Bulletin de veille n° 9

Retardateurs de flamme

Janvier 2023

Objectifs : Recherche de rapports, articles scientifiques, réglementation sur les retardateurs de flamme. Plus spécifiquement sur : la caractérisation, les techniques d'analyse, le vieillissement, les émissions dans l'atmosphère, les risques chimiques.

La validation des informations fournies (exactitude, fiabilité, pertinence par rapport aux principes de prévention, etc.) est du ressort des auteurs des articles signalés dans la veille. Les informations ne sont pas le reflet de la position de l'INRS.
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Sources surveillées

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Rapports et articles (sources : INRS-Biblio, google scholar, Web of Science, Lens, Les Techniques de l'ingénieur, internet)

W. J. Lee, S. H. Cha and D. H. Kim
Preparation and Characterization of Cardanol-Based Flame Retardant for Enhancing the Flame Retardancy of Epoxy Adhesives
Polymers, Vol. 14, n° 23, Dec 2022, p. 12.
Epoxy resin has a versatile set of applications due to its excellent properties. However, its easily flammable property limits further applications. A bio-based flame retardant, cardanyl diphenylphosphate (CDPP), was successfully synthesized via condensation reaction between cardanol and diphenyl phosphoryl chloride. The chemical structure of CDPP was confirmed via H-1 nuclear magnetic resonance and Fourier transform infrared spectroscopy. To overcome the flammable property of epoxy resin, different amounts of CDPP were incorporated into the epoxy resin. The thermal stability of epoxy resin with CDPP was reduced due to its phosphorus component, which had a relatively weak bond. Meanwhile, the measured char residue of epoxy resin with CDPP was increased compared to its calculated value, which indicated that CDPP promoted the formation of char residue. The limiting oxygen index of epoxy resin with CDPP was enhanced as the amount of CDPP increased from 22.1% for EP0 to 32.7% for EP10. The maximum value of the heat release rate per unit area and total heat release values of EP10 decreased by 23.23% and 12.02%, respectively, as compared to those of EP0. Additionally, single lap shear strength confirmed the improvement in the adhesion property of EP5. The lap shear strength increased to 7.19 MPa for EP5 compared to 6.27 MPa for EP0. This behavior might be due to the higher polarity of the phosphorus components. Based on the findings gathered in the present study, the incorporation of a bio-based flame retardant (CDPP) in epoxy resin has the potential for improving flame retardancy and adhesion property, which will be promising for the industrial area.
https://doi.org/10.3390/polym14235205

H. Alshemmari, Y. N. Kavil, A. Sheredah and S. Rajagopalan
Inevitable human exposure of flame retardants on the potential health risk and assessment of PBDEs in soils collected from Sulaibiya, Kuwait
Arabian Journal of Geosciences, Vol. 15, n° 24, 2022/12/16 2022.
Owing to the increase in inflammable polymer materials and related requirements, global demand for polybrominated diphenyl ethers (PBDEs) rose rapidly from the 1970s to the 1990s. BFRs would pollute the soil with dry or wet deposits, as well as landfills. The current research focuses on the levels of PBDEs in the agricultural and non-agricultural soils of Sulaibiya, Kuwait. The study expands the threats of PBDE toxicity to humans as well. The findings will lead to a deeper understanding of PBDE transport practices, environmental effects, and health hazards. The prevalent concentration of BDE-209 congeners can be found in both areas. The average concentrations along the Sulaibiya agricultural and non-agricultural regions were 121.26 ng/g and 50.29 ng/g, respectively, at the current observed sites. The total cancer risk was in the range of 7.67 × 10−9–1316.53 × 10−9 for adults and 10.04 × 10−9–1723.08 × 10−9 for children in the agricultural region. The correspondent total cancer risk in the non-agricultural regions was in the range of 6.14 × 10−9–240.31 × 10−9 for adults and 8.05 × 10−9–314.53 × 10−9 for children. Regardless of the severity of the dismantling activities, the soil organic matter (SOM) of most of the obtained soil samples along agricultural soils varied from 0.2 to 2.1%. As a result, the SOM composition of the samples in this analysis can predominantly be traced to agricultural practices. PCA study was also performed to identify the relationship of soil parameters with the level of PBDEs along with the observed locations.
https://doi.org/10.1007/s12517-022-10942-5

