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EDITORIAL

Bio-Based Halogen-Free Flame Retardant Polymeric Materials

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1 About the Special Issue Editor

Xin Wang received his PhD in Safety Science and Engineering from the University of Science and Technology of China (USTC) in 2013. He is currently employed as an Associate Professor of the State Key Laboratory of Fire Science (SKLFS) at the University of Science and Technology of China (USTC). His research activities are focused on fire-safe polymer composites, including flame retardant polymer nanocomposites, smoke suppression of polymers, and sustainable flame retardant technologies. To date, he has authored or co-authored 150 papers in peer-reviewed international journals (total citations 8280, H index = 55), 1 monograph, 5 invited book chapters and 12 patents in these fields. He serves as editorial board members of the *Journal of Renewable Materials*. He was also awarded the 2nd Prize of National Natural Science Award awarded by the Chinese Government (2017).

The extensive utilization of polymeric materials in our daily life is driven by their superior comprehensive properties. However, polymeric materials are apt to be ignited with a fast flame spread rate as well as the release of massive toxic gases and smoke during combustion. As a consequence, the relatively high fire hazards of polymeric materials account for a large number of property losses and casualties in polymer-related fire accidents every year worldwide. Thus, fire safety requirements on polymeric materials are currently attracting increasing attention in terms of difficulty of ignition, low heat release rate and low production of toxic gases and smoke. Over the past few decades, flame retardant technology from bio-based resources has gained increasing interest owing to increasing awareness of environmental protection and sustainable development. Bio-based halogen-free flame retardants are currently a hot research area because they are safe, non-toxic and sustainable flame retardants. This special issue, which consists of 12 articles, including one review article, written by research groups of experts in the field, focuses on the latest advances in bio-based halogen-free flame retardant polymeric material applications.

Ding et al. reviewed the latest progress of flame retardant bio-based benzoxazines in recent years, including their synthesis methods, flame retardancy, thermal stability and other physical and chemical properties. In addition, we briefly presented the challenges and future development prospects of flame retardant bio-based benzoxazines.

Zhang et al. studied the effect of montmorillonite (MMT) on the properties of a layered double hydroxide (LDH)-intumescent flame retardant (IFR) flame retardant poly (lactic acid) (PLA) system. The results showed that the addition of MMT into PLA composites helped to form more stable carbon layers in the combustion process, thus reducing the pHRR of PLA composites. This study can provide a new guidance strategy for further optimizing the properties of IFR polymers.

Li et al. successfully synthesized a bio-based phosphorus-nitrogen flame retardant (Cy-HEDP) inspired by the structure of DNA. The results showed that when the addition of Cy-HEDP was 15 wt%, the modified epoxy resin could pass the UL-94 V-0 rating, and the heat release and smoke emission of epoxy resin were reduced significantly. This study provides inspiration for the development of bio-based flame retardants.

Chen et al. successfully introduced beta-cyclodextrin (β-CD) into layered tin phenylphosphonate (SnPP) to obtain a hybrid flame retardant and applied it to enhance the thermal stability and flame retardancy of epoxy resin (EP). When the amount of β-CD@SnPP was 6 wt%, the peak heat release rate (PHRR), total heat release (THR), and smoke production rate (SPR) of the EP composites were reduced by 28.4%, 33.0% and 44.8%, respectively. The good flame retardancy and smoke suppression are ascribed to the excellent charring capability of the β-CD@SnPP hybrid.

Greiner et al. synthesized a novel flame retardant substructure based on phosphorylated salicylic acid (SCP) and added it into RTM6, a high-performance epoxy resin used in resin transfer molding processes as a composite matrix. All tested flame retardants decreased the PHRR by up to 54% for neat resin samples. The excellent mechanical properties showed the applicability of these flame retardants in carbon fiber reinforced composite materials.

Guo et al. presented an isosorbide-derived polyphosphonate (PICPP) as a flame retardant for poly (lactic acid) (PLA). PLA composites containing 10 wt% PICPP achieved a high limiting oxygen index of 30.0% and UL-94 V-0 classification, indicating that PICPP was an efficient bio-based flame retardant agent for PLA.

Zhang et al. synthesized a phosphorus-containing eugenol-derived flame retardant (DOPO-GE) and mixed it with a bisphenol A epoxy prepolymer. When the phosphorus content was 1.0%, the residual yield of the thermosets at 750°C in nitrogen increased from 13.9% to 30.6%, implying excellent charring ability. When the phosphorus content was only 0.5%, the limiting oxygen index was as high as 30.3% with UL94 V-0 achieved.

Wang et al. synthesized a vanillin-derived, DOPO-containing bisphenol (VDP) as a reactive flame retardant for epoxy thermosets. With a phosphorus content of 0.5%, the heat release rate, total heat release rate and smoke production are markedly reduced. Additionally, the impact strength increased by 34%, and the flexural strength increased by 23%.

Zhang et al. reported phytate-based flame retardants, aluminum phytate (PA-Al) and iron phytate (PA-Fe), and introduced them into rigid polyurethane foam (RPUF). Cone calorimetry analysis showed that the THR of RPUF/PA-Al30 decreased by 17.0% and total smoke release (TSR) decreased by 22.0% compared with pure RPUF, demonstrating a low fire risk and good smoke suppression.

Wang et al. used boric acid, borax and disodium octaborate to modify craft paper-based packaging materials for archive conservation. The modified craft paper showed much higher flame retardancy than the pristine paper, without sacrificing the tensile strength and elongation at break. This study provides a facile way to improve the fire safety of archival packaging materials by applying environmentally friendly flame retardants.

Yu et al. fabricated plywood by immersing veneers in a flame retardant mixture consisting of phosphoguanidine, guanidine sulfamate, disodium octaborate tetrahydrate and dodecyl dimethyl benzyl ammonium chloride. The burning behaviors and fire risk of flame retardant plywood were studied by cone calorimeter and LOI tests, which showed good fire resistance.

Luo et al. used lignin-modified ammonium polyphosphate (L-APP) as a flame retardant additive for poly (L-lactic acid) (PLLA). With an L-APP loading of 20 wt%, the PLLA composites showed an LOI of 30.8% and a UL-94 V-0 level. This study promotes the value-added utilization of lignin and the application of PLLA in the field of flame retardant materials.

In summary, bio-based flame retardants made from various renewable feedstocks represent one of the most promising directions for next-generation flame retardants, and, due to their sustainability, they have attracted extensive attention and achieved significant progress during the past few decades. The field of bio-based flame retardants for polymers is experiencing rapid growth, which should continue for the coming decade.

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