Bulletin de veille n° 13

Retardateurs de flamme

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Objectifs : Recherche de rapports, articles scientifiques. 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.
Les liens mentionnés dans le bulletin donnent accès aux documents sous réserve d'un abonnement à la ressource.

Sources surveillées

INRS-Biblio
Google Scholar
Lens.org
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Internet

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

R. Baron, L. Geoffroy, N. Gay, G. Fontaine, B. Fayolle and S. Bourbigot
Thermal ageing of flame-retardant high-density polyethylene designed for railway application
Polymer Degradation and Stability, 2025/01/19
Intumescent flame-retardant high-density polyethylene was subjected to accelerated ageing at 120°C. The unaged sample was compared to samples aged at different exposure times with respect to their fire properties such as critical flux at extinguishment, heat release rate and smoke opacity and toxicity in addition to char morphology and physicochemical properties. Findings showed that thermo-oxidation occurred after 43 days of exposure, leading to char structural changes for all the fire/smoke tests conducted but at different ageing times. The char structural change highly affected the heat release rate after 59 days. However, the critical flux at extinguishment and smoke toxicity after the maximum exposure time (96 days) were not significantly modified.
https://doi.org/10.1016/j.polymdegradstab.2025.111202

X. Zhu, Z. Wang, Z. Fang, Z. Xu, B. Luo, H. Yang, K. Wang and B. Guo
Flame-retardant polymer electrolytes enhancing the safety of lithium batteries
Journal of Energy Storage, Vol. 108, 2025/02/01
Flame-retardant polymer electrolytes have become indispensable in improving the safety of lithium-ion batteries and other energy storage systems. With the growing incidence of battery fires and explosions, these materials offer a promising solution to address the safety concerns associated with high-energy-density batteries. This review provides a comprehensive overview of the development of flame-retardant polymer electrolytes and their pivotal role in enhancing lithium-ion battery safety. These electrolytes improved battery safety through various mechanisms, such as free radical scavenging, condensed phase formation, heat absorption, and gas dilution. Additionally, they contribute to electrochemical performance by facilitating lithium-ion conduction, expanding the electrochemical stability window, and enhancing cycle stability. The review also highlights the challenges involved in optimizing flame-retardant polymer electrolytes, particularly the need to balance safety with electrochemical performance. By exploring these issues, we aim to provide valuable insights into the practical applications of flame-retardant polymer electrolytes for high-performance lithium batteries and identify future research directions that focus on enhancing safety, performance, and scalability for next-generation energy storage technologies.
https://doi.org/10.1016/j.est.2024.115080

M. Andruschko, M. Luksin, P. Frank, T. Paululat, U. Jonas and S. Fuchs
A set of intrinsically flame retardant, halogen-free styrenic copolymers: Synthesis, characterization, processing, and properties
Polymer Degradation and Stability, Vol. 232, 2025/02/01
Halogen-free, intrinsically flame retardant copolymers with glass transition temperatures in the range of 93 - 97 °C were synthesized from styrene, elemental sulfur, and organophosphorus comonomers in a facile radical bulk polymerization process. The copolymers were characterized using multidetector size exclusion chromatography (SEC), elemental analysis (EA), thin layer chromatography (TLC), UV/Vis spectroscopy, and 1H, 13C, and 31P nuclear magnetic resonance (NMR) spectroscopy. SEC revealed number average molar masses (Mn) ranging from 14 - 18 kg/mol, and weight average molar masses (Mw) from 41 - 62 kg/mol. The phosphorus contents ranged from 0.1 - 0.6 wt.%, while the sulfur contents were 0.4 - 0.7 wt.%, with covalently bound sulfur being predominantly present in the lower molar mass fractions. Structural details of the formed sulfur-containing moieties in the copolymers were elucidated with homonuclear correlation spectroscopy (COSY) and 1H/13C heteronuclear single-quantum correlation spectroscopy (HSQC) techniques, indicating the presence of PS-substituted 1-phenylethyl sulfanyl units with a mono-, di- or trisulfidic arrangement. Thermogravimetric analyses (TGA) showed slightly decreased decomposition onset temperatures for all copolymers compared to that for polystyrene, and no or only minimal formation of residual masses above 500