S. Pellerin, F. Samyn, S. Duquesne and V. Landry
Preparation and Characterisation of UV-Curable Flame Retardant Wood Coating Containing a Phosphorus Acrylate Monomer
Coatings, Vol. 12, n° 12, 2022/11/29 2022, p. 1850.
The application of a flame retardant coating is an effective solution to enhance the fire retardancy of wood flooring. However, finding the right balance between reducing the flame propagation and good overall coating properties while conserving wood appearance is complex. In order to answer this complex problem, transparent ultraviolet (UV)-curable flame retardant wood coatings were prepared from an acrylate oligomer, an acrylate monomer, and the addition of the tri(acryloyloxyethyl) phosphate (TAEP), a phosphorus-based monomer, at different concentrations in the formulation. The coatings' photopolymerisation, optical transparency, hardness, water sorption and thermal stability were assessed. The fire behaviour and the adhesion of the coatings applied on the yellow birch panels were evaluated, respectively, using the cone calorimeter and pull-off tests. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analyses were performed on the collected burnt residues to obtain a better understanding of the flame retardancy mechanism. Our study reveals that phosphorus monomer addition improved the coating adhesion and the fire performance of the coated wood without impacting the photopolymerisation. The conversion percentage remained close to 70% with the TAEP addition. The pull-off strength reached 1.12 MPa for the coating with the highest P-monomer content, a value significantly different from the non-flame retarded coating. For the same coating formulation, the peak of heat release rate decreased by 13% and the mass percentage of the residues increased by 37% compared to the reference. However, the flame-retarded coatings displayed a higher hygroscopy. The action in the condensed phase of the phosphorus flame retardant is highlighted in this study.</jats:p>
https://doi.org/10.3390/coatings12121850

B. A. Howell
Thermal Degradation of Organophosphorus Flame Retardants
Polymers, Vol. 14, n° 22, 2022/11/15 2022, p. 4929.
The development of new organophosphorus flame retardants for polymeric materials is spurred by relatively low toxicity, effectiveness, and demand for replacement of more traditional materials. To function, these compounds must decompose in a degrading polymer matrix to form species which promote modification of the solid phase or generate active radical moieties that escape to the gas phase and interrupt combustion propagating reactions. An understanding of the decomposition process for these compounds may provide insight into the nature of flame retardant action which they may offer and suggest parameters for the synthesis of effective new organophosphorus flame retardants. The thermal degradation of a series of organophosphorus esters varying in the level of oxygenation at phosphorus-alkyl phosphate, aryl phosphate, phosphonate, phosphinate-has been examined. Initial degradation in all cases corresponds to elimination of a phosphorus acid. However, the facility with which this occurs is strongly dependent on the level of oxygenation at phosphorus. For alkyl phosphates elimination occurs rapidly at relatively low temperature. The same process occurs at somewhat higher temperature for aryl phosphates. Elimination of a phosphorus acid from phosphonate or phosphinate occurs more slowly and at much higher temperature. Further, the acids formed from elimination rapidly degrade further to evolve volatile species.
https://doi.org/10.3390/polym14224929

H. Chen, S. Zhu, R. Zhou, X. Wu, W. Zhang, X. Han and J. Wang
Thermal Degradation Behavior of Thiol-ene Composites Loaded with a Novel Silicone Flame Retardant
Polymers, Vol. 14, n° 20, 2022/10/14 2022, pp. 4335-4335.
A novel silicone flame retardant PMDA was synthesized and blended with a commercial thiol-ene (TE) to obtain a flame-retardant TE (FRTE) composite. The cone calorimeter measurement showed the incorporation of PMDA improved the flame retardancy of the TE composite at concentrations of 5 wt%. The thermal stability and degradation mechanism of FRTE in nitrogen was studied by thermogravimetric analysis. The degradation behaviour of TE containing a PMDA flame retardant was found to be changed. The kinetics of thermal degradation was evaluated by Kissinger method and Flynn-Wall-Ozawa method. The results showed that the activation energies of the FRTE degradation were higher than those of neat TE. However, the degradation mechanism of the TE matrix was not changed by the incorporation of flame-retardant PMDA. In this study, the

flame-retardant mechanism of PMDA flame-retardant TE polymer was explained by using two kinetic analysis methods.
https://doi.org/10.3390/polym14204335

