenyl phosphate) (RDP), MOF, resorcinol, and graphene oxide (GO) [76] in PLA solution-casted films was successful in achieving good fire retardancy performance. Investigations also unraveled high potential of PLA nonwoven mats with intumescent features when ammonium polyphosphate (APP) was blended with lignin and starch carbohydrates [77].

In the light of above discussion, this short communication intends to place stress on the importance of research on flame retardancy of PHA-based family as potential era of survey in the field. Though kinetic study on thermal degradation of PHB was addressed in two reports, flame retardancy of neat PHA has never been reported. Except a work on the blend of PHB with poly(butylene adipate-co-terephthalate) (PBAT) filled with combination of nano-iron oxide and antimony oxide with emphasis being placed on superiority of additives [78, 79], no report is available in the literature on flame behavior of PHA-based systems. This is why we pictured here a potential framework for research on flame retardancy of PHA-based composites, looking at present from the future window. Figure 2 provides a comprehensive comparison of some physical and structural characteristics of PLA and PHA [80]. Although the density of PLA and PHA are the same, glass transition temperature (Tg) of PLA is well above room temperature, notifying suitableness of PHA for usage in moderate temperature. PHA behaves like ductile materials at room temperature due to low Tg, however, its Tg can be changed for lower or higher levels by incorporation of additives and plasticizers. Moreover, PHA is a semi-crystalline biodegradable polyester; while PLA possesses somehow an amorphous structure. Water permeability of PHA stands lower than PLA, due to the presence of crystalline domains, which offers PHA as a potential candidate for packaging industry. Thus, comparison between thermal stability and flame retardancy performances of PHA and PLA would be motivating.

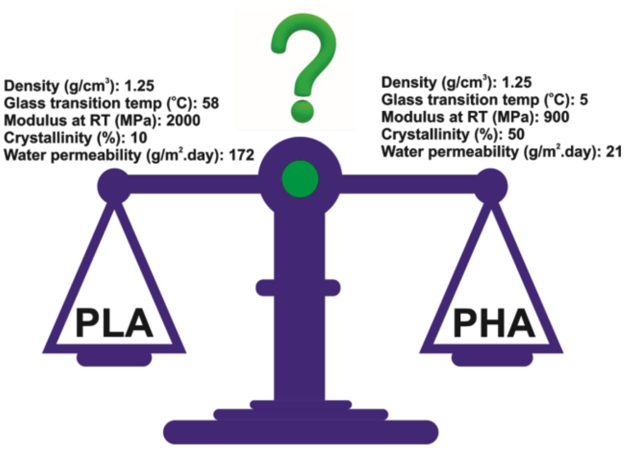

Figure 2 : General comparison of final properties of PLA and PHA

2- CONCLUSION:

Biodegradable polymers appeared as candidates for wide variety of fields thanks to their environmental-friendly and almost respectable properties. However, inadequate flame retardancy and mechanical strength of biopolymers have opened doors to substantial research in recent years to tackle their drawbacks. In the meanwhile, some promising outcomes have positioned them in the way commercialization. PLA belongs to the first generation of biodegradable polyesters, which is produced from food supply resources, mainly corns. However, substantial volume of corn is required in synthesis of PLA, which remains an unsolved problem in their large-scale production. Furthermore, PLA products suffer from very high flammability, along with insufficient mechanical properties-what suggests blending them with additives to reimburse their defects. These severe drawbacks highlights the need for synthesis of PHA as the second generation of fully biodegradable polyesters through microorganisms to eliminate the usage of corn. PHA has been found many potential applications in wide variety of fields thanks to biocompatibility, biodegradability, and low permeability against H_2O, CO, and O_2. Though researchers and technologists alike have addressed flame retardancy of PLA, no report is available on flame retardancy of PHA. This communication intends to encourage researchers working on flame retardancy of biobased polymers to take direction towards PHA.

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Eco-ignifugation de textiles à l'aide de biomacromolécules

Nous proposons ci-dessous une courte introduction d'une revue intéressante sur l'ignifugation de textiles à base de biomacromolécules. La version complète est disponible ici :

Basak S, Ali SW. Sustainable fire retardancy of textiles using bio-macromolecules. Polymer Degradation and Stability.2016; 133:47-64.

Dr. Santanu Basak est chercheur à l'Institut de Recherche sur les Technologies du Coton (ICAR-Central Institute for Research on Cotton Technology), Bombay, Inde. Il travaille dans le domaine de l'ignifugation "écologique" des matériaux textiles depuis plus de 10 ans et a publié plusieurs contributions remarquées sur ce sujet.

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L'ignifugation des textiles est confrontée à de nombreux défis en raison des problèmes de toxicité, de cancérogénicité et de génération d'effluents liés aux agents utilisés. Pour répondre à ces problèmes, depuis quelques années, différentes biomacromolécules ont été étudiées comme agents ignifuges pour textiles, notamment cellulosiques. C'est l'objet de cette revue de présenter les travaux réalisés dans ce domaine.