°C. Selected copolymers were extruded and injection molded on a laboratory scale. UL 94 vertical flame testing demonstrated a good flame retardant performance for most copolymer types, alongside with short after-flaming times and intensive melt dripping. Increased melt flow caused by polymer decomposition, probably initiated by the sulfur moieties in the copolymer structures, and cooling are considered the main condensed-phase flame retardant processes involved. Two copolymers of the set display a UL 94 V-0 classification.
https://doi.org/10.1016/j.polymdegradstab.2024.111141

Y. Huang, J. He and R. Yang
Preparation and characterization of HNTs@ZIF enhanced intrinsic flame retardant RTV silicone rubber
Polymer Degradation and Stability, Vol. 230, 2024/12/01
Phenylphosphonyl dichloride (BPOD) and 3-aminopropyltriethoxysilane (APTES) were used to prepare phosphorus-nitrogen hexaethoxysilane (BPTES). BPTES was then used for cross-linking and curing hydroxyl-terminated room-temperature vulcanized (RTV) silicone rubber, providing intrinsic flame retardancy. In addition, halloysite (HNTs) is a kind of tubular silicate, taking advantage of its large aspect ratio, HNTs were used as a template to load ZIF67 on the surface of halloysite to obtain HNTs@ZIF tubular filler. It was added to the above system as a reinforcing and flame-retardant filler by physical blending, and the RTV elastomer with excellent performance was prepared. The successful preparation of phosphorus-containing crosslinkers (BPTES) was demonstrated by FT-IR. After the introduction of the new crosslinker, RTV not only has improved flame retardant performance, but also improved mechanical properties. The tensile strength and elongation at break of RTV with 20 wt.% BPTES are increased by 151 % and 211 %, respectively. The peak heat release rate (pHRR) and the peak of smoke production rate (pSPR) are reduced by 55.9 % and 48.6 %, respectively, and the thermal stability is also improved. In addition, the successful preparation of HNTs@ZIF was confirmed by FT-IR, XRD, XPS, and TEM. By introducing 2 wt.% HNTs@ZIF into 20 wt.% BPTES cured RTV, the intrinsically flame-retardant RTVs with enhanced performance were prepared. It is worth noting that when 2 wt.% HNTs@ZIF is added, the flame retardant and smoke suppression properties of phosphorus-containing silicone rubber are further improved. Because the ZIF contains cobalt metal ions that can be catalyzed into carbon. The pHRR and pSPR decrease by 18.3 % and 16.3 %, respectively, and the total heat release (THR) and total smoke production (TSP) decrease by 23.6 % and 24.4 %, respectively. This work will provide enlightenment for the study of intrinsic flame-retardant RTVs enhanced by modified halloysite.
https://doi.org/10.1016/j.polymdegradstab.2024.111036