Y. Xiang, Y. Gao, G. Xu, M. He, S. Qin and J. Yu
Thermal degradation behavior and flame retardant properties of PET/DiDOPO conjugated flame retardant composites
Frontiers in chemistry, Vol. 10, 2022/10/07 2022, p. 1018998.
PET/DIDOPO conjugated flame retardant composites were prepared by melt blending of styrene bridged DOPO (DIDOPO) into polyethylene terephthalate (PET). The flame retardancy, rheological behavior, and thermal degradation behavior of the composite were characterized by vertical combustion test (UL-94), limit oxygen index test (LOI), rotational rheometer, and thermogravimetry (TG). The results showed that the flame retardant composite with V-0 grade was obtained when the amount of DIDOPO is 12.5wt%, and the corresponding LOI value was 56.87% higher than that of PET. The thermogravimetry-fourier infrared spectroscopy (TG-FTIR) test results showed that DIDOPO could promote the degradation of PET/DIDOPO materials, and release phosphorus-containing free radicals to quench the flame, therefore slowing down the combustion process, and mainly playing the key flame retardant role in gas-phase.
https://doi.org/10.3389/fchem.2022.1018998

B. S. Regmi and A. Apblett
Spectroscopic characterization, thermal, and flame retarding properties of melaminium cyanoacetate monohydrate
Polymer Bulletin, 2022.
FTIR and Raman spectra of melaminium cyanoacetate have been recorded and analyzed. Band assignments are given based on the melamine and cyanoacetic acid molecules. The ring breathing vibrations of the triazine ring show frequency shift toward the high wavenumber side. This change is attributed to an increase in rigidity of the ring as a consequence of protonation and the formation of donor-acceptor types of hydrogen bonding interactions. Notably, this melaminium cyanoacetate salt also contributes to the efficient flame-retardant properties of polyurethane foam substrate as revealed by the flammability test and thermogravimetric analysis.
https://doi.org/10.1007/s00289-022-04594-4

J. X. Liu, D. L. Cui, D. L. Yang, J. Y. Li, Z. Y. Yang, J. Z. Su, C. X. Ren, Y. Y. Niu and P. Xiang
Organophosphorus Flame Retardant TCPP Induces Cellular Senescence in Normal Human Skin Keratinocytes: Implication for Skin Aging
International Journal of Molecular Sciences, Vol. 23, n° 22, Nov 2022.
Tris (1-chloro-2-propyl) phosphate (TCPP) is one of the most frequently detected organophosphorus flames in the environment. Continuous daily exposure to TCPP may harm human skin. However, little is known about the adverse effects of TCPP on human skin. In this study, we first evaluated the detrimental effects and tried to uncover the underlying mechanisms of TCPP on human skin keratinocytes (HaCaT) after 24 h exposure. We found that TCPP caused a concentration-dependent decrease in HaCaT cell viability after exposure to 1.56-400 mu g/mL for 24 h, with an IC50 of 275 mu g/mL. TCPP also promoted the generation of intracellular reactive oxygen species (ROS) and triggered DNA damage, evidenced by an increase of phosphorylated histone H2A.X (gamma H2A.X) in the nucleus. Furthermore, the cell cycle was arrested at the G1 phase at 100 mu g/mL by upregulation of the mRNA expression of p53 and p21 and downregulation of cyclin D1 and CDK4 expression. Additionally, both the senescence-associated-beta-galactosidase activity and related proinflammatory cytokine IL-1 beta and IL-6 were elevated, indicating that TCPP exposure caused cellular senescence may be through the p53-dependent DNA damage signal pathway in HaCaT cells. Taken together, our data suggest that flame-retardant exposure may be a key precipitating factor for human skin aging.
https://doi.org/10.3390/ijms232214306

J. Z. Sun, D. H. Zhang, K. Wei, F. Tan, M. He, D. M. Bao and S. H. Qin
Synthesis and Characterization of P-PPD-Ph-Conjugated Flame Retardant
Frontiers in Chemistry, Vol. 10, Jul 2022.
The conjugated flame retardants have rarely been studied. A conjugate flame-retardant 4, 4'-{1 '', 4 ''-phenylene-bis [amino- (10'''-oxy10'''-hydro-9'''-hydrogen- 10'''lambda(5)-phosphaphenanthrene-10 ''-yl)-methyl]}-diphenol (P-PPD-Ph) was synthesized and added into the polylactic acid (PLA) matrix. The P-PPD-Ph-conjugated flame-retardant structure was tested by FTIR, H-1, and P-31 NMR analysis. The thermal and rheological properties of PLA/P-PPD-PH-conjugated flame-retardant composites were investigated. The results showed that P-PPD-Ph-conjugated flame retardant affects PLA/P-PPD-PH-conjugated flame-retardant composites for promoting the formation of a carbon layer when the P-PPD-Ph-conjugated flame-retardant content was 15% and the residual carbon ratio for PLA/P-PPD-PH-conjugated flame-retardant composites increased by 4.2%.
https://doi.org/10.3389/fchem.2022.956322