Parmi ces retardateurs de flamme biosourcés, certaines sont des extraits de plantes, telles que la sève de bananier ou le jus obtenu à partir de feuilles d'épinard. Différentes sources de protéines ont également pu être étudiées pour développer des retardateurs de flamme, par exemple à base de lait (la caséine et le lactosérum, c'est-à-dire la partie liquide issue de la coagulation du lait ont été utilisés) ou provenant de plumes de poulet (riches en kératine) ou de champignons (hydrophobines, protéines riches en acide aminé cystéine). De l'acide désoxyribonucléique (ADN), extrait de sperme de hareng, a aussi été utilisé pour ignifuger des tissus de coton.

Toutes ces biomacromolécules, contenant du carbone, de l'oxygène, de l'azote et parfois aussi du phosphore, ont en commun une décomposition thermique lente, étalée sur une large plage de température et conduisant à une production de char importante. Ainsi, l'ADN est un biopolymère contenant des bases azotées (adénine, guanine, cytosine et thymine) ainsi que des unités désoxyriboses et des groupes phosphates. La déshydratation des unités désoxyriboses est catalysée par l'acide phosphorique formé suite aux premières étapes de décomposition (rupture des liaisons phosphodiesters) et un char intumescent est formé, dont l'expansion est favorisée par libération de composés azotés.

Déposé sur des tissus de coton, l'ADN conduit à une augmentation l'indice limite d'oxygène, une diminution de la vitesse de combustion verticale et à une production accrue de char. La texture du tissu fut même conservée après combustion.

Special Issue "Innovative Flame Retardants" - in "Molecules" journal

Deadline for manuscript submissions: **30 September 2019**

Guest editors: Rodolphe Sonnier, Laurent Ferry, Henri Vahabi

Special Issue Information

Dear Colleagues,

The research focuses more and more on the development of biobased materials to attain the requirements of sustainability. Developing biosourced materials in the future includes polymers as well as additives. Among these additives, flame retardants are the most important market. Bioresources are numerous and provide many opportunities to develop innovative flame retardants. Solutions based on carbohydrates, polyphenols, lipids or proteins are currently investigated.

To be commercially successful, biobased flame retardants must obviously be as efficient as oil-based ones. However, cost may also be a major drawback. Indeed, the development of biobased flame retardants often needs various extraction, purification and functionalization steps. A solution to be competitive may be to provide multifunctionalities. For instance, combining flame retardancy with anti-ageing, plasticizing, crosslinking, conductive properties and so on would be highly desirable. Alongside biobased ones, there are other innovative flame retardants based on various elements or from different classes of materials which offer new opportunities.

This special issue aims to gather high-quality papers about innovative flame retardants. Especially, all aspects of biobased flame retardants are considered, i.e. their extraction, synthesis and functionalization as well as the assessment of their fire retardancy properties and their environmental impact. Papers on other innovative flame retardants are also welcomed. Multifunctional additives combining several properties (including flame retardancy) will be privileged.

Guest Editors

For more information:
https://www.mdpi.com/journal/molecules/special_issues/Flame_Retardants

Special Issue

Flame Retardants and Flame-Retardant Polymers/Composites (FR&FRPC)

Composites Part B : Engineering

Due to the low manufacturing cost and wide range of performances, polymers and polymer composites are increasingly important in our everyday life and can be found all around us. Many of these polymer materials are, however, highly flammable, which poses increased fire risk to people's lives and our society. The flammability of polymers and polymer composites is a serious issue and severely limits their applications. It has been identified as the root cause of many severe fire incidents, which cause over 40,000 deaths worldwide every year with the total fire loss around 1% of the gross domestic products of the world. Adding flame retardants has been approved as an effective strategy to address the fire issues associated with these flammable polymers and composites. Development of flame retardants and flame-retardant polymers/composites has become an important topic for composite materials and their applications.

Composites Part B: Engineering has recently identified flame retardants and flame-retardant polymer/composites as one of its 20 focused topics for the journal. This Special Issue is purposely organised to announce this decision. We want our flame retardants research community to be aware that ***Composites Part B: Engineering*** is now dedicated to publishing the latest progress on flame retardants and flame-retardant polymer composites.

We are pleased to have four world renowned top scientists on flame retardants as our Guest Editors. The Special Issue will feature the latest technological and science advances and also the future challenges and opportunities on flame retardant materials. The topics focus on ecofriendly flame retardants, flame retardant polymer composites, new flame retardancy technologies, characterisation and evaluation of fire performances and smoke toxicity, and fire modelling/simulations. The Special Issue aims to provide an excellent platform to share the latest advances in this research field. We anticipate it to be of great value to our researchers, engineers and government policy makers.