Í. Cacho, I. Uria, P. España, S. Arnaiz and A. Lopez-Urionabarrenechea
Laser-induced Breakdown Spectroscopy and Multivariate Data Analysis Applied to in-line Sorting of Brominated Plastics from Waste Electric and Electronic Equipment
Journal of Polymers and the Environment, 2024/10/22.
The presence of Persistent Organic Pollutants (POP) in consumer products such as electrical and electronic equipment represents a major obstacle for the recycling of the materials they contain at their end-of-life. Current technologies applied to recover plastics from waste electric and electronic equipment (WEEE) struggle to meet the requirements from recyclers regarding restrictions on some of these POPs, mainly brominated flame retardant (BFR) content. In this study, laser-induced breakdown spectroscopy (LIBS) technique combined with partial least squares regression (PLSR) was investigated for the real-time classification of WEEE plastics based on their total bromine (Br) content, in order to foster their reintroduction into the market as secondary raw materials. With this aim, a classification method was trained and tested in a sorting prototype using mixed plastic samples from TV set and computer monitor housings containing an average of 1.34% of Br. Regardless of polymer colour and type, up to 56% of the tested material could be segregated into a single fraction with a final Br concentration of 1,280 mg/kg. The achieved values met the requirements established in the CENELEC EN 50625 series of standards for the depollution of BFRs (< 2,000 mg/kg of Br) and the concentration of polybrominated diphenyl ethers (PBDEs) was estimated to be 213 mg/kg. These findings demonstrate the potential of the LIBS technique together with multivariate data analysis to ensure WEEE plastic sorting and depollution compliance with current regulations, reducing disposal rates and ultimately contributing to its circularity.
https://doi.org/10.1007/s10924-024-03438-8

Ó. Gómez, N. Ramírez, L. Vallecillos and F. Borrull

Determining personal exposure to high production volume chemicals (HPVCs) and polycyclic aromatic hydrocarbons (PAHs) with silicone wristbands: A pilot study

Environmental Research, Vol. 263, 2024/12/15

High production volume chemicals (HPVCs) and polycyclic aromatic hydrocarbons (PAHs) are semi-volatile organic compounds (semi-VOCs) of great environmental concern because of their presence worldwide and health problems resulting from long-term exposure to some of them. It is essential to have robust analytical methods to monitor the concentrations of these compounds not only in environmental samples but also individual exposure. In this pilot study we develop and validate a multiresidue analytical method based on ultrasound-assisted extraction and gas-chromatography mass spectrometry for the simultaneous determination of 56 semi-VOCs using silicone wristbands (SWBs) as personal passive samplers. The developed method provided recoveries between 43% and 114% on sampled SWBs and method detection and quantification limits in the range of 0.1–35 ng/g and 0.3–119 ng/g, respectively. A preliminary study was performed with a small group of adults living in the industrial city of Tarragona (north-eastern Spain) to evaluate the applicability of SWBs for monitoring individual exposure to the studied HPVCs and PAHs. Benzothiazoles, benzenesulfonamides, UV stabilisers and phenolic antioxidants were determined for the first time in SWBs. Phthalates (PAEs), stood out above the rest, accounting for 52% of the total concentrations. Diethylhexyl phthalate was the compound found at the highest concentrations with values between 1.1 and 82 µg/g. Carcinogenic and non-carcinogenic dermal risk assessment was performed for adults and considering two scenarios (low and high). PAHs were the compounds with the highest carcinogenic and non-carcinogenic dermal risk regardless of the exposure scenario. The second family of compounds that contributed the most to the total risk were PAEs but high punctual concentrations of these compounds caused significant differences between exposure scenarios.

https://doi.org/10.1016/j.envres.2024.120107

H. Tong, W. Wang, G. Wang, X. Wang, D. Yu, B. Chen and K. Pei

Synthesis and characterization of non-ionic flame-retardant waterborne polyurethane

RSC Advances, Vol. 14, n° 44, 2024, pp. 32031-32040.