L. Wang, Y. Q. Yu, G. Q. Liu, B. W. Hu and J. H. Lu
Degradation of Tetrabromobisphenol S by thermo-activated Persulphate Oxidation: reaction Kinetics, transformation Mechanisms, and brominated By-products
Environmental Technology, 2022.
Brominated flame retardants (BFRs) are a group of contaminants of emerging environmental concern. In this study, systematic exploration was carried out to investigate the degradation of tetrabromobisphenol S (TBBPS), a typical emerging BFRs, by thermally activated persulfate (PDS) oxidation. The removal of 5.0 mu M TBBPS was 100% after 60 min oxidation treatment under 60 degrees C. Increasing the temperature or initial PDS concentration facilitated the degradation efficiency of TBBPS. The quenching test indicated that TBBPS degradation occurred via the attack of both sulphate radicals and hydroxyl radicals. Natural organic matter (NOM) decreased the removal rate, however, complete disappearance of TBBPS could still be obtained. Six intermediate products were formed during reactions between TBBPS and radicals. Transformation pathways including debromination, beta-Scission, and cross-coupling were proposed. Brominated disinfection by-products (DBPs) in situ formed during the degradation of TBBPS were also investigated, such as bromoform and dibromoacetic acid. The presence of NOM reduced the formation rates of brominated DBPs. Results reveal that although thermo-activated PDS is a promising method for TBBPS-contaminated water, it can lead to potential brominated DBPs risks, which should be paid more attention to when SO4 center dot--based oxidation technology is applied.
https://doi.org/10.1080/09593330.2022.2135027

A. L. Mei Liu, Lingling Meng, Gaoxin Zhang, Xiaoling Guan, Jiang Zhu, Yingming Li, Qinghua Zhang, Guibin Jiang
Exposure to Novel Brominated Flame Retardants and Organophosphate Esters and Associations with Thyroid Cancer Risk : A Case–Control Study in Eastern China
Environmental Science and Technology, Vol. 56, n° 24, 2022.
Novel brominated flame retardant (NBFR) and organophosphate ester (OPE) exposure may engender adverse effects on human health. However, present epidemiological information regarding the effects of such exposure is limited and controversial. In this case–control study, 481 serum samples were collected from patients with thyroid cancer (n = 242) and healthy controls (n = 239) in Shandong Province, eastern China. The levels of NBFRs and OPEs, thyroid hormones, and serum lipid parameters were measured in all the participants. Pentabromotoluene, 2,3-dibromopropyl 2,4,6 tribromophenyl ether, decabromodiphenylethane (DBDPE), tris (2-chloroethyl) phosphate (TCEP), and triphenyl phosphate (TPP) were widely detected (detection frequency > 60%) in all the participants. A significantly high risk association was found between exposure of NBFRs and OPEs (namely 1,2,3,4,5-pentabromobenzene, DBDPE, tri-n-propyl phosphate, tri[(2R)-1-chloro-2-propyl] phosphate, tris (1,3-dichloro-2-propyl) phosphate, and tris (2-butoxyethyl) phosphate) and thyroid cancer in both males and females. In the females of the control group, TCEP levels exhibited a significantly positive association with thyroid-stimulating hormone and a negative association with triiodothyronine (T3), free triiodothyronine (FT3), and free thyroxine (FT4) levels. Weighted quantile sum

regression evaluated the mixed effects of the compounds on thyroid hormones levels and thyroid cancer. As a result, TPP accounted for the majority of the T3, thyroxine, and FT3 amounts. Our results suggest that NBFR and OPE exposure contributes to alterations in thyroid function, thereby increasing thyroid cancer risk.
https://doi.org/10.1021/acs.est.2c04759

