

Phosphorus-containing (bio) compounds in combination with expandable graphite: Flame retardancy and smoke/toxicity suppression of flexible polyurethane foams through synergistic effects

vorgelegt von

M. Sc.

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an der Fakultät III – Prozesswissenschaften

der Technischen Universität Berlin

zur Erlangung des akademischen Grades

Doktorin der Naturwissenschaften

- Dr. rer. nat. -

genehmigte Dissertation

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Tag der wissenschaftlichen Aussprache: 16. Dezember 2022

Berlin 2023

To my parents

I can do all this through Him who gives me strength.

Bible (NIV) – Philippians 4:13

Acknowledgements

First of all, I would like to thank God. He has given me strength and encouragement and has accompanied me through the ups and downs.

This endeavor would not have been possible without my esteemed supervisor - Prof. Dr. habil. Bernhard Schartel. I am extremely grateful that he gave me an opportunity to start my Ph.D. in his group. Although I am not so familiar with the topic at the beginning, thanks for his patience in teaching and guiding me over the years. I know sometimes I was not confident enough in my work, but he always encourages me and believes in me to get the work done.

I would like to express my deepest appreciation to Prof. Dr.-Ing Dietmar Auhl for agreeing to supervise my work and progress, providing me with invaluable feedback and reviewing this doctoral dissertation.

Thanks should also go to all my colleagues in the working group 7.5 at BAM over the years, Dr. Alexander Battig, Weronika Tabaka, Sandra Falkenhagen, Dr. Robert Gleuwitz, Dr. Benjamin Zirnstein, Dr. Yi Tan, Dr. Xuebao Lin, Vitus Hupp, Dr. Lars-Hendrik Daus, Sebastian Goller, Maria Jauregui, Daniel Rockel and Bettina Strommer... I appreciate for their friendly help with my project and, scientific and non-scientific discussions. I really had great memories with them over the years. I would like to extend my sincere thanks to Patrick Klack for providing the technical support and the workshop team, especially Michael Schneider and Tobias Lauterbach, for cutting the samples.

I would like to offer my special thanks to Dr. Simone Krüger and Tina Raspe for their assistance with the smoke density chamber measurements and Dietmar Schulze for his contribution to the mechanical testing for the materials.

I had the pleasure of collaborating with our Chinese partners at the University of Science and Technology China (USTC), especially Prof. Yuan Hu, Dr. Chao Ma and Feng Zhou. They provided me a lot of resources and I learned more about the topic from them during my 5-month stay in China.

In addition, I would like to express gratitude to Dr. Doris Pospiech and Andreas Korwitz from Leibniz Institute of Polymer Research Dresden (IPF Dresden) for supporting my research ideas and giving me precious advice on my idea during my two stays in Dresden.

Lastly, I would like to acknowledge my family, especially my parents. They have given me a lot of support and freedom to achieve my dreams and goals in Germany. I would also want to give a big thank to my best friend Kayee Poon who is always there for me, always encourages me and believes in me.

May Almighty God continue to bless you all.

Zusammenfassung

Polyurethan-Weichschaum (FPUF) ist aufgrund seiner offenzelligen Struktur anfällig für Brände. FPUF besteht hauptsächlich aus Kohlenwasserstoffen, die brennbar sind. Um den Flammschutz zu verbessern, wurden in der Industrie häufig halogenierte Flammschutzmittel, wie chlor- und bromhaltige Verbindungen, in FPUF eingesetzt. Da halogenierte Flammschutzmittel giftig für Lebewesen und die Umwelt sind, werden sie durch halogenfreie Flammschutzmittel ersetzt. Daher synthetisierte der Kooperationspartner eine Reihe neuartiger phosphor-stickstoffhaltiger 9,10-Dihydro-9-oxa-10-phosphaphenanthren-10-oxid (DOPO)-Derivatsalze und ein neuartiges flüssiges phosphorhaltiges Flammschutzmittel (P-FR) - Bis([dimethoxyphosphoryl]methyl)phenylphosphat (BDMPP) und setzte sie in FPUF ein. Das Brandverhalten dieser FPUF wurde im ersten Teil dieser Arbeit untersucht.

Diese wissenschaftliche Arbeit konzentriert sich hauptsächlich auf die Erhöhung der Flammwidrigkeit und die Unterdrückung des Rauches von FPUF während der Verbrennung durch die Nutzung des Synergieeffekts zwischen halogenfreien (biobasierten) phosphorhaltigen Flammschutzmitteln und expandierbarem Graphit (EG). Der Clou ist, dass ein phosphorgepfropftes Polyol auf Sojabasis synthetisiert und zusammen mit EG in FPUF eingesetzt wurde. Der Brandrückstand zeigt, dass es einen synergistischen Effekt von Phosphor und EG in der kondensierten Phase gibt, und die Konzentration der Phosphorverbindung zeigt ein nichtlineares Verhalten in Bezug auf die Flammhemmung. Neben dem mit Phosphor gepfropften Polyol auf Sojabasis wurde dem FPUF auch BDMPP zusammen mit EG zugesetzt. Die Ergebnisse der Brandtests von FPUF, die BDMPP und EG enthalten, zeigen ebenfalls einen hervorragenden Synergieeffekt zwischen P-FR und EG.

Da die übermäßige Ausbeutung von Erdöl in den letzten Jahrzehnten ein heißes Thema ist, ist die Verwendung erneuerbarer Ressourcen wie Pflanzenöle ein Ansatz, um die Verwendung von petrochemischen Produkten zu reduzieren. Neben Sojaöl wurde auch Rizinusöl verwendet, um den biologischen Gehalt von FPUF zu erhöhen. In Kombination mit anderen handelsüblichen Flammschutzmitteln und Additiven wurden das Brandverhalten und das Rauchverhalten von FPUF untersucht. Die Kombination von P-FR und EG zeigt auch in diesen Systemen einen vielversprechenden Synergieeffekt in FPUF.

Das Verständnis der Brandphänomene von Polyurethanschaum (PUF) ist ein Schlüssel zur Verbesserung seines Flammschutzes. Daher wurden in der Arbeit die chemischen Komponenten und die physikalische Struktur von PUF klar dargestellt und das Brennverhalten von PUF vorgeschlagen, wenn es einem Wärmestrom von oben ausgesetzt wird. Der Synergieeffekt zwischen P-FR und EG wurde detailliert beschrieben, und die Verwendung von erneuerbaren Rohstoffen in PUF wurde diskutiert, um Einblicke in das Thema Nachhaltigkeit zu geben.

Die Kombination von P-FR und EG ist in der Regel auch die erste Wahl in der Industrie, um die Flammhemmung von PUF extrem zu verbessern. Drei industrielle Benchmark-PUFs, die P-FR und EG

enthalten und in verschiedenen Anwendungen eingesetzt werden, um die höchsten Anforderungen zu erfüllen, wurden untersucht und analysiert. Es wurde somit der Aktuelle Stand der Technik diskutiert. Die Kombination von P-FR und EG stellt die klassenbeste Mehrkomponente in Bezug auf Flammschutz und Rauchverhalten in PUFs ist.

Anhand verschiedener Brandtests wurde in dieser Arbeit der Synergieeffekt zwischen P-FR und EG in PUF, insbesondere FPUF, umfassend untersucht, um in Zukunft wissenschaftsbasiert ein effektiveres Mehrkomponenten-Flammschutzsystem für PUF zu entwickeln.

Abstract

Flexible polyurethane foam (FPUF) is prone to fire due to its open-cell structure, and the chemical composition of FPUF is mainly composed of hydrocarbons which are flammable. To improve the flame retardancy, halogenated flame retardants, such as chlorine- and bromine-containing compounds, were commonly used in FPUF in the industry. Since halogenated flame retardants are poisonous to the living organisms and the environment, they are being replaced by halogen-free flame retardants. Therefore, the cooperation partner synthesized a series of novel phosphorus-nitrogen-containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivative salts and a novel liquid phosphorus-containing flame retardant (P-FR) - bis([dimethoxyphosphoryl]methyl) phenyl phosphate (BDMPP) and applied them in FPUF. The fire behavior of these FPUF foams were investigated in the first part of this work.

This scientific work mainly focuses on enhancing the flame retardancy and suppressing smoke of FPUF during burning by using the synergistic effect between halogen-free (bio-based) P-FRs and expandable graphite (EG). The highlight is that a phosphorus-grafted soybean-based polyol was synthesized and was applied in FPUF along with EG. The fire residue reveals that there is a synergistic effect of P-FR and EG in the condensed phase, and the concentration of phosphorus compound exhibits non-linear behavior in terms of flame retardancy. Apart from the phosphorus-grafted soybean-based polyol, BDMPP was also added into FPUF along with EG. The results from the fire tests of FPUF containing BDMPP and EG also show an excellent synergistic effect between P-FR and EG.

As overexploitation of petroleum is a hot topic in recent decades, using renewable resources such as plant oils is an approach to reduce the use of petrochemical products. Besides soybean oil, castor oil was used to increase the biological content of FPUF. Combined with other commercial flame retardants and additives, fire performance and smoke behavior of the FPUF were investigated. The combination of P-FR and EG shows also in these systems a very promising synergistic effect in FPUF.

Understanding the fire phenomena of polyurethane foam (PUF) is a key to improve its flame retardancy. Therefore, the work clearly depicted the chemical components and the physical structure of PUF and proposed the burning behavior of PUF when it is subjected to a heat flux on top. The synergistic effect between P-FR and EG was described in detail, and the use of renewable feedstocks in PUF was discussed to provide insights into the topic of sustainability.

The combination of P-FR and EG is generally the first choice used in the industry for greatly enhancing flame retardancy of PUF. Three industrial benchmark PUFs containing P-FR and EG used in different applications to fulfill challenging demands were investigated and analyzed. Thus, the current state-of-the-art was discussed. The combination of P-FR and EG is the best-in-class multicomponent in terms of flame retardancy and smoke behavior in PUFs.

Through different fire tests, this work comprehensively investigated the synergistic effect between P-FR and EG in PUF, especially FPUF, to enable evidence-based development of more effective multicomponent flame retardant system for PUF in the future.