Waterborne polyurethane (WPU) offers many advantages and is widely used in coatings, leathers, adhesives, biomaterials, and other consumer products. However, WPU is highly flammable. Many reactive flame retardants have been developed, but their char formation efficiency is still unsatisfactory, and the melt dripping during combustion has not been effectively suppressed. In this paper, a novel phosphorus-containing flame retardant with dihydroxy groups, (6-((4-hydroxyphenyl)((4-hydroxyphenyl)amino)methyl) dibenzo[c,e][1,2]oxaphosphinine 6-oxide) (PHAD), was successfully synthesized and incorporated into WPU molecular chain as a chain extender, thereby synthesizing a series of non-ionic flame-retardant waterborne polyurethane (NFRWPU) emulsions. The chemical structure of NFRWPU was successfully characterized by Fourier transform infrared spectroscopy and nuclear magnetic resonance. With the help of a thermogravimetric analyzer, scanning electron microscope and other instruments, some key performance parameters of NFRWPU in applications were investigated, including: physical, mechanical, and thermal stability and flammability. Some important experimental results include: both the particle size and viscosity of the emulsion increase gradually with increasing PHAD content, and when the PHAD content reaches 12%, the average particle size of emulsion increases to 106.6 nm with a viscosity of 89 mPa s; with the addition of PHAD, the tensile strength of NFRWPU initially increased and then decreased, while the elongation at break showed a continuous downward trend. The maximum tensile strength reached 22.63 MPa, and the minimum elongation at break dropped to 1060%; the addition of PHAD improved the thermal stability and flame retardancy of the film, with the highest limiting oxygen index value reaching 25.6% and the maximum carbon residue increasing to 6.5%. All these results indicate that NFRWPU is a promising flame retardant WPU considering the comprehensive performance.

http://dx.doi.org/10.1039/D4RA05873A

A. Balasch, A. Peris, C. Reche, T. Moreno and E. Eljarrat
Dermal exposure assessment of formal e-waste dismantlers to flame retardants and plasticizers using passive sampling methodologies
Environment International, Vol. 192, 2024/10/01
The recycling of e-waste can lead to the release of organic chemicals when materials containing additives are subjected to dismantling and grinding. In this context, the exposure of workers from a Catalonian e-waste facility to flame retardants and plasticizers (including organophosphate esters (OPEs), polybrominated diphenyl ethers (PBDEs), novel brominated flame retardants (NBFRs) and dechloranes) was assessed using T-shirts and wristbands as passive samplers. The study area includes an area exclusively dedicated to cathodic ray-tube (CRT) TVs dismantling, and a grinding area where the rest of e-waste is ground. All the families of compounds were detected in both T-shirts and wristbands, with the highest concentration levels corresponding to OPEs, followed by PBDEs, NBFRs, and dechloranes. The CRT area presented higher concentration levels than the grinding area. The compounds with higher concentrations in T-shirts were 2-ethylhexyl diphenyl phosphate (EHDPP), diphenyl cresyl phosphate (DCP) and triphenyl phosphate (TPHP), and the total concentration of all groups ranged between 293 and 8324 ng/dm2-h (hour). In the case of the wristbands, the most abundant compounds were DCP, TPHP, and BDE-209, with total concentrations between 188 and 2248 ng/dm2-h. The two sampling methods appear to be complementary, as T-shirts collect coarser particles, while wristbands also capture volatile compounds. Based on normalized surface and time concentrations, the estimated daily intake (EDI) through dermal contact was calculated and carcinogenic and non-carcinogenic risks (CR and non-CR) associated with this activity assessed. The results show median CR 29 and 16 times below the threshold in CRT and grinding areas respectively. The non-CR medians were 2 and 3 times below the threshold, although in the CRT area one exceptional value surpassed the threshold, suggesting that risk can exist for some workers in the facility.
https://doi.org/10.1016/j.envint.2024.109021

S. Y. Kılıç, N. Taşci, M. F. Demirkan, F. Yuksel and G. Y. Çiftçi
The new polycyclotriphosphazenes: Synthesis, characterization, thermal and photophysical properties
Journal of Molecular Structure, Vol. 1309, 2024/08/05
Polyamides are used as high-performance materials in industry and electronics. Researchers have recently been focusing on this area and trying to synthesize more stable and high-performance molecules by polymerizing various groups into the backbone skeleton. In this work, we report the design, synthesis, and characterization of paracetamol derivatives of cyclotriphosphazene (DSPCT and DSHY) and polycyclotriphosphazenes (DSTPC and DSAC) for the first time. The structures of new products were fully characterized by MALDI-TOF Mass analysis, FT-IR, 1H and 31P NMR spectroscopies and single crystal X-ray (for DSPCT and DSHY) crystallography. The crystallization behaviours of the polyamides were studied by X-ray diffraction, and a scanning electron microscope was used to observe the morphology of the DSTPC and DSAC. Thermal degradation properties for DSHY, DSTPC and DSAC were determined by DSC and TGA techniques. Polyamides and the DSHY compound exhibited superior thermal stability with an initial decomposition temperature range of ca. 251–302 °C. Additionally, spectral characterization and photophysical behaviours (fluorescence quantum yields and lifetimes) of the all new compounds were also comprehensively investigated using UV–Vis and fluorescence spectroscopies (steady-state and time-resolved fluorescence).
https://doi.org/10.1016/j.molstruc.2024.138161