W. H. Fukai Chu, Lei Song, Yuan Hu
State-of-the-Art Research in Flame-Retardant Unsaturated Polyester Resins: Progress, Challenges and Prospects
Fire Technology, 2022.
Unsaturated polyester resins (UPR) are broadly applied in chemical, construction, transportation and electrical fields, etc. However, UPR materials are extremely flammable. Through radiation, conduction and convection, the released heat brings serious thermal hazards to surrounding life and the environment. Meanwhile, the combustion of UPR also releases a vast of toxic pyrolysis gases and smoke, causing extremely serious non-thermal hazards, endangering life and health, reducing fire visibility and hindering escape and rescue efforts. Therefore, the flame retardant modification of UPR materials is an inevitable measure to reduce its flammability and broaden its application breadth. In this review, the flammability of UPR materials is firstly analyzed from the perspective of their compositions and structures. Meanwhile, based on the differences in preparation methods of flame retardant UPR (FR-UPR) in literature research, it is divided into additive flame retardant, intrinsic flame retardant and interfacial flame retardant methods. The relationship between the highly efficient flame retardant structures and the properties, and the gaseous-phase flame retardant and condensed-phase mechanisms in FR-UPR composites are analyzed. Compared with traditional additive flame retardants, polymeric flame retardants, nanosheet flame retardants and intrinsic flame retardant method are important directions for the future development of FR-UPR composites. In addition, the interfacial flame retardant method can effectively improve the interfacial adhesion and flame retardant properties of fiber-reinforced UPR composites, and also has application prospects. This review analyzes the current challenges faced by FR-UPR, and looks forward to its possible future development directions to guide the preparation and application of high-performance FR-UPR.
https://link.springer.com/article/10.1007/s10694-022-01337-9

Y. Z. Lizheng Qin, Shun Gong, Shikun Zhao, Zhiwen Cao, Jianping Deng
Synthesis and Characterization of a New Copolymer Consisting of Polyamide 1210 and Reactive Phosphorus−Nitrogen Flame-Retardant
Macro-Molecular Rapid Communications, 2022.
The thermal stability and reactivity of organophosphorus flame-retardants play a critical role in synthesizing copolymerized flame-retardant polyamides. Herein, this work successfully synthesizes a flame-retardant CEPPA-DDA salt (CDS) with both good thermal stability and high reactivity by reacting 2-carboxyethyl phenyl phosphonic acid (CEPPA) with 1,12-dodecanediamine (DDA). Flame-retardant polyamide 1210 (FRPA) is further prepared by copolymerizing the CDS, DDA, and sebacic acid (SEA). The test results show that the introduction of CDS can significantly improve the flame-retardant properties of FRPA. Specifically, the flame-retardant polyamide 1210 (FRPA-7) with 7 wt% CDS addition can reach V-0 grade according to UL-94 standard, accompanying limiting oxygen index value of 30.2% and tensile strength of 38.62 MPa. Compared with pure polyamide 1210, the peak heat release rate and total heat release rate of FRPA-7 reduce by 24.11% and 9.40%, respectively. This study provides a simple strategy to prepare flame-retardant polyamides with high flame retardancy and good mechanical properties, which are expected to show great potentials in future industrial applications.
https://doi.org/10.1002/marc.202200644

J. E. Andrew B. Hawkey, Zade R. Holloway, Erica Pippen, Olivia Jarrett, Bruny Kenou, Theodore A. Slotkin, Frederic J. Seidler, Edward D. Levin
Developmental exposure to the flame retardant, triphenyl phosphate, causes long-lasting neurobehavioral and neurochemical dysfunction
Birth Defects Research, 2022.
Human exposures to organophosphate flame retardants result from their use as additives in numerous

consumer products. These agents are replacements for brominated flame retardants but have not yet faced similar scrutiny for developmental neurotoxicity. We examined a representative organophosphate flame retardant, triphenyl phosphate (TPP) and its potential effects on behavioral development and dopaminergic function. Female Sprague–Dawley rats were given low doses of TPP (16 or 32 mg kg−1 day−1) via subcutaneous osmotic minipumps, begun preconception and continued into the early postnatal period. Offspring were administered a battery of behavioral tests from adolescence into adulthood, and littermates were used to evaluate dopaminergic synaptic function. Offspring with TPP exposures showed increased latency to begin eating in the novelty-suppressed feeding test, impaired object recognition memory, impaired choice accuracy in the visual signal detection test, and sex-selective effects on locomotor activity in adolescence (males) but not adulthood. Male, but not female, offspring showed marked increases in dopamine utilization in the striatum, evidenced by an increase in the ratio of the primary dopamine metabolite (3,4-dihydroxyphenylacetic acid) relative to dopamine levels. These results indicate that TPP has adverse effects that are similar in some respects to those of organophosphate pesticides, which were restricted because of their developmental neurotoxicity.
https://doi.org/10.1002/bdr2.2125