Index of abbreviations

ATH	Aluminum trihydrate
BDMPP	Bis([dimethoxyphosphoryl]methyl) phenyl phosphate
CAS	Castor oil
CO	Carbon monoxide
CuO	Copper (II) oxide
DOPO	9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DTG	The first derivative of TG
EG	Expandable graphite
EHC	Effective heat of combustion
FPUF	Flexible polyurethane foam
FTIR	Fourier transform infrared spectroscopy
HCN	Hydrogen cyanide
HRR	Heat release rate
LOI	Limiting oxygen index
MA	Melamine
MARHE	Maximum average heat emission
MHD	Magnesium hydroxide
NMR	Nuclear magnetic resonance spectroscopy
OP	Exolit [®] OP560 polyol
P-FR	Phosphorus-containing flame retardant
PHRR	Peak heat release rate
PUF	Polyurethane foam
RPUF	Rigid polyurethane foam
SDC	Smoke density chamber
SEM	Scanning electron microscopy

2,4-TDI	2,4-Toluenediisocyanate
2,6-TDI	2,6-Toluenediisocyanate
TDI	Toluenediisocyanate
TG	Thermogravimetry
TGA	Thermogravimetry analysis
THR	Total heat release
TSR	Total smoke release
UL 94 HBF	Underwriters Laboratories 94 horizontal burning test

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1 Introduction

Synthetic polymeric materials can be seen almost everywhere in people's daily life due to their low cost, ease of processing and versatility. There are different kinds of polymeric materials used in various applications according to their different physical and mechanical properties. Many household items around us are made of synthetic polymers, such as flexible polyurethane foams (FPUFs). FPUF is a material widely used in consumer goods with excellent cushioning effect such as mattresses, upholstered furniture, car seats and packaging. [1] In a fire situation, the high thermal inertia of flexible polyurethane foam (FPUF) because of its chemical composition and physical structure in nature results in rapid heating of the first layer, which reduces ignition time and accelerates flame spread, limiting the application of FPUF. In addition, burning FPUF releases large amounts of toxic gases, such as carbon monoxide (CO) and hydrogen cyanide (HCN), which can cause human death. [2-3] Therefore, the goal of this research was set to enhance the flame retardancy and to reduce the smoke toxicity in flexible polyurethane foams (FPUFs) by designing, constructing, and modifying the polyols and flame retardants based on the theory and technology of synergism, catalytic carbonization, and catalytic conversion. This scientific work is summarized in papers that present different approaches on the flame retardancy enhancement of FPUF to enable a wide range of applications and to reduce potential fire risk to people.

This scientific work is summarized in 7 papers as listed below.

1. Shicong Ma, Yuling Xiao, Feng Zhou, Bernhard Schartel, Yin Yam Chan, Oleg P. Korobeinichev, Stanislav A.Trubachev, Weizhao Hu, Chao Ma and Yuan Hu. Effects of novel phosphorus-nitrogen-containing DOPO derivative salts on mechanical properties, thermal stability and flame retardancy of flexible polyurethane foam. *Polym Degrad Stabil.* 2020, 177. Doi: 10.1016/j.polymdegradstab.2020.109160.
2. Feng Zhou, Chao Ma, Kang Zhang, Yin Yam Chan, Yuling Xiao, Bernhard Schartel, Manfred Doring, Bibo Wang, Weizhao Hu and Yuan Hu. Synthesis of ethyl (Diethoxymethyl)phosphinate derivatives and their flame retardancy in flexible polyurethane foam: Structure-flame retardancy relationships. *Polym Degrad Stabil.* 2021, 188. Doi: 10.1016/j.polymdegradstab.2021.109557.
3. Yin Yam Chan, Chao Ma, Feng Zhou, Yuan Hu and Bernhard Schartel. A liquid phosphorous flame retardant combined with expandable graphite or melamine in flexible polyurethane foams. *Polym Advan Technol.* 2022, 33, 326-339. Doi: 10.1002/pat.5519.
4. Yin Yam Chan, Chao Ma, Feng Zhou, Yuan Hu and Bernhard Schartel. Flame retardant flexible polyurethane foams based on phosphorous soybean-oil polyol and expandable graphite. *Polym Degrad Stabil.* 2021, 191. Doi: 10.1016/j.polymdegradstab.2021.109656.

5. Yin Yam Chan, Andreas Korwitz, Doris Pospiech and Bernhard Schartel. Flame retardant combinations with expandable graphite/phosphorus/CuO/castor oil in flexible polyurethane foams (This article was submitted to ACS Applied Polymer Materials on 11.11.2022.)
6. Yin Yam Chan and Bernhard Schartel. It takes two to tango: Industrial benchmark PU-foams with expandable graphite/P-flame retardant combinations (This article was accepted by Kautschuk Gummi Kunststoffe on 23.10.2022 and is being published.)
7. Yin Yam Chan and Bernhard Schartel. It takes two to tango: Synergistic expandable graphite – phosphorus flame retardant combinations in polyurethane foams. *Polymers*. 2022, 14, 2562. Doi:10.3390/polym14132562.

The simplest way to enhance the flame retardancy of materials is to physically mix the flame retardant additives into the polymer matrix. In the past, the addition of halogenated flame retardants into polymers was the most common approach to improve the flame retardancy. Due to the toxicity of halogenated flame retardants, they have been replaced by halogen-free flame retardants, such as phosphorus-containing flame retardant (P-FR). [4] Paper 1 and Paper 2 are studies related to the flame retardancy of the additive novel P-FR in FPUF. A novel 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivative salts and a novel liquid phosphorous flame retardant, bis([dimethoxyphosphoryl]methyl) phenyl phosphate (BDMPP), are synthesized by the cooperation partner in Paper 1 and Paper 2, respectively. They were simply used as single additive flame retardants to improve the fire performance of FPUF in both gas phase and the condensed phase. The investigation of the fire behavior, in particular the cone calorimeter analysis, was my work contribution in Paper 1 and Paper 2.

The flame retardancy of P-FR is limited when its concentration is further increased. [5] Therefore, system combining P-FR with other flame retardants is an effective approach. In Paper 3, BDMPP was combined with expandable graphite (EG) or melamine (MA) in FPUF. BDMPP is effective in both gas phase and condensed phase and cooperated well with EG and MA in the polymer matrix to enhance the flame retardancy of FPUF. The combination of P-FR and MA created a layered residue which provides thermal protection to the material underneath during burning. The synergistic effect between P-FRs and EG was clearly recognizable from the results of fire tests.

Due to the growing focus on sustainability issues, more and more industries have paid more attention and started to use renewable resources instead of petroleum-derived raw materials for over a decade. [6] A renewable resource is a supply of a substance that can be replenished. Since the raw materials used in conventional FPUF are derived from petroleum, the synthesis of reactive flame-retarded bio-based polyols is a solution that kills two birds with one stone to produce FPUF for a wide range of applications. [7] On the one hand, the renewable biomass content is increased. On the other hand, the flame retardancy is improved. Paper 4 presents a good example in terms of the need for sustainability and flame retardancy in FPUFs. Modified vegetable oils, such as palm oil, sunflower oil, linseed oil, rapeseed oil, can be used

as substitute for polyol production due to their certain similarities in chemical structure. [8] In Paper 4, soybean oil was successfully modified into reactive phosphorus-containing polyol. In the formulation of FPUF, the petrochemical polyether polyol was partially replaced by the phosphorus-containing soybean oil-based polyol up to 80 %. The foam samples with modified soybean oil-based polyol still show excellent physical and mechanical properties. Furthermore, the combination of phosphorus-containing bio-based polyol and EG in FPUF provided excellent synergistic effect in charring, resulting in improved flame retardancy.

The objective of Paper 5 was to find out the synergism among different combinations of commercial flame retardants and additives (EG, P-FR, copper (II) oxide) in terms of flame retardancy and smoke behavior in FPUF. The results showed that the combination of EG and P-FR greatly improved the char yield, thereby providing better flame retardancy for FPUF. Regarding sustainability, the petrochemical polyol was partially replaced by castor oil in the formulation of FPUF to enhance the bio-based content. Paper 5 provides a multi-component strategy in FPUF that not only improves the flame retardancy but also simultaneously reduce the smoke and toxic gas emission.

Paper 6 and Paper 7 present the state-of-the-art of the flame retardancy of PUF. The most prominent highlight among the papers is the synergistic effect between P-FRs and EG in FPUFs. The binding effect by P-FR strengthens the structure of expanded graphite residue, thereby providing impressive protection to the material underneath during burning. According to the results of the work from Paper 3 to Paper 5, combination of P-FR and EG in FPUF is an effective way to significantly increase flame retardancy and reduce amount of smoke released. Three industrial benchmark P-FR/ EG polyurethane foam products used in different applications (Railways/ships, buildings, and lightweight structure) were investigated in Paper 6, showing remarkable results in terms of flame retardancy. In addition, many published research studies in recent years have found a synergistic effect between P-FR and EG. [9-13] However, comprehensive studies on the interaction between P-FR and EG in PUF during burning are insufficient. Therefore, the feature article (Paper 7) reveals in detail the burning process of the synergistic effect between P-FRs and EG in PUFs, providing a better understanding for the successful development of flame-retardant PUF. To gain a deeper understanding and modify the flame retardancy of PUFs according to their burning behavior, the temperature-thickness relationship of PUFs at different burning stages is illustrated. Moreover, current and future topics related to the use of renewable feedstocks to increase the bio-based content in PUF and isocyanate-free approaches are discussed in the article to provide potentially sustainable ways for future PUF production. [14, 15]

2 Scientific background – Fire behavior and flame retardancy

Various synthetic polymers are generally high molecular weight hydrocarbon, and most of them are highly flammable, raising public concern about potential fire risks. [16-18] Among different fire safety measures, actively enhancing the flame retardancy of polymeric materials is one of the approaches to deal with the fire risk problem. Accordingly, many studies in recent decades have focused on improving the flame retardancy of polymers through flame retardants to reduce the probability of fire accidents. Fuel, oxygen, and heat are indispensable for a continuous combustion. Flame retardant is a substance inhibits or disrupts the combustion cycle. In the past, halogen-based flame retardants were commonly used as additives because of their excellent performance in improving the fire retardancy of polymer even at low concentrations. Nonetheless, the use of halogen-based flame retardants in consumer goods was already banned in some countries due to their toxicity, persistence, and bioaccumulation. Inhalation of halogens, especially bromine, has adverse effects on environment and human health. Therefore, more halogen-free flame retardants have been developed and used in polymers. Furthermore, scientists found that two or more flame retardants used in a polymeric system may induce synergistic effect to enhance the flame retardancy. In order to understand the fire behavior to better design promising flame-retardant systems, the fire development of polymeric materials during burning is discussed in the next paragraphs.

Figure 1 depicts the typical four stages of a fire scenario. They are ignition, developing fire, fully developed fire and decay. [19] Once the polymer is ignited, the heat from the ignition source on the polymeric materials causes the rising of temperature. When the temperature is high enough, the chemical bonds keep breaking and volatile fragments keep generating to a certain concentration. If the products are flammable as burning fuels and at the same time a sufficient concentration is reached, a flame forms and may initially grow by flame spread to a continuation of flaming combustion in the stage of developing fire. The temperature gets higher as more and more material melts and volatilizes to fuel the fire. In the stage of fully developed fire, which is the penultimate stage of the fire growth, the flame may stabilize to become a steady state. When the fuel is consumed so that the flame cannot sustain, the stage of decay occurs and reduces the overall temperature.

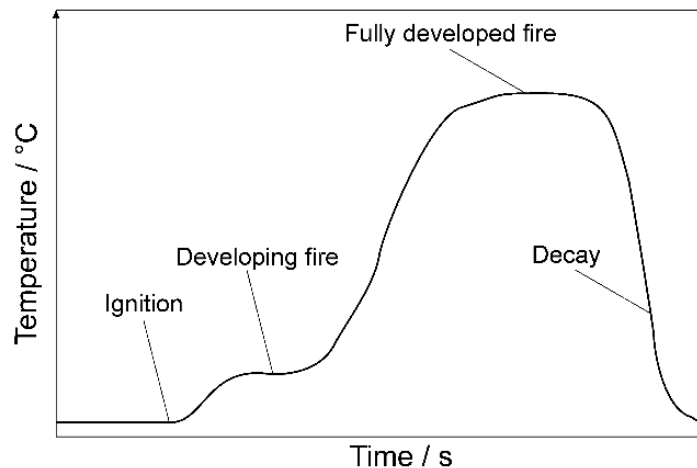


Figure 1 Stages in a fire scenario

Due to incomplete combustion of polymeric materials, not only carbon dioxide and water, but also CO and smoke are the main products produced.