Topics of Interest

1. Flame Retardants
2. Flame Retardant Polymer/Composites
3. Flame Retardant Technologies
4. Characterisation and Evaluation of Fire Performance and Smoke Toxicity
5. Model/Simulation for Polymer Degradation and Combustion
6. Others

Full research papers and review articles are all welcome

Important Dates

Submission opening**: 4 April 2019**

Paper submission deadline: **31 July 2019**

Final decision notification: **30 September 2019**

Submission Instructions

This Special Issue solicits both original research and review studies related to FR&FRPC. All submitted papers must be clearly written in excellent English and contain original or review work, which has not been published or is currently under review by any other journals or conferences. Papers must not exceed 25 pages including figures, tables, and references. A detailed submission guideline is available as "Guide to Authors" at the journal website: www.journals.elsevier.com/composites-part-b-engineering/.

All manuscripts and any supplementary material should be submitted through Elsevier Editorial System by click “Submit Your Paper” in the journal website. When instructed to “Start New Submission”, authors must select "VSI: Flame Retardants" when they reach the "Select Issue Type".

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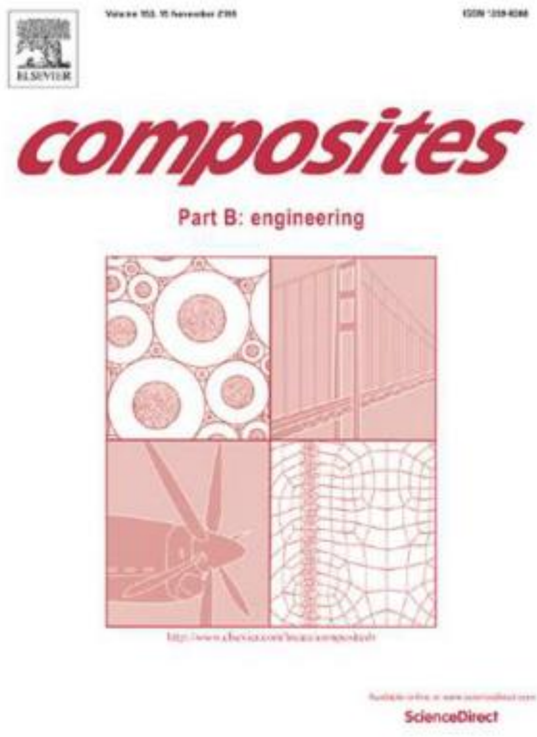

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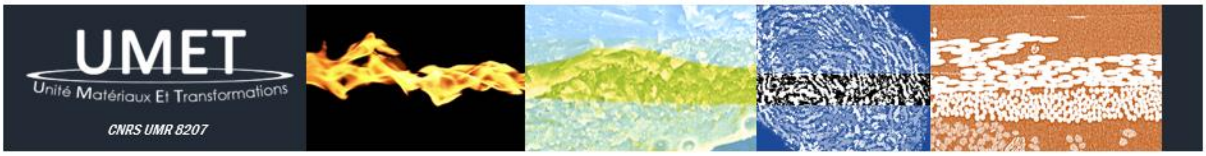
27ème rencontres du GDR Feux

12 & 13 décembre 2019 - UMET, Lille

Organisé conjointement par le GDR Feux et le GT « Dégradation et comportement au feu des matériaux organiques » de la SCF



SAVE THE DATE

La thématique de la sécurité incendie requiert l'étude à différentes échelles de processus physico-chimiques complexes tels que la pyrolyse ou encore les phénomènes de transferts et de propagation. La sécurité incendie passe également par le développement de systèmes et matériaux de plus en plus complexes qui doivent répondre à une législation qui évolue notamment en prenant en compte les notions de développement durable. Afin d'échanger sur les dernières avancées dans ces domaines, nous vous convions à participer aux **27ième rencontres du GDR Feux** organisées conjointement avec le **groupe « Dégradation et comportement au feu des matériaux organiques » de la Société Chimique de France** qui auront lieu à Lille (Campus Cité Scientifique, Villeneuve d'Ascq), les **12 et 13 Décembre 2019.**

Le thème central de ces rencontres concernera **« l'Expérimentation et la modélisation multi-échelles pour les feux »**. Il concerne à la fois l'approche top-down pour laquelle les chercheurs s'interrogent sur le comportement global de l'incendie en isolant à l'échelle du laboratoire les mécanismes fins (dégradation, émission d'aérosols, développement de métrologie pour la détermination des propriétés des matériaux, …) et l'approche bottom-up pour laquelle les chercheurs développent des matériaux incluant des retardateurs de flamme dont ils cherchent ensuite à caractériser le comportement à la petite échelle pour pouvoir l'étendre à la pleine échelle.

Cette rencontre sera l'occasion d'échanger sur : la métrologie pour la détermination des propriétés des matériaux, le couplage entre le comportement des matériaux en condition d'incendie et leur tenue mécanique, le couplage entre réaction au feu des matériaux et conditions environnementales (vieillissement), le couplage solide/flamme (caractérisation des émissions), l'analyse des fumées à différentes échelles,…

Dates importantes :

Ouverture de l'appel à communications : 02/09/2019

Ouverture des inscriptions : 15/09/2019

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