W. G. Tianyi Ma, Yuping Wang, Wenqing Wang, Rui Wang
Thermal degradation and flame retardancy prediction of Fe, Al, and Cu-based metal-organic framework and polyethylene terephthalate nanocomposites using DFT calculation
Polymer, Vol. 263, n° 16, 2022.
In this research, Fe3+, Al3+, and Cu2+ containing MOFs were synthesized and added into polyethylene terephthalate (PET), respectively, namely Fe-MOF-PET, Al-MOF-PET, and Cu-MOF-PET. Fe-MOF-PET was studied as the model sample to discuss the effect of metal cations of MOF on the thermal degradation mechanism. It indicated that Fe3+ would coordinate with the Cdouble bondO of PET and attract the C–O bond of the ester group to occur the homolytic reaction according to quantum chemical simulation combining the experimental data, including the pyrolysis chromatography-mass spectrometry (Py-GC-MS) and thermogravimetric infrared spectroscopy (TG-IR). Furthermore, the thermal degradation reaction of Fe3+ as the standard pathway was applied to predict flame retardant properties of different MOF-PET composites. The flame retardant order, Fe-MOF-PET > Al-MOF-PET > Cu-MOF-PET, was also successfully proved by the cone calorimeter (CONE), limiting oxygen index (LOI), and vertical flame test (VFT), respectively. The worse result of Cu2+ was attributed to the “one point” fracture reaction pathway of Cu-MOF-PET, which was different from the “two points” fracture of Fe-MOF-PET and Al-MOF-PET. This research provided an effective tool for predicting the flame retardant properties of MOFs in different polymer matrix using density functional theory (DFT).
https://doi.org/10.1016/j.polymer.2022.125496

A. Q. Hoang, N. M. Tue, M. B. Tu, G. Suzuki, H. Matsukami, L. H. Tuyen, P. H. Viet, T. Kunisue, S. Sakai and S. Takahashi
A review on management practices, environmental impacts, and human exposure risks related to electrical and electronic waste in Vietnam: findings from case studies in informal e-waste recycling areas
Environmental Geochemistry and Health, 2022.
Electrical and electronic waste (e-waste) has become a global concern, especially in developing countries. In this review, we conducted a literature survey of e-waste management practices, processing activities, and adverse effects in Vietnam, an emerging country in Southeast Asia, by gathering data from peer-reviewed articles published between 2009 and 2021. This is the first review paper to comprehensively discuss management and research aspects regarding e-waste in an Asian developing country. Due to the lack of an effective management and recycling system, a certain portion of Vietnamese e-waste has been processed by informal sectors without appropriate recycling and pollution control technology, resulting in localized contamination and human exposure to toxic chemicals. Primitive processing activities, such as manual dismantling, open burning, and plastic recycling, have been identified as important contributors to the environmental emission and human exposure to toxic elements (notably As, Mn, Ni, Pb, Zn) and organic pollutants like flame retardants, PAHs, PCBs, and dioxin-related compounds. Informal e-waste processing from these small-scale workshops can release pollutants at similar levels compared to large-scale facilities in

developed countries. This fact suggests an urgent need to develop management best practices for e-waste in Vietnam as well as other emerging and developing countries, in order to increase recycling efficiency and minimize their adverse impacts on environmental and human health.
https://doi.org/10.1007/s10653-022-01408-4