To improve fire safety, flame retardants are commonly used in polymers, textiles, and coatings to inhibit or prevent the development of the propagation of fire. However, since compatibility and flame-retardant interactions vary from one polymer to another, there is no all-purpose flame retardants suitable for all polymeric materials. For FPUF, there are some commercial flame retardants such as metal hydroxides, P-FRs, MA, and intumescent products commonly used. These flame retardants act differently under various modes of action, and they are generally categorized into three approaches: Condensed phase, endothermic and gas phase modes of action. [20-21]

Condensed phase mode of action:

Non-flammable char is produced in the polymer through the dehydration of the flame retardant to generate double bonds during the pyrolysis process. Carbonaceous char layer is formed by cyclization, cross-linking, aromatization, and graphitization to act as a physical hinderance preventing the heat and mass transfer from the gas phase to the unburned material underneath. [22] In addition, the intumescent effect of char is triggered in the presence of three basic ingredients: acid source, charring agent and blowing agent. The gaps trapped in the intumescent char provide superior flame retardancy to the system.

Endothermic mode of action:

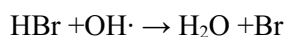
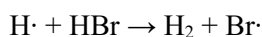
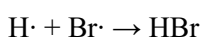
Heat is absorbed by endothermic decomposition of metal hydroxides to prevent reaching the pyrolysis temperature of the material. [21] Aluminum trihydrate (ATH) and magnesium hydroxide (MHD) are common mineral-based flame retardants that undergoing endothermic reaction under high temperature. During the endothermic decomposition of these mineral fillers, heat is absorbed, and non-flammable water vapor is generated to further quench and slow down the pyrolysis process of the material. The released water vapor also effectively dilutes surrounding combustible gases such as oxygen in the flame

zone. The endothermic decomposition reactions of ATH and MHD are described in equation (1) and equation (2), respectively. [23-25]

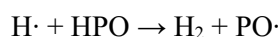
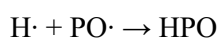


Gas phase mode of action:

Gas phase flame retardants reduce the heat released in the gas phase by scavenging reactive free radicals, such as $\text{H}\cdot$ and $\text{OH}\cdot$, during combustion. [26] Halogen-based flame retardants provide the most effective flame retardancy to various polymers in the gas phase. Halogen can be readily released under fire condition to inhibit free radical reactions, which are exothermic to maintain the flame. Bromine is taken as an example:



Nonetheless, halogen-based flame retardants release toxic and corrosive gases, especially hydrogen halides, and large amount of smoke during burning. Therefore, less toxic alternatives such as phosphorus compounds are used as flame retardants in polymers. [4] Phosphorus-containing compounds is a halogen-free flame retardant which is a less toxic alternative. Phosphorus derivatives act not only a char promoter via dehydration to induce cyclization, crosslinking, aromatization/ graphitization in the condensed phase, but also in the gas phase, depending on their chemical structures and their interactions with the polymer. [27] Radical scavengers such as $\text{PO}\cdot$, $\text{HPO}\cdot$ and $\text{PO}_2\cdot$ combined with free radicals in the gas phase to reduce the heat released during burning. However, polymeric materials with P-FRs increase the release of smoke and CO during burning.



A lot of above-mentioned flame retardants are additives. Since these additives are generally required in high amounts to achieve satisfactory flame retardancy, they can adversely affect the final mechanical properties of the polymer in practical applications. To solve this problem, reactive flame retardants have been developed and applied to polymers. Reactive flame retardants can be chemically joined to the polymer backbone to reduce the impact on the mechanical properties of the material. Reactive flame retardants with specific functional groups should be tailored for certain types of polymers.

2.1 Flame retardancy of polyurethane foams

Polyurethane is a large molecule composed of multiple urethane groups in the molecular backbone. Figure 2 shows the typical synthetic route of polyurethane by the hydroxyl groups from polyol and isocyanate group to form the repeating urethane linkage via polyaddition reaction. Polyurethane can be linear, branched, or crosslinked depending on the chemical structure of polyols and isocyanates. [28] Using different ratios of different types of polyols and isocyanates and different kinds of additive, polyurethanes can be produced for different applications ranging from rigid and flexible foams, coating, adhesives, sealants to elastomers. [29]

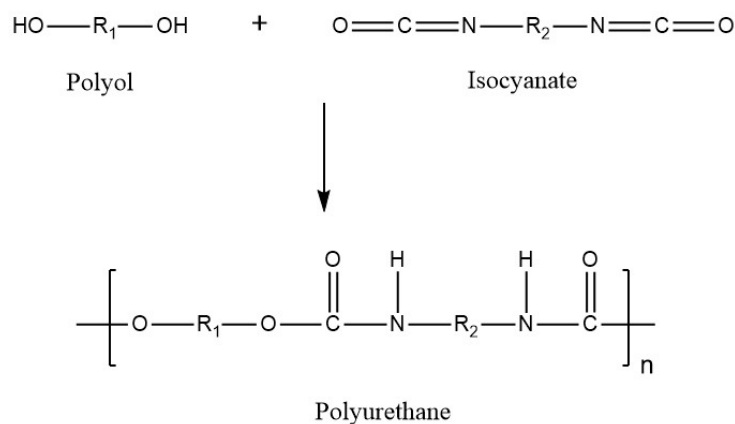


Figure 2 Typical synthetic route of polyurethane

2.1.1 Factors affect the flammability of polyurethane foams

The chemical composition of polyurethane, shown in Figure 2, is mainly hydrocarbons, and its cellular structure, low density and large surface area make PUF vulnerable to fire. In a real fire scenario, burning droplets of PUF can ignite surrounding objects to increase the spread of the fire. Due to incomplete combustion, the entire material is not consumed. Tiny and lightweight unburned particles called smoke are emitted in the air. Apart from smoke, toxic gases such as HCN and CO released by PUFs are the leading cause of death due to the inhalation in fires. [3]

Among a wide range of applications, PUF occupies the largest market share of polyurethane products. Polyurethane foam is generally divided into two categories: rigid polyurethane foam (RPUF) and flexible polyurethane foam (FPUF). RPUF has extremely low thermal conductivity due to its closed-cell structure serving as a perfect thermal insulation material for buildings and refrigeration. Due to the flexibility of FPUF by its open-cell structure, it is commonly used as a cushioning material for furniture, car seats and packaging. [6]

RPUF has better flame retardancy than FPUF because RPUF has higher apparent density and crosslink density. More char is produced in RPUF during burning to protect the material underneath. [30] On the other hand, FPUF collapses at the start of burning and then turns into a pool fire. [31] After the flame was extinguished, there were only fragile tiny fragments reminded in Figure 3.

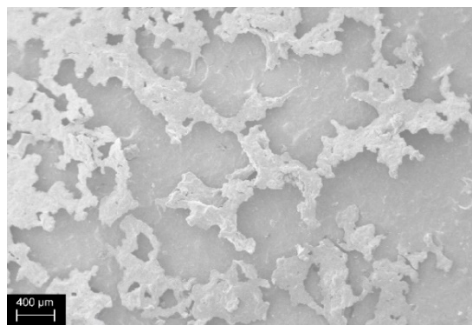


Figure 3 SEM image of residue from FPUF.

The flammability of PUF is largely determined by its main chemical components - polyol and diisocyanate. [32] The chemical structure of polyol have great influence on flammability. The functionality of polyol directly affects crosslinking density of PUF. Higher functionality of polyol means that a greater number of hydroxyl group reacts with isocyanate group to form more urethane linkage. More urethane linkages in PUF result in higher crosslink density and require more energy to break the crosslinks. Therefore, the flammability of PUF is reduced with higher crosslink density. The flame retardancy of PUFs with aromatic based polyols is significantly higher compared to PUFs based on aliphatic polyols. It is because aromatic hydrocarbons have higher hydrolytic and thermal stability compared to aliphatic hydrocarbons. Aromatic structures are more easily charred during burning. [33] Isocyanate index is the equivalent ratio of isocyanate to alcohol in the formulation. If a significant excess of isocyanate is present in the polymer matrix, trimerization of the excess isocyanate forms isocyanurate rings, shown in Figure 4. Isocyanate rings promote charring during burning to improve flame retardancy by providing protective layers for unburned parts.

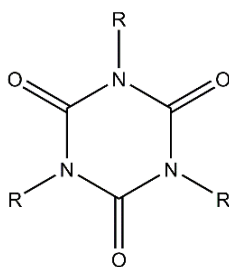


Figure 4 Chemical structure of isocyanurate.

2.2 Synergistic effect of flame retardants

Most of the additive flame retardant may influence adversely the mechanical properties of polymers. In order to achieve satisfactory fire performance, high loading of flame retardants, especially metal hydroxides, is usually necessary to be added to the polyurethane foam. [34] When the combination of two or more flame retardants in a polymer matrix performs better overall flame retardancy than the sum of the effects of individual flame retardants, it is called synergistic effect. [35] Due to the synergistic effect of combination of flame retardants, less flame retardants can be added to reduce the adverse impact on mechanical properties of the material. Systems such as Br-Sb₂O₃, Br-NH₃ and P-N are

advantageous combinations of synergistic effect in polymers. [36-37] The non-halogenated combination P-FR/EG is a perfect match to trigger strong synergistic effect in FPUF. P-FRs decomposed into glassy polyphosphate that binds the fluffy expanded graphite together to form a reinforced thermal protective char layer for the unburned material underneath. EG alone significantly reduced peak heat release rate (PHRR) in FPUF, but PHRR is even lower in the combination of P-FR and EG. The char residue yield after burning greatly increased. The increase content of phosphorus at the same amount of EG enhanced the weight percentage of char residue, but greater amount of phosphorus increased the total smoke release (TSR).

2.3 Materials

i. Polyols and isocyanates

Polyols and isocyanates are the main chemical components for the polymerization of FPUF and RPUF. Polyol shown in Figure 5 is an organic compound containing multiple OH functional groups to build the soft segment of PUF. Isocyanate is a major component commonly used to build the hard segments of PUF. However, the type of polyol and isocyanates used in FPUF and RPUF are different due to their physical and mechanical properties. For example, the isocyanate used in FPUF is usually an 80:20 mixture of 2,4-toluenediisocyanate (2,4-TDI) and 2,6-toluenediisocyanate (2,6-TDI) as displayed in Figure 6. Apart from polyols and isocyanates, some additives also need to be added for successful foaming, such as blowing agents, surfactants, and catalysts. Since FPUF is the main material of this study, the composition of FPUF is detailly described as follows. The mechanical properties of FPUF are highly influenced by the types of polyols and isocyanates. The functionality of polyol used for FPUF is about 2-3 because FPUF has a lower crosslink density. Long chain polyols contribute to the flexibility and elasticity of the foam. Isocyanate forms the hard segments in the polymer network to provide strength and rigidity to the foam. [38] The open-cell structure shown in Figure 7 containing cell windows, struts, and strut joins provides a cushioning function in nature.