I. Mohammadi Dehcheshmeh, A. Poursattar Marjani, F. Sadegh, M. E. Soltani, M. Safaeirad and M. Frediani
Synthesis and characterization of flame retardant unsaturated polyester-allyloxysilane resin for wood coatings
Scientific Reports, Vol. 14, n° 1, 2024/06/11
Fireproof coatings are the simplest, most efficient, and oldest method for protecting a wide range of flammable products, such as wood. Furthermore, surface ignition is the initial phase, so surface protection is essential to reduce fire propagation. Furthermore, delaying the spread of flames can help to save someone when a fire starts. This project synthesized flame-resistant resin starting from tetraallyloxysilane monomer as a halogen-free monomer, an intrinsic flame retardant co-curing agent. The following step synthesized polyester resin

using terephthalic acid as a heat-resistant resin. Unsaturated polyester was used by bulk radical polymerization. FT-IR and 1H-NMR analysis showed the successful synthesis of the desired monomer and polymeric compound. The thermal degradation and flame retardancy of pure unsaturated polyester resin (UPE) and allyloxysilane-unsaturated polyester (AUPE) were investigated by thermogravimetric analysis (TGA/DTG/DSC). The burning test and the thermal stability of the coating layers were evaluated using standard UL 94. Physical properties of resins were evaluated using Heat Deflection Temp tests (HDT) ISO 75-A, ASTM 648, Hardness ASTM D2583, Volumetric shrinkage ASTM 3521, and Water absorption ASTM D570. The results of the tests show the successful synthesis and their flame retardant properties.
https://doi.org/10.1038/s41598-024-62765-x

H. Liu, W. Wang, L. Yan and Z. Xu
Flammability degradation behavior and ageing mechanism of flame-retardant cable sheath under different ageing conditions
Polymer Degradation and Stability, Vol. 230, 2024/12/01
The durability of fire-resistant performance is a great challenge for long-life wire and cable sheath materials. The commonly used flame-retardant cable sheath materials were aged by thermal, salt spray and hygrothermal accelerated methods. The effects of different environmental factors on the fire protection performance of cable sheath materials were investigated by cone calorimeter, limiting oxygen index, UL94, plastic smoke density, scanning electron microscope and Fourier transform infrared spectroscopy tests, and the ageing mechanism of cable sheath materials was proposed. The results show that the three accelerated ageing methods have a weakening effect on the fire resistance and charring properties of cable sheath materials. Among them, hygrothermal ageing treatment has the most serious impact on the fire-resistant performance compared with the unaged cable sheath material, including a decrease by 16.0 % in limiting oxygen index grade, an increase by 13.8 % in total heat release, a decrease by 75.8 % in light transmittance, and a decrease by 47.4 % in char residue at 800 °C. The deterioration of fire protection performance for cable sheath materials depends on the complex environmental conditions. The weakening effect of hygrothermal ageing is the strongest, followed by salt spray ageing, and the thermal ageing is the smallest. This work can provide strategic guidance for an in-depth analysis of the fire risk of ageing cables in complex environments.
https://doi.org/10.1016/j.polymdegradstab.2024.111019