S. K. Lu, J. B. Liu, L. J. Zeng, L. H. Ai and P. Liu
Preparation and Characterization of Cyclodextrin Coated Red Phosphorus Double-Shell Microcapsules and Its Application in Flame Retardant Polyamide 6
Polymers, Vol. 14, n° 19, Oct 2022.
Using the melamine borate and crosslinked beta-cyclodextrin as shell materials, the double-shell microcapsules (Mic-DP) of red phosphorus (RP) was prepared, and its flame-retardant effect on polyamide 6 (PA6) was investigated. Compared with RP, Mic-DP showed lower hygroscopic and better inoxidizability. The limiting oxygen index (LOI) of PA6/13%Mic-DP was 27.8%, and PA6/13%Mic-DP reached V-0 rating. After the addition of 13% Mic-DP, the total exothermic (THR), peak exothermic (PK-HRR), and average effective thermal combustion (AV-EHC) rates of PA6 decreased. In addition, in order to investigate its flame-retardant mechanism, the pyrolysis gas chromatography-mass spectrometry (Py-GC-MS), scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) methods were used, and the results showed that mic DP acted as a flame retardant in the gas and condensed phases. The Mic-DP exhibited good compatibility and dispersibility in PA6.
https://doi.org/10.3390/polym14194101

J. Andrzejewski and S. Michalowski
Development of a New Type of Flame Retarded Biocomposite Reinforced with a Biocarbon/Basalt Fiber System: A Comparative Study between Poly(lactic Acid) and Polypropylene
Polymers, Vol. 14, n° 19, Oct 2022.
A new type of partially biobased reinforcing filler system was developed in order to be used as a flame retardant for polylactic acid (PLA) and polypropylene (PP)-based composites. The prepared materials intended for injection technique processing were melt blended using the novel system containing ammonium polyphosphate (EX), biocarbon (BC), and basalt fibers (BF). All of the prepared samples were subjected to a detailed analysis. The main criterion was the flammability of composites. For PLA-based composites, the flammability was significantly reduced, up to V-0 class. The properties of PLA/EX/BC and PLA/EX/(BC-BF) composites were characterized by their improved mechanical properties. The conducted analysis indicates that the key factor supporting the effectiveness of EX flame retardants is the addition of BC, while the use of BF alone increases the flammability of the samples to the reference level. The results indicate that the developed materials can be easily applied in industrial practice as effective and sustainable flame retardants.
https://doi.org/10.3390/polym14194086

J. Y. Zhao, Z. X. Zhan, M. J. Lu, F. B. Tao, D. Wu and H. Gao
A systematic scoping review of epidemiological studies on the association between organophosphate flame retardants and neurotoxicity
Ecotoxicology and Environmental Safety, Vol. 243, Sep 2022.
Organophosphate flame retardants (OPFRs) are increasingly and widely used as substitutes for brominated flame retardants in daily life. The chemical structure of OPFRs is very similar to that of organophosphorus pesticides, leading to concerns about their neurotoxicity. A few epidemiological studies have been published with incon-sistent results on this topic, and a systematic scoping review is needed to provide an overview or map of the current evidence on the relationship of OPFRs with neurodevelopmental toxicity. Therefore, MEDLINE (accessed through PubMed), Web of Science, and CNKI (Chinese National Knowledge Infrastructure) were systematically searched for articles published in the last two decades. Nine eligible articles were included in the present sys-tematic scoping review for adherence to the predefined PECOS (population, exposure, comparison, outcome, study design) statement. Six studies were conducted in the USA, and the remaining three studies were conducted in Austria, Norway and China. A total of 2 581 children (1 203 females and 1 378 males) were included. Half of the included studies focused on the adverse effects of OPFR exposure on cognition in children, while others primarily focused on the behaviors of children. In summary, the

current evidence suggests inverse associations between early-life exposure to OPFRs and the childhood intelligence quotient and internalizing behavior and positive relationships of OPFR exposure with externalizing behavior. However, some differences in the timing of sample collection for exposure measurements, in the individual OPFR metabolites available, in the neuro-developmental scales for outcome measurement, and in the statistical methods used to analyze the data are noted. In addition, further studies are warranted to evaluate some important issues, such as sex differences in the association, exposure-sensitive periods, and cumulative exposure risk assessment.
https://doi.org/10.1016/j.ecoenv.2022.113973