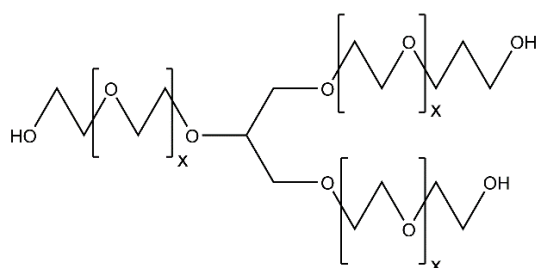


Figure 5 Chemical structure of petrochemical polyol.

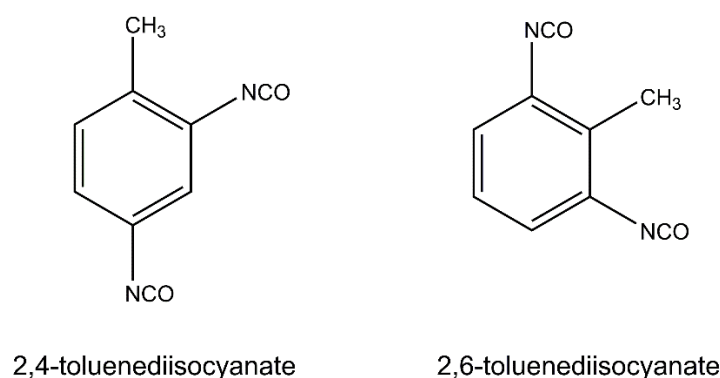


Figure 6 Chemical structure of 2,4-toluenediisocyanate and 2,6-toluenediisocyanate.

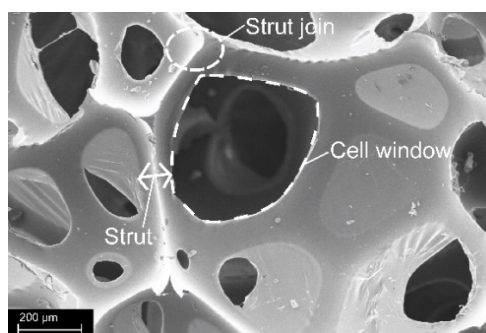


Figure 7 SEM image of cell structure of FPUF.

ii. Catalyst, foaming stabilizer and blowing agent

Besides polyol and diisocyanate, catalyst, foaming stabilizer and blowing agent are also important to the foaming process. [39] Amine catalysts and organic tin complex catalysts are most widely used catalyst in polyurethane foam production. Amine catalysts balance the reaction, help to reduce foam defects, and improve the structural stability of the final foam. Organic tin complex catalysts facilitate the gel reaction in the foaming process. Foaming stabilizer is used to stabilize the bubble formation to control the cell size. It is used to maintain the cell structure by increasing the resilience of the cell wall. Foaming stabilizers are organic/ inorganic silicone-based complexes. There are two types of blowing agent: physical and chemical. Physical blowing agents form gas bubbles by introducing inert gas (e.g. carbon dioxide, nitrogen) or low-boiling-point liquid (e.g. cyclopentane, hydrofluorocarbon, dichloromethane) in the polymer matrix through gas release or evaporation of the liquid. Water is usually used as a chemical blowing agent in polyurethane. As shown in Figure 8, it is a condensation reaction of water and isocyanate to release carbon dioxide (CO_2) gas as a blowing agent in FPUF.

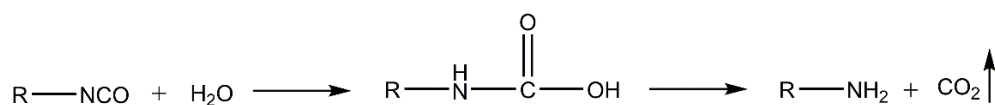


Figure 8 Condensation reaction between isocyanate group and water

iii. Synthesis of flexible polyurethane foams

FPUF is typically prepared by one-pot method with two components (Component A and component B) shown in Figure 9. Component A consists of polyol, amine catalyst, tin catalyst, foaming stabilizer and blowing agent and component B is TDI. Component A is mixed homogenously by a high-speed mechanical mixer. Component B (TDI) is then poured into the mixed component A and stirred subsequently at high speed for 5 s. The mixture is transferred to a mold during the subsequent expansion. Afterwards, the foam is placed in an oven at 80 °C for 24 h to complete curing.

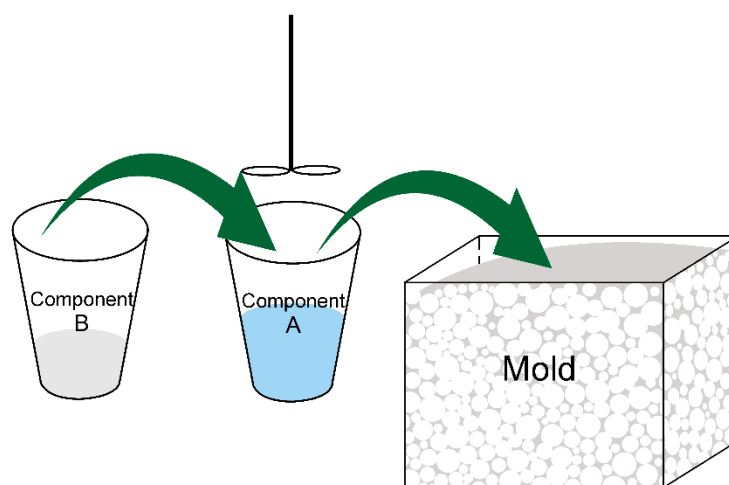


Figure 9 Schematic diagram of the synthesis of FPUF

iii. Plant oils

Soybean oil and castor oil, which are shown in Figure 10, were used in this work. A plant oil molecule composed of a triacylglycerol and linked to three fatty acids, which has structural similarities to petrochemical polyol. (See Figure 5). [40] Therefore, the plant oil is an alternative source for polyurethane production as it is a renewable resource. Soybean oil consists of unsaturated bonds on fatty acids which can be modified into polyols by simple chemical reactions such as epoxidation and hydrolysis. Castor oil has hydroxyl groups in nature. It can be replaced directly with the petrochemical polyol in the formulation. Since castor oil is not suitable for human consumption, it does not compete with edible oil, and thus it is more sustainable.

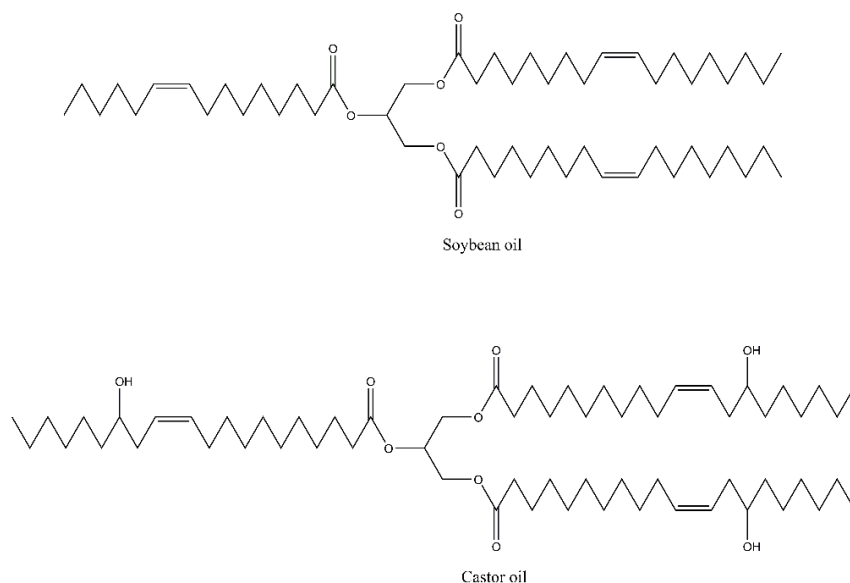


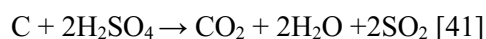
Figure 10 Chemical structure of soybean oil and castor oil.

iv. Flame retardants and smoke suppressants

Due to the flammability of FPUF, adding flame retardants is a common way to reduce the fire risk. For this purpose, several flame retardants and smoke suppressants (EG, P-FRs, MA, and nano metal oxide) were added to FPUF in this work.

Expandable graphite (EG)

Graphite is in layered structure in natural. As shown in Figure 11, Intercalant such as sulfuric acid is added between the layers. Sulfuric acid decomposes into gases under elevated temperature. These gases force to increase the distance between the graphite layers and thus expanding the graphite into several hundred times of its original size. Instead of the decomposition of sulfuric acid, Camino et al. [41] suggested that the expansion of EG is due to the reaction of carbon in the graphite with sulfuric acid to form blowing gases, as shown in the chemical equation below. As shown in Figure 12, expanded graphite has a porous and bulky worm-like structure which provides excellent thermal insulation for the unburned part. Sufficient EG provides excellent flame retardancy, which greatly reduces the fire risk. Moreover, EG is an effective smoke suppressant for FPUF by increasing the residence time of smoke precursors in the pyrolysis zone into aromatic char. [42]



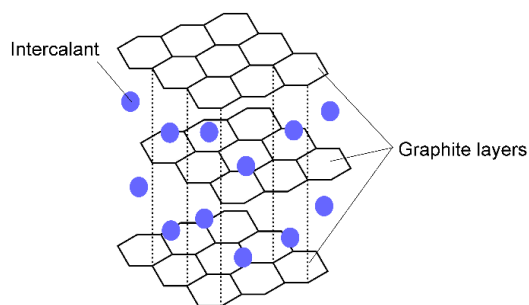


Figure 11 Chemical structure of expandable graphite

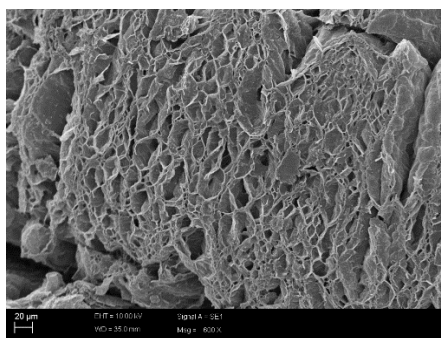


Figure 12 SEM image of the surface of expanded graphite

Phosphorus-containing flame retardants (P-FR)

P-FRs generally act in the gas phase and condensed phase. In the gas phase, phosphorous compounds decompose into free phosphorous radicals to quench the other free radicals generated to inhibit the combustion process during burning of materials. In the condensed phase, the presence of phosphorus compounds in a polymer matrix promotes carbonization to stabilize the char. [27] The phosphocarbonaceous char is formed by linking polyaromatic macromolecules and phosphate groups to act as a protective layer for the material underneath. [43] However, the increasing concentration of P-FRs exhibit nonlinear behavior in terms of flame retardancy. [5, 44] Therefore, the flame retardancy of P-FR is optimized in a certain amount of phosphorus content (See Figure 13). The effectiveness of P-FRs in higher concentration is limited when used alone. It usually gives synergy in multicomponent flame retardant systems, for instance P-EG which is mentioned in chapter 2.2.