C. E. Enyoh, T. O. Maduka, M. S. Rana, S. C. Osigwe, S. C. Ihenetu and Q. Wang
Chemicals from Brominated Flame Retardants: Analytical Methods, Occurrence, Transport and Risks
Applied Sciences, 14, Issue, 2024
Brominated flame retardants (BFRs) are synthetic chemicals widely used to reduce the flammability of consumer products, including electronics, textiles, and furniture. Despite their effectiveness in fire prevention, BFRs pose significant environmental and health risks due to their persistence, bioaccumulation, and potential toxicity. This review provides a comprehensive examination of BFRs, focusing on recent advancements in analytical methods for their detection and quantification in environmental and biological samples. The study explored the physicochemical properties that influence BFR distribution and transport in various matrices, including soil, water, air, sediments, and biota. The review also summarizes current knowledge on the occurrence and environmental fate of BFRs, highlighting their mobility and long-range transport. Furthermore, the study discusses the health risks associated with BFR exposure, emphasizing their endocrine-disrupting effects and impact on reproductive and neurological functions. By integrating findings from recent studies, this review aims to enhance the understanding of BFR behavior and inform regulatory strategies to mitigate their adverse effects on human health and the environment.
https://doi.org/10.3390/app14177892

W. Ren, J. Liang, M. Huang, W. Qian, M. Zhao, F. Qiao, L. Cui, Z. Zhang, J. Wang, C. Zhou, Z. Wang, Q. An and D. He

Thermally-stable and flame-retardant metal-organic framework-based separator for high-performance lithium-ion batteries

Chemical Engineering Journal, Vol. 498, 2024/10/15

Safety hazards hinder the development of lithium-ion batteries (LIBs), in which the failure of separator is a key point. However, commercial polyolefin separators display poor thermal stability and flame-retardant property. Aramid nanofiber (ANF) is a promising material for safer separators in batteries due to its excellent thermal stability and remarkable flame retardancy, but the pure ANF separator often shows low ionic conductivity because of the tightly packed fibers. Metal-organic framework (MOF) is a promising candidate for increasing the porosity and ionic conductivity of ANF separator due to its ultrahigh porosity and ultrahigh specific area. Herein, a thermally-stable and high-performance composite separator is fabricated by combining MOF pore-forming agent and ANF network skeleton. The MOF/ANF1composite separator with 10 wt% ANF shows excellent thermal-stability (melting-point above 300 °C and decomposition temperature above 500 °C) and remarkable flame-retardant property. And it exhibits high ionic-conductivity of 1.01 mS·cm−1, contributed to the superior long-term cycling performance of the coin cell with the capacity of 147.3 mAh·g−1 after 200 cycles at 1 C, almost 25.4 % higher than that of the coin cell with PP separator for LIBs. The strategy of this research provides new ideas for the design of high-safety LIBs.

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M. Altaf, M. N. Ahmed, A. Iqbal and A. A. Khan

Synthesis and characterization of novel organoclay-epoxy based flame retardant nanocomposites

Journal of Reinforced Plastics and Composites, Aug 2024.

In this study, cost-effective, widely spread, and nontoxic fillers were used to improve the flame retardancy of epoxy nanocomposites. A novel and environmentally benign cation exchange approach was used for the modification of bentonite nanoclay with positively charged L-serine, used to synthesize nanocomposites. Modification of clay was confirmed by using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy. X-ray diffraction (XRD) technique proved increase of d-spacing from 12.82 & Aring; to 14.42 & Aring; as a result of cation exchange. Field emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDS) were used to investigate microstructure of the nanocomposites. Reduction in weight loss, with 28.0 % to 34.0 % increase in char yield of epoxy nanocomposites was determined by the thermogravimetric analysis (TGA). Underwriters laboratories (UL-94) V-0 ratings of nanocomposites indicated improved flame retardancy. Nanofillers significantly reduced the loading of aluminum tri-hydroxide (ATH) and improved the flame retardancy through its synergistic effect.

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