S. Y. Seunghwan Wi, Beom Yeol Yun, Yujin Kang, Sumin Kim
Fire retardant performance, toxicity and combustion characteristics, and numerical evaluation of core materials for sandwich panels
Environmental Pollution, Vol. 312, 2022.
According to fire accident statistics, fires in buildings are increasing. The flame-retardant performance of insulation materials is considered an important factor for preventing the spread of fire and ensuring evacuation. This study evaluated the flame-retardant performance and combustion characteristics of four types of organic thermal insulation used as core materials in sandwich panels. The flame-retardant performance evaluation based on total heat release and heat release rate revealed that phenolic foam (PF) satisfied the criteria for non-combustible grade insulation. An analysis of the hazardous gases released while combustion of the four insulation materials indicated that a significant amount of CO was released—an average of 19,000 ppm or higher—in the rigid urethan foam (PIR) and spray-type polyurethane foam (SPU). The fractional effective dose (FED) value was derived from the gas analysis results according to ISO 13344. PIR and SPU had an average FED value of 2.0 or higher and were identified as very dangerous in the case of fire accidents. Moreover, the evacuation time in the case of a fire in a warehouse-type building was comprehensively analyzed considering the material, size, and height for the four types of insulation. PIR was the most vulnerable to fire, and for PF, the danger limit was not reached until the end of the simulation.
https://doi.org/10.1016/j.envpol.2022.120067

C. Marianne, V. Christelle, V. Henri and F. Michel
Retardateurs de flamme conventionnels et biosourcés pour les polymères
n° ref. article : af6051, 2018.
L’industrie des polymères occupe aujourd’hui une place primordiale au niveau mondial. En effet, les polymères sont partout ; ils sont utilisés dans tous les aspects de la vie quotidienne grâce à leurs propriétés spécifiques concurrençant ainsi les matériaux traditionnels. Cependant ils possèdent une vulnérabilité certaine à l’égard des incendies. Il est donc nécessaire de renforcer leur comportement au feu par l'ajout de composés retardateurs de flamme. Dans cet article les différentes familles de retardateurs de flamme utilisés dans l’industrie des polymères sont présentées à l’exclusion des phosphorés et halogénés : leurs mécanismes d’action sont détaillés et des exemples d’application sont donnés. Une partie est consacrée aux retardateurs de flamme biosourcés dont le développement constitue un champ d’investigation peu développé, mais actuellement en plein essor.
https://www.techniques-ingenieur.fr/base-documentaire/materiaux-th11/adjuvants-des-plastiques-42138210/retardateurs-de-flamme-conventionnels-et-biosources-pour-les-polymeres-af6051/

F. Laurent and L.-C. José-Marie
Retardateurs de flammes RF des matériaux polymères
Techniques de l'ingénieur Adjuvants des plastiques, Vol. base documentaire : TIB138DUO, n° ref. article : am3237, 2016.
Les retardateurs de flamme sont des composés chimiques améliorant la réaction au feu des polymères et composites et permettant leur utilisation en conformité avec la réglementation incendie. Le développement des retardateurs de flamme est conditionné par leur action propre sur la réaction au feu, leur capacité à ne pas dégrader les autres propriétés des matériaux, mais aussi par leurs impacts environnementaux et toxicologiques. L’article détaille la problématique de l’inflammabilité des polymères, les mécanismes généraux d’action des différentes familles de retardateurs de flamme ainsi que les effets de synergie. En dernier lieu, les

aspects environnementaux, liés notamment au cycle de vie des polymères, sont évoqués.
https://www.techniques-ingenieur.fr/base-documentaire/materiaux-th11/adjuvants-des-plastiques-42138210/retardateurs-de-flammes-rf-des-materiaux-polymeres-am3237/

N. Claire and M. Raphaël
Retardateurs de flamme phosphorés commerciaux pour les polymères
Techniques de l'ingénieur Adjuvants des plastiques, Vol. base documentaire : TIB138DUO, n° ref. article : af6047, 2016.
Les retardateurs de flamme sont des additifs essentiels dans la formulation des matériaux polymères. Avec l'application des nouvelles règles environnementales et sanitaires, les retardateurs de flamme à base de phosphore trouve une place privilégiée dans le marché de ces additifs. Après une description des mécanismes d'action des retardateurs de flamme dans les matériaux polymères, les différentes méthodes de caractérisation du potentiel ignifugeant de ces additifs sont présentées. Ensuite, les retardateurs de flamme phosphorés commerciaux sont passés en revue en mettant en avant l'intérêt de leur structure chimique (organique versus inorganique, degré d'oxydation, aromaticité, synergie d'atomes).
https://www.techniques-ingenieur.fr/base-documentaire/materiaux-th11/adjuvants-des-plastiques-42138210/retardateurs-de-flamme-phosphores-commerciaux-pour-les-polymeres-af6047/