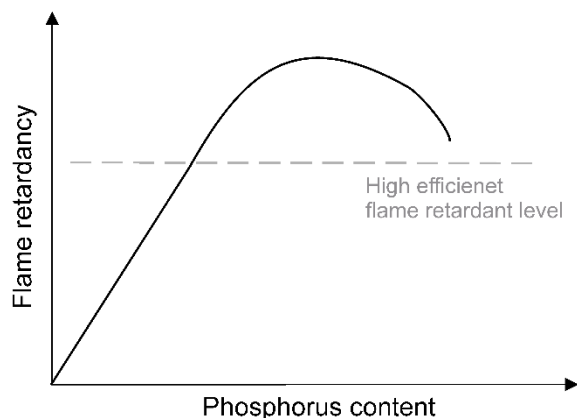


Figure 13 Flame retardancy against phosphorus content

Melamine

Melamine (MA), an organic compound containing high content of nitrogen, acts as a heat sink to increase the heat capacity of the system and inert diluent released in the flame during the decomposition process. [45] MA effectively increases the time to ignition. Apart from enhancing the flame retardancy, Price et al. [46] found that MA reduces the amount of aromatic smoke precursors thereby suppressing smoke in PFUF. However, the increasing amount of MA increases the viscosity and thus decreases the growth and rising height of FPUF during foaming. Therefore, the physical structure and the mechanical properties is further degraded due to the embedding of higher concentration of MA in the FPUF matrix. [47]

Nano metal oxides

Transition metal nanoparticles can catalyze the pyrolysis gas product such as smoke, HCN and CO at high temperature. [48-50] Metal compounds such as copper, zinc, nickel, and iron have good adsorption and catalytic conversion capabilities for HCN which can be converted into N_2 , CO_2 and H_2O etc.

2.4 Methods

Different measurements and tests were performed to characterize the materials from different perspectives, such as morphology of the unburned and burned materials, mechanical properties, decomposition behavior, flammability, dripping behavior, fire performance and smoke behavior.

2.4.1 Nuclear magnetic resonance spectroscopy (NMR)

Nuclear magnetic resonance (NMR) is a spectroscopy analysis to determine the molecular structure of chemical substances based on the interaction of nuclear spins in a magnetic field. NMR was mainly used to determine the hydrogen and phosphorus spectra of the synthesized polyol in Paper 4.

2.4.2 Thermogravimetric analysis (TGA)

Pyrolysis is the thermal decomposition process of materials at elevated temperature in an inert atmosphere. During pyrolysis of organic materials, volatile products are released in the gas phase while solid residue remains in the condensed phase as carbon char. 10 mg powdered samples in an alumina crucible were heated up at a steady heating rate of 10 K min^{-1} under constant nitrogen flow (i.e. 30 mL/min). Figure 14 displays the curve of thermogravimetry (TG) and the first derivative of the TG curve (DTG). The mass loss curve of FPUF generally consists of two decomposition steps. The first decomposition step is attributed to the hard segment derived from the isocyanates. The second decomposition step at higher temperature is related to the soft segment from polyols.

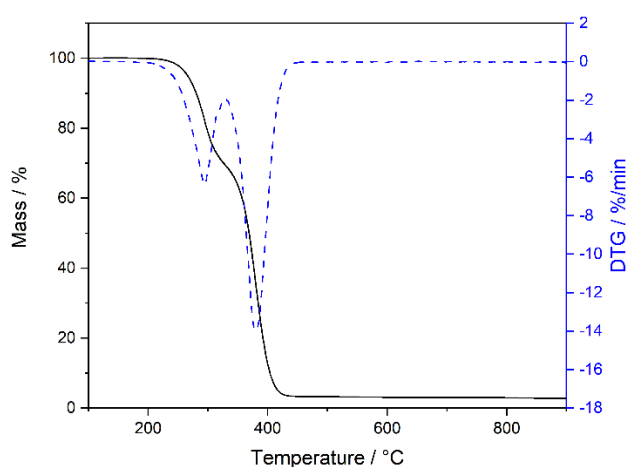


Figure 14 TG and DTG curves of FPUF

2.4.3 Thermogravimetry coupled with Fourier transform infrared spectroscopy

The combination of TGA and Fourier transform infrared spectroscopy (FTIR) allows simultaneous analysis of gaseous reaction products produced during the pyrolysis of materials. It is a useful tool for understanding the chemical reactions between flame retardants and polymers during thermal decomposition that take place in the pyrolysis zone. FTIR measures the wavelength range in the infrared region that a sample absorbs.

2.4.4 Flammability – limiting oxygen index (LOI)

Limiting oxygen index (LOI) is done to characterize the flammability according to ISO 4589-2. A test specimen with the dimensions of 100 mm x 10 mm x 10 mm is burned vertically at the upper end in a glass cylinder at room temperature under a constant flow of mixture of oxygen and nitrogen at specific concentration. Varying the oxygen concentration until its specimen burns at the lowest oxygen concentration. The lowest oxygen concentration represents the LOI value. FPUF is very flammable due to its chemical composition and physical structure. The general LOI value for FPUF ranged from 16 to 19 vol.-%. [51]

2.4.5 Underwriters Laboratories 94 horizontal burning test (UL 94 HBF)

The test uses a small flame source to determine the burning behavior of FPUF specimens in the horizontal direction according to ISO 9772. Specimen dimensions of 150 mm x 50 mm x 10 mm is used for testing. Measurement determines the tendency of the material to extinguish or spread the flame once the specimen is ignited. The dripping behavior is observed whether the cotton pad is ignited by burning drops. [52, 53] The setup of UL94 HBF is shown in Figure 15.

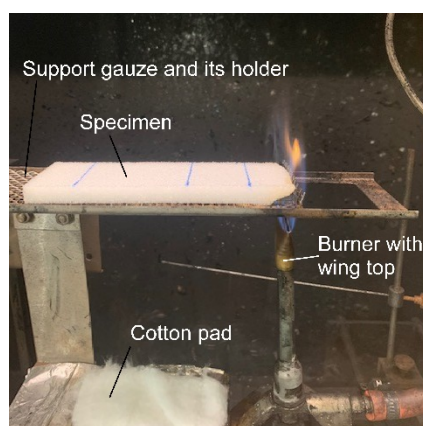


Figure 15 Setup of UL 94 HBF test

2.4.6 Cone calorimeter

The burning behavior of the materials under forced flaming conditions were studied in accordance with ISO 5660. Cone calorimeter, shown in Figure 16, is a tool used to study the fire performance of materials in a fire scenario of developing fire under dynamic airflow condition. The specimen size for foam is 50 mm x 100 mm x 100 mm. The bottom and sides of foam specimens are wrapped with a single layer of aluminum foil. To obtain meaningful data for comparison, a specimen placed horizontally on a sample holder is exposed horizontally to a heat flux 25 kW m^{-2} with a spark ignitor in 25 mm spacing with a cone heater. The load cell under the sample holder records the mass loss throughout the test. The effluents released from the specimen are piped and analyzed for O_2 , CO_2 and CO content. Moreover, there are thermocouple, pressure sensor, smoke measurement and a sample probe to collect different valuable data such as heat release rate (HRR), total heat release (THR), apparent effective heat of combustion (EHC), total smoke release (TSR), carbon monoxide yield, char yield and maximum average heat emission (MARHE) can be collected in the measurement. [19, 54, 55]

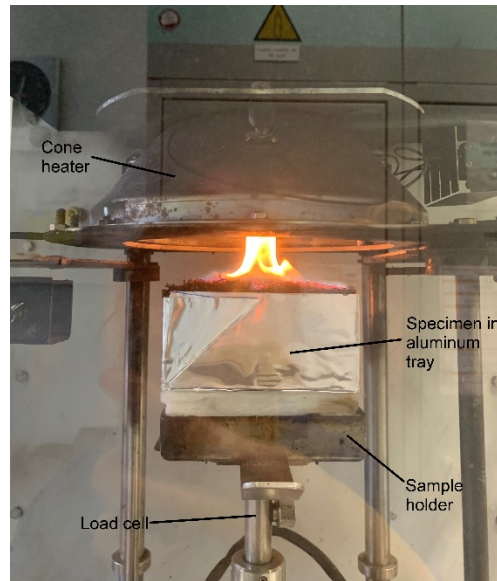


Figure 16 Burning sample on the load cell of cone calorimeter

2.4.7 Scanning electron microscopy (SEM)

The morphology of the foam before burning and its residue after burning was investigated by SEM. SEM images samples in nanometer scale by emitting electron beam. There is an interaction between the emitted electron beam and the sample, resulting in different signals depending on the surface topography. These signals are received and processed to present the morphology of samples. The specimens are sputter-coated with 15 nm of gold to increase the conductivity of the samples, resulting in higher resolution images.

2.4.8 Mechanical test

The compression strength, tensile strength as well as elongation at break of FPUF were measured by a Universal Testing Machine. The compression strength was determined by following ISO 3386-1. The specimen size for compression is 40 mm x 30 mm x 10 mm. Tensile strength and elongation at break were evaluated using type 1A specimens with a thickness of 10 mm according to ISO 1798.

2.4.9 Smoke density chamber (SDC) coupled with FTIR

SDC is a sealed test chamber equipped with a photometric instrument. [56] SDC measures the specific optical density under conditions of static accumulation in accordance with ISO 5659. The specimen size for foam samples is 75 mm x 75 mm x 25 mm in the SDC measurement. The foam specimen is exposed to a heat flux of 25 kW m^{-2} in a separation of 25 mm to the cone heater, with or without the use of a pilot flame depending on the fire scenario. The SDC is combined with FTIR to analyze qualitatively and quantitatively the gases evolved from materials during burning in such mentioned condition.

3 Discussion of the results

3.1 Main messages from the publications

Due to the high flammability of FPUF, several flame-retardant systems were designed and prepared to improve the flame retardancy of FPUF for a wide range of applications. Five first-authorship and two co-authorship articles were published detailing the studies on different flame-retardant FPUF systems.

Paper 1 and Paper 2 from the academic partner, University of Science and Technology of China (USTC), investigated the morphology, mechanical properties, thermal stability, and flame retardancy of FPUF with self-synthesized P-FRs. The novel flame retardants synthesized by our academic partner performs well in both gas phase and condensed phase due to the presence of phosphorus.

Paper 3 summarizes a study on a liquid phosphorous flame retardant – bis([dimethoxyphosphoryl]methyl) phenyl phosphate (BDMPP) combined with EG or MA incorporated in FPUF. The results show that BDMPP worked in gas phase with reduced value of EHC. MA alone already greatly reduced the peak heat release rate as it undergoes endothermic reaction to increase the heat capacity of the system. EG is an effective smoke suppressant that significantly reduces the TSR from $392 \text{ m}^2 \text{ m}^{-2}$ to $52 \text{ m}^2 \text{ m}^{-2}$. EG also reduced the MARHE from 320 kW m^{-2} to 109 kW m^{-2} . The char yield from the combination of BDMPP and EG in PFUF is greater than the sum of the individual effects. The combination of BDMPP and MA in FPUF produces layered structure residue, which is an excellent fire protection during burning. Therefore, the combination of BDMPP with EG or MA provided synergistic effect on flame retardancy of FPUF.

In Paper 4, phosphorus-containing soybean-oil-based polyol was synthesized to enhance the flame retardancy and bio-based content of FPUF. Apart from replacing petrochemical polyol with flame-retardant bio-based counterpart, another flame retardant, EG was also added to the system. Notably, the synergistic effect between the phosphorus-containing soybean-oil-based polyol and EG provides excellent char yield during burning. The char yield percentage is one of the decisive factors regarding the flame retardancy of a material. The increase in char residue provided a protective layer for the underlying unburned FPUF, thereby significantly improve the flame retardancy. The main mechanism behind is that the phosphorus-containing soybean-oil-based polyol acts as a gluing agent to bind and strengthen the loose expanded graphite. Therefore, the structural integrity is maintained. Even if only 20 wt.% of polyether polyol was replaced by phosphorus-containing soybean-oil-based polyol and additional 10 wt.% of EG in FPUF, the char residue was twice than that of the sample with only 10 wt.% of EG. For the sample containing 80 wt.% of phosphorus-containing soybean-oil-based polyol and an additional 10 wt.% of EG, the char residue was 3.6 times higher than the sample with only 10 wt.% of EG. In addition to flame retardancy, EG also significantly reduced the smoke emission, as shown by the result from cone calorimeter and smoke density chamber.

In Paper 5, several flame retardants and additives were used in FPUF. The results showed the combination of P-FR and EG was the most effective system in flame retardancy among different flame retardant combinations. The synergistic effect between P-FR and EG in FPUF created a superior thermal barrier resulting in high char yield after burning in cone calorimeter measurement due to incomplete pyrolysis. EG acted as a smoke suppressant and reduced the amount of toxic gases (CO and HCN) released. The presence of castor oil (CAS) enhanced the bio-based content and maintain the physical and mechanical properties of FPUF.

Paper 6 presents a scientific analysis of fire performance and smoke behavior on three industrial P-EG PUFs. These materials show extremely low heat release rate and smoke emission which means less fire hazard. Since the value of MARHE is less than 90 kW m^{-2} or even lower, they meet the requirement of EN 45545. The high char yield of expanded graphite was used as a protective layer to shield the underlying material from heat, resulting in insufficient pyrolysis temperature and eventually incomplete burning. The combination of P-FR and EG was proved to be the state-of-the-art in PUF flame retardant systems for various applications such as damping, construction and lightweight structure.

The main highlight from a series of scientific works is the synergistic effect between P-FR and EG in FPUF. Therefore, a comprehensive study on the combination of EG and P-FRs in PUFs is presented in Paper 7. The feature article first introduces the general fire hazard of PUFs, the difference between FPUF and RPUF, the difference between polyisocyanurates foam and PUF, the flammability and smoke toxicity during burning of PUFs, and the commercial flame retardants for PUFs. The burning process of FPUF and RPUF is described in detail with texts and diagrams. FPUF and RPUF behave differently during burning due to crosslink density, apparent density, and cellular structure. The char formed due to the high crosslinking density of RPUF provides protection for the underlying material. However, due to the low crosslink density of FPUF collapses easily into pool fire and burns fiercely with almost none of the residue remained after burning. Therefore, the RPUF has better flame retardancy than FPUF. Polyol and diisocyanate are the main components for polyurethane synthesis. The crosslink density depends on the chemical properties and the amount of polyol and diisocyanate in PUFs. PUFs with EG and P-FR were discussed individually in terms of burning behavior. The burning behavior of PUF with the combination of EG and P-FR was discussed in depth. The combination of PUF with EG and phosphorous compounds has such excellent flame retardancy because the phosphorous compounds turn into glassy polyphosphates that act as binder to maintain the integrity of the carbonaceous char. Moreover, the phosphorus functions as a bridge to bind the aromatic char into a larger molecule. As a result, this enhanced carbonaceous char provides better protection for the material underneath and less mass and heat is transferred. Furthermore, current and future topics regarding green solution for flame retardants and PUFs were discussed. However, there are still some challenges to be overcome regarding the recycling of flame-retardant PUF, as well as the potential health concerns of P-FRs.

4 Publications

4.1 Effects of novel phosphorus-nitrogen-containing DOPO derivative salts on mechanical properties, thermal stability and flame retardancy of flexible polyurethane foam

Shicong Ma, Yuling Xiao, Feng Zhou, Bernhard Schartel, Yin Yam Chan, Oleg P. Korobeinichev, Stanislav A. Trubachev, Weizhao Hu, Chao Ma and Yuan Hu. *Polym Degrad Stabil.* **2020**, 177. Doi: 10.1016/j.polymdegradstab.2020.109160.

Status: This article was accepted and published.

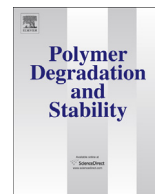
<https://doi.org/10.1016/j.polymdegradstab.2020.109160>

Authors' contributions:

- Shicong Ma
 - Formal analysis
 - Conceptualization
 - Writing – Original draft
- Yuling Xiao
 - Software
 - Validation
- Feng Zhou
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- Bernhard Schartel
 - Methodology
- Yin Yam Chan
 - Investigation
- Oleg P. Korobeinichev
 - Data curation
- Stanislav A. Trubachev
 - Supervision
- Weizhao Hu
 - Resources
- Chao Ma
 - Visualization
 - Writing – review & editing
- Yuan Hu
 - Supervision

Abstract

In this work, a series of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivative salts containing phosphorus and nitrogen were synthesized, and their effects on mechanical properties, thermal stability and flame retardancy of flexible polyurethane foam (FPUF) were investigated. Studies have shown that the addition of DOPO derivatives will increase the tensile strength, compression set, and compression hardness of FPUF, but it will lead to a decrease in elongation at break. Thermogravimetric analysis showed that the initial decomposition temperature of FPUF containing DOPO derivatives was reduced, but the char residue was significantly improved. A series of combustion tests indicated that the addition of DOPO derivative salts can improve the flame retardancy of FPUF, of which 10-hydroxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide dicyandiamide salt (D-DICY) exhibited the best flame retardancy. When the load of D-DICY was 20 phr, the limiting oxygen index (LOI) of foam reached 24.5%, and the peak heat release rate and total heat release were decreased by 55.7% and 52.9%, respectively. Furthermore, based on the analysis of the gas phase combustion products and the char residue of the condensed phase, the possible flame retardant mechanism was proposed.



Effects of novel phosphorus-nitrogen-containing DOPO derivative salts on mechanical properties, thermal stability and flame retardancy of flexible polyurethane foam

Shicong Ma^a, Yuling Xiao^a, Feng Zhou^a, Bernhard Schartel^b, Yin Yam Chan^b, Oleg P. Korobeinichev^c, Stanislav A. Trubachev^{c,d}, Weizhao Hu^a, Chao Ma^{a,*}, Yuan Hu^{a,**}

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ARTICLE INFO

Article history:

Received 8 February 2020

Received in revised form

28 March 2020

Accepted 29 March 2020

Available online 3 April 2020

Keywords:

Flexible polyurethane foam

DOPO derivative salts

Mechanical properties

Thermal stability

Flame retardancy

ABSTRACT

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1. Introduction

Flexible polyurethane foam (FPUF) is one of the most important components of polyurethane materials, accounting for about 40% of its market share [1,2]. Based on its low density, high resilience, excellent gas permeability and low thermal conductivity, FPUF is widely used in bedding, shoes, architectural decoration, textile industry and other fields [3]. However, FPUF is highly flammable, and its limiting oxygen index is only 16–18% [4]. The large surface area and good permeability of foam will accelerate the spread of fire during combustion, which greatly limits its application [5]. Therefore, it is important to find or synthesize a suitable flame retardant

to impart flame retardancy to FPUF.

At present, the commonly used FPUF flame retardants can be divided into two types: additive and reactive flame retardants. The former mainly includes triethyl phosphate, dimethyl methyl phosphate (DMMP), tris(2-chloroisopropyl) phosphate ester (TCPP), trichloroethyl phosphate (TCEP), melamine, expandable graphite, and aluminum hydroxide [6,7]. The latter mainly includes flame retardant polyols and flame retardant isocyanates [8]. The additive flame retardants are introduced into the foam through simple physical and mechanical mixing, which has little effect on the foaming formula and exhibit good flame retardancy under low load. Therefore, they are widely used in FPUF [9]. At present, the most widely used FPUF flame retardants are halogen-based flame retardants, which have high thermal stability, low price, and have little effect on the mechanical properties of foam [10]. However, halogen-based flame retardants have many disadvantages that

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cannot be ignored. First, they will produce a large amount of smoke and corrosive hydrogen halide gas during combustion. Second, halogen-based flame retardants may generate extractable organic halides (EOX), polybrominated dibenzodioxins (PBDD) and polybrominated dibenzofurans (PBDF). Among them, EOX is an environmentally persistent organic compound, which is lipophilic, hydrophobic, and difficult to degrade. And PBDD and PBDF are easy to accumulate in the human body and damage the human immune and regeneration system [11]. Therefore, the use of halogen-free flame retardants has become the future development trend [12].

In the field of halogen-free flame retardants, compounds containing single flame retardant element are increasingly unable to meet application requirements, hence, the development of flame retardants is increasingly focused on the synergy of multiple flame retardant elements. Among them, phosphorus-nitrogen synergistic flame retardants have become one of the main research directions [13]. Generally, they have the advantages of heat insulation, low toxicity, low smoke generation and low corrosion [14]. Liang et al. synthesized a series of organic phosphorus compounds and studied the flame retardancy of different compounds on FPUF. The results showed that the synthesized phosphoramidates exhibited higher flame retardancy than the corresponding phosphates [5]. Chen et al. synthesized a series of phosphorus-containing melamine salts and applied to FPUF. Among them, 2-carboxyethyl(phenyl)phosphinic acid melamine salt (CMA) showed the best flame retardancy. When its load was 20 phr, the LOI of the foam reached 23.5% [15]. Rao et al. prepared a melamine salt with high flame retardancy from diphenylphosphinic acid (DPPA) and melamine (MA). When its addition amount was 20 phr, the LOI of FPUF increased to 24.5% [16]. However, the 2-carboxyethyl (phenyl) phosphinic acid and the diphenylphosphinic acid mentioned above have certain limitations in practical applications, mainly due to the relatively expensive price and less supply in industry. In comparison, as a commonly used and industrialized phosphorus-containing flame retardant, DOPO has great advantages in practical applications [17]. There are some researches on the use of DOPO and its derivatives to flame retard FPUF [18,19]. Przystas et al. evaluated the flame retardancy of several bridged DOPO on FPUF. When the addition amount of them was 7.5%, the horizontal combustion test level of FPUF was HF-1. In contrast, the horizontal combustion level of FPUF containing conventional flame retardants TCP and TCEP was HF-2 [20]. Sabyasachi et al. investigated the flame retardancy of novel DOPO phosphoramidate to FPUF. When its load was 10 phr, the horizontal combustion test level of FPUF can reach HF-1 [21].

In this work, DOPO was first oxidized to 10-hydroxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-OH), then DOPO-OH was reacted with nitrogen-containing compounds (melamine, dicyandiamide, and urea) through a hydrothermal reaction to synthesize a series of phosphorus-nitrogen-containing DOPO derivative salts and apply it to FPUF. Their effects on the structure, mechanical properties, thermal stability, and flame retardancy of FPUF was evaluated. By analyzing the products in the gas phase and the condensed phase, the flame retardant mechanism is explained.

2. Experimental

2.1. Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was provided by Shandong Mingshan Fine Chemical Industry Co. Ltd (Shandong, China). Melamine, dicyandiamide, urea and dibutyltin dilaurate (DBTDL) were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ethanol and hydrogen peroxide were supplied by Aladdin Holdings Group Ltd. Polyether

polyol 330, triethylenediamine (A33, 33%), silicone surfactant and toluene diisocyanate (TDI 80/20) were supplied by Jiangsu Lvyuan New Material Co., Ltd., China. Distilled water was obtained from our laboratory.

2.2. Synthesis of DOPO derivatives

DOPO-OH was synthesized according to reference [22]. 108 g (0.5 mol) of DOPO was added to a three-necked flask, and then 100 mL of 30% hydrogen peroxide solution was slowly dropped into the three-necked flask at 60 °C. After the addition was completed, the temperature was raised to 80 °C and the reaction was continued for 8 h. The product was filtered and washed 3 times with acetone, and dried in a vacuum oven at 80 °C for 24 h.

The synthesis method of DOPO derivative salts was similar. Herein, the reaction between DOPO-OH and dicyandiamide was taken as an example. 58 g (0.25 mol) of DOPO-OH and 300 mL of mixed solvent of water and ethanol (1: 1 by volume) were added to a three-necked flask. After DOPO-OH was completely dissolved, 21 g (0.25 mol) of dicyandiamide was added in portions at room temperature. Then the reaction was continued for 6 h. Finally, the mixture was evaporated under reduced pressure and the obtained product was dried in a vacuum oven at 70 °C for 24 h. The obtained DOPO derivative salts were all white solid powders. The yields of D-Mel, D-DICY, and D-Urea were 92.7%, 85.1%, and 81.5%, respectively.

The abbreviations of the salts produced by the reaction of DOPO-OH with melamine, dicyandiamide, and urea are D-Mel, D-DICY, and D-Urea respectively. The chemical structure of the DOPO derivative salts are shown in Fig. 1.

2.3. Preparation of FPUF

The pure and DOPO derivatives-containing FPUF were prepared by the one-pot and free-rise method. Briefly, polyol 330, distilled water, catalyst (DABCO and DBTDL), silicone oil and flame retardant were added into a 1 L plastic cup and thoroughly mixed by mechanical stirring. TDI 80/20 was then added to the plastic cup with vigorous agitation for 6s, and the mixture was immediately poured into an open plastic mold to create a free foaming foam. The foam was heated at 80 °C for 24 h. The NCO/OH ratio is 1.05 and the formulation of FPUF is shown in Table 1. The abbreviations of the three DOPO derivatives-containing FPUF are FPUF/D-D, FPUF/D-M, and FPUF/D-U.

2.4. Measurements

Fourier transform infrared spectra (FTIR) was measured on a Nicolet 6700 spectrometer (Nicolet Instrument Company, U.S.) in a wavenumber range of 4000 to 500 cm^{-1} using KBr disk method.

Nuclear magnetic resonance (NMR) spectra was recorded on a Bruker AV400 NMR spectrometer (400 MHz) using deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) as the solvent.

The density of FPUF was tested according to the standard of ISO 845:2006. The sample was left more than 72 h before testing and the volume of sample was larger than 100 cm^3 .

Thermogravimetric analysis (TGA) was performed using a Q5000 thermal analyzer (TA Co., U.S.). The test conditions were a rise from room temperature to 800 °C at an increase rate of 20 °C/min under nitrogen atmosphere.

The limiting oxygen index (LOI) was tested in accordance with ISO 4589-1:1996 and tested on an HC-2 oxygen index meter (Jiang Ning Analytical Instrument Company, China). The size of the test sample was $130 \times 10 \times 10 \text{ mm}^3$.

Vertical combustion test was performed on a CFZ-2 instrument (China Jiangning Analytical Instrument Co., Ltd.) according to

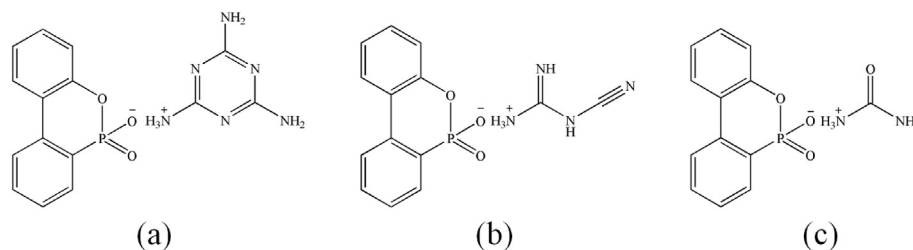


Fig. 1. The chemical structure of D-Mel (a), D-DICY (b) and D-Urea (c).

Table 1

Formulations of pure FPUF and DOPO derivatives-containing FPUF.

Sample	polyol 330 (php)	Flame retardants (php)	H ₂ O (php)	DABCO (php)\	DBTDL (php)	SZ580 (php)	TDI (80/20) (php)
Pure FPUF	100	0	3	0.6	0.10	0.5	41
FPUF/D-M-10	100	10	3	0.6	0.10	0.5	41
FPUF/D-M-20	100	20	3	0.7	0.12	0.6	41
FPUF/D-D-10	100	10	3	0.9	0.12	0.6	41
FPUF/D-D-20	100	20	3	1.2	0.15	0.7	41
FPUF/D-U-10	100	10	3	1.2	0.13	0.6	41
FPUF/D-U-20	100	20	3	1.5	0.16	0.7	41

California Technical Bulletin 117 (TB 117–2000). The size of the test sample was $12 \times 3 \times 0.5$ inch³.

Cone calorimetry test was performed on a fire-resistant test technical equipment according to ISO 5660-1 standard under an external heat flux of 25 kW/m². The sample size was $100 \times 100 \times 25$ mm³.

Scanning electron microscope (SEM) images of the samples were taken on a FEI Sirion 200 scanning electron microscope under high vacuum conditions with an acceleration voltage of 10 kV.

Tensile properties was performed according to ISO 1798: 2008, and the tensile speed was 500mm/min⁻¹. The width and thickness of the sample were 10 mm, and the gauge length was 40 mm.

Compression set test was performed according to ISO 1856: 2000. The foam was compressed between two metal plates to 50% of its original thickness and left at 70 °C for 22 h. The size of the test sample was $50 \times 50 \times 25$ mm³. 25% of compression hardness was measured in accordance with ISO 2439: 1997.

The Nicolet 6700 FTIR spectrometer was combined with a TGA Q5000IR thermogravimetric analyzer to characterize the thermogravimetric analyzer-Fourier transform infrared spectrum (TG-IR). Under nitrogen atmosphere, the heating rate was 20 °C/min⁻¹ and the flow rate was 30mL/min⁻¹.

Laser Raman spectroscopy (LRS) measurement was performed on a SPEX-1403 laser Raman spectrometer (SPEX Co., United States) at room temperature. Wave numbers range from 2000 to 500 cm⁻¹.

3. Results and discussion

3.1. Characterization of DOPO derivatives

The chemical structure of the synthesized DOPO derivatives was characterized by FTIR and NMR. The FTIR spectrum of DOPO and its derivatives are shown in Fig. 2 and the corresponding NMR spectrum is shown in Fig. 3. In the FTIR spectrum of DOPO (Fig. 2a), the absorption peak at 1450–1650 cm⁻¹ corresponds to the skeletal vibration of the benzene ring, and the peak at 2385 cm⁻¹ is attributed to the stretching vibration of the P–H bond [23]. It can be seen from the spectrum of DOPO-OH (Fig. 2a) that the characteristic peak of the P–H bond disappears while the characteristic peak of P–OH bond appears at 927 cm⁻¹, indicating that DOPO is oxidized to DOPO-OH [24]. From the FTIR spectrum of D-Mel (Fig. 2b), the

absorption peak at 3389 cm⁻¹ is attributed to the asymmetrical stretching vibration of –NH₂ [25]. The stretching vibration of C=N in triazine ring is observed at 1660 cm⁻¹. The characteristic peak at 893 cm⁻¹ corresponds to the deformation vibration of triazine ring [26]. The spectrum of D-DICY shows absorption peaks at 2209/2160 cm⁻¹ and 1638 cm⁻¹, which are related to the tensile vibration of the C≡N and C=N bonds [27]. The adsorption peaks of D-Urea at 3440 cm⁻¹ and 3342 cm⁻¹ are attributed to the antisymmetric and symmetrical tensile vibration of –NH₂ group [28]. The combined absorption peak at 1610 cm⁻¹ is attributed to the tensile vibration of C=O bond and the bending vibration of –NH₂ group [29]. The ¹H NMR (Fig. 3a) and ³¹P NMR (Fig. 3b) spectrum of DOPO and DOPO-OH are shown in Fig. 3. Chemical shifts from 7.36 to 8.26 ppm represent the resonance of phenyl groups [30]. The disappearance of hydrogen on the P–H bond (8.89 ppm and 6.50 ppm) and the appearance of hydrogen on the –OH bond (11.42 ppm) indicate that DOPO has been oxidized to DOPO-OH. In addition, the change in the chemical shift of the single peak of phosphorus also confirms that DOPO has reacted [22]. The ¹H NMR (Fig. 4a and b and c) and ³¹P NMR spectra (Fig. 4d and e and f) of DOPO derivative salts are displayed in Fig. 4. It can be seen that the chemical shift of hydrogen on the P–OH bond does not appear in the spectrum of the DOPO derivative salts, and the chemical shift of phosphorus has shifted. The above results prove that P–OH has reacted with amine groups.

3.2. Morphology and mechanical properties of FPUF

In order to study the influence of DOPO derivative salts on the structure of FPUF, the surface morphology of FPUF was characterized by SEM. It can be seen that the surface of pure FPUF is smooth (Fig. 5e), while the agglomeration can be observed from the images of DOPO derivatives-containing FPUF (Fig. 5f, g and h). From Fig. 5a, b, c and d, the foam size of the FPUF modified by the DOPO derivative is almost the same as the pure FPUF, which indicates that the structure of the FPUF is maintained after the addition of DOPO derivative salts.

The tensile and compressive properties of pure FPUF and DOPO derivative-added FPUF were tested to evaluate the effects of additives on the mechanical properties of the foam. The relevant data are listed in Table 2 and the stress-strain curve of FPUF is displayed in Fig. 6. Compared with pure FPUF, the tensile strength, 50%

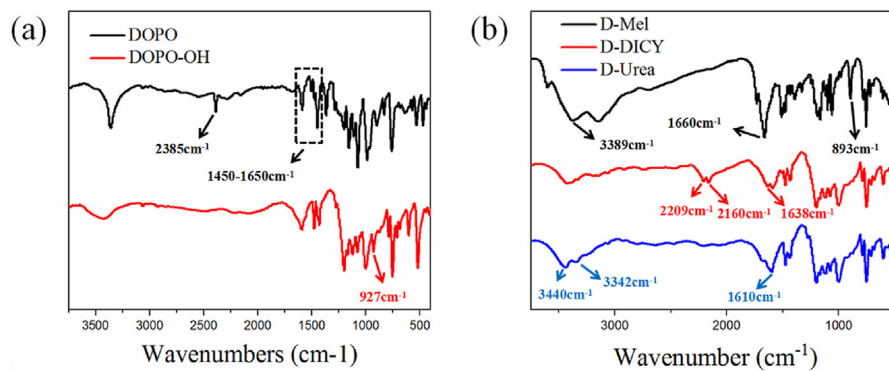


Fig. 2. FTIR spectrum of DOPO and DOPO-OH (a), D-Mel, D-DICY and D-Urea (b).

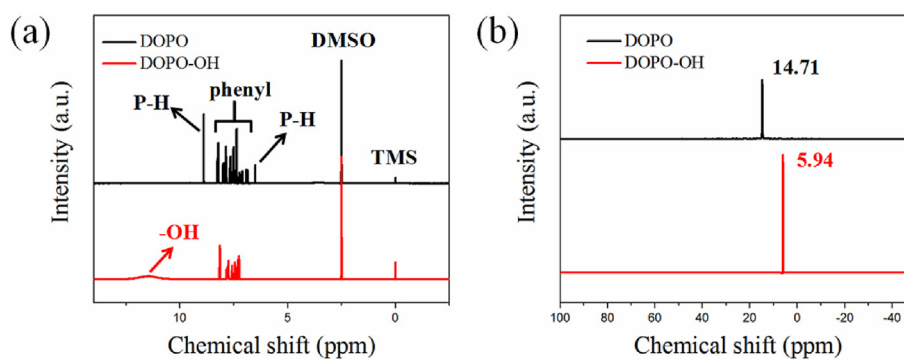


Fig. 3. ¹H (a) and ³¹P (b) NMR spectrum of DOPO and DOPO-OH.

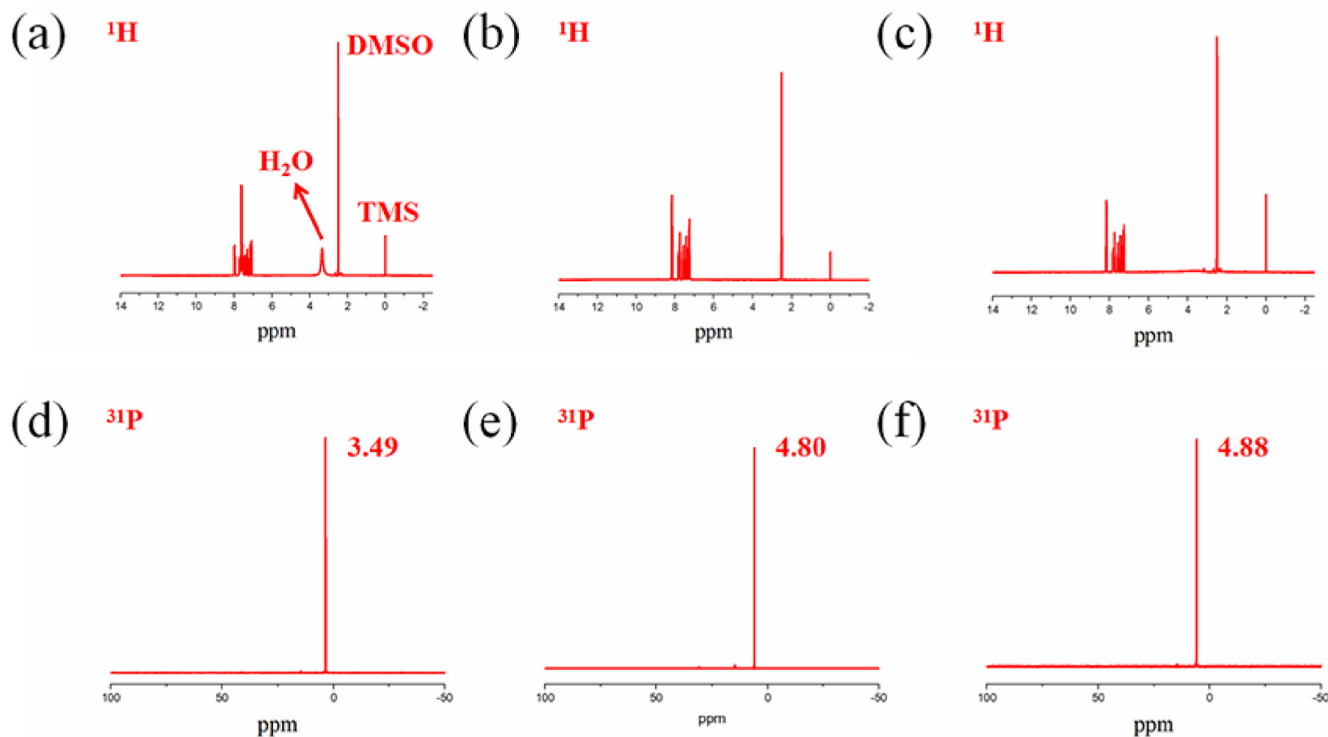


Fig. 4. ¹H and ³¹P NMR spectrum of D-Mel (a and d), D-DICY (b and e) and D-Urea (c and f).

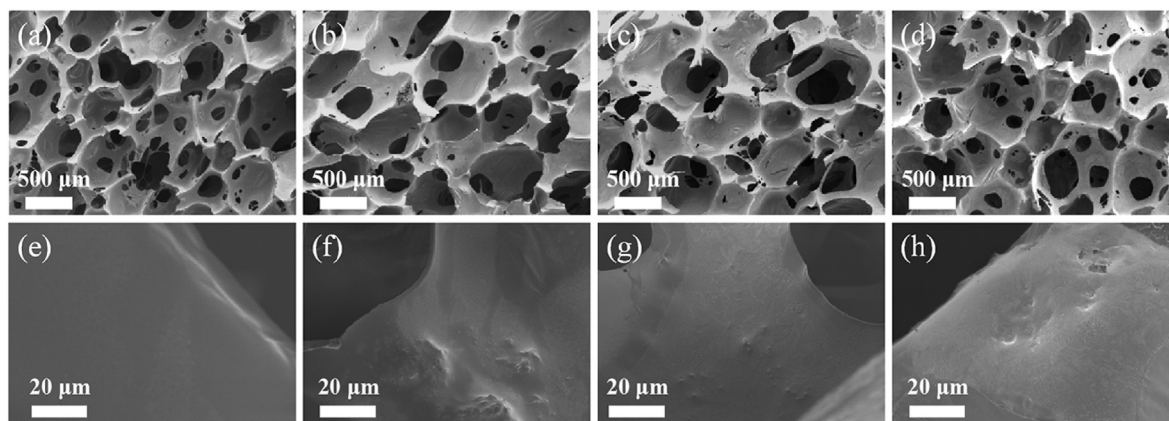


Fig. 5. SEM images of pure FPUF (a and e), FPUF/D-M-20 (b and f), FPUF/D-D-20 (c and g), FPUF/D-U-20 (d and h).

compression set and 25% compression hardness of FPUF modified by DOPO derivative salts are improved, and the elongation at break is reduced. The reasons for the above results can be summarized as follows. DOPO derivative salts dispersed in FPUF can act as reinforcing particles to improve the strength of the matrix and hinder the movement of the polyurethane molecular chain, thus improving the tensile strength, compression set and compression hardness of FPUF [31]. However, the DOPO derivative salts in the polyurethane matrix will cause agglomeration due to the problem of dispersibility, which will cause the foam to break more easily during the stretching process. Therefore, the elongation at break of the foam decreases [32]. The density of FPUF is also showed in Table 3. It can be observed that the addition of DOPO derivatives will increase the density of FPUF. This is because when the additives are mixed into the FPUF, the quality of the foam is increased without affecting the volume of the foam, thereby increasing the density of the foam [21].

3.3. Thermal stability of the DOPO derivatives and FPUF

TGA and DTG curves of DOPO and its derivatives are shown in Fig. 7a and the relevant characteristic data are listed in Table 3. It can be seen that the initial decomposition temperature (T_i) of the DOPO derivative salts are all higher than 270 °C, showing good thermal stability. And the char residue is also significantly improved compared to DOPO. Because the thermal decomposition temperature of nitrogen-containing substances in DOPO derivative salts is low, their maximum decomposition rate temperature (T_{max}) is slightly lower than that of DOPO-OH [33]. The TGA and DTG curves of pure FPUF and FPUF with DOPO derivatives are shown in Fig. 7b and the corresponding data are listed in Table 4. All curves present typical two-step decomposition process. The first maximum mass loss occurs at 220–280 °C, which is due to the degradation of hard segments. The second stage of maximum mass

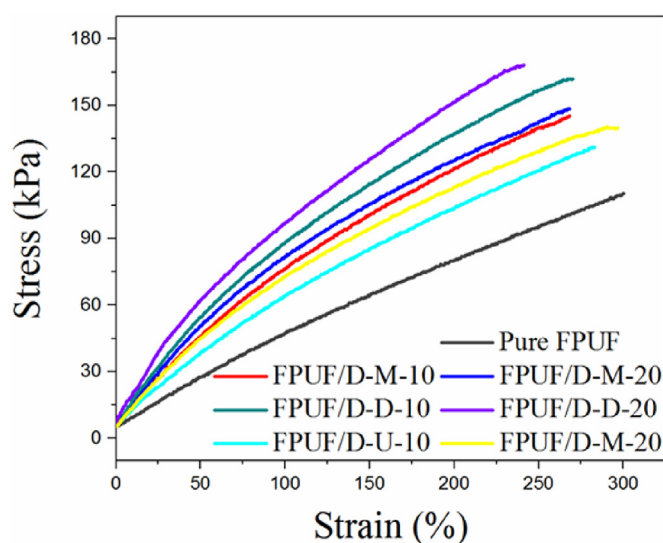


Fig. 6. Stress-strain curves of pure FPUF and DOPO derivatives-containing FPUF.

loss appears at 360–420 °C, which corresponds to the thermal decomposition of soft segments [34]. The results show that the T_i of FPUF modified by DOPO derivative salts is slightly lower than that of pure FPUF, which is due to the premature decomposition of the additives [35]. Furthermore, the introduction of additives can increase the char residue of FPUF. This is mainly because the phosphoric acid, polyphosphoric acid, etc. generated by DOPO derivative salts will cover the surface of the FPUF [36]. These foam-covering compounds reduce the rate of thermal decomposition of the carbon skeleton and suppress the release of volatile gases. In addition, it can also provide additional covalent bonds to catalytic the cross-linking of the skeleton to form a carbon layer network [37]. In

Table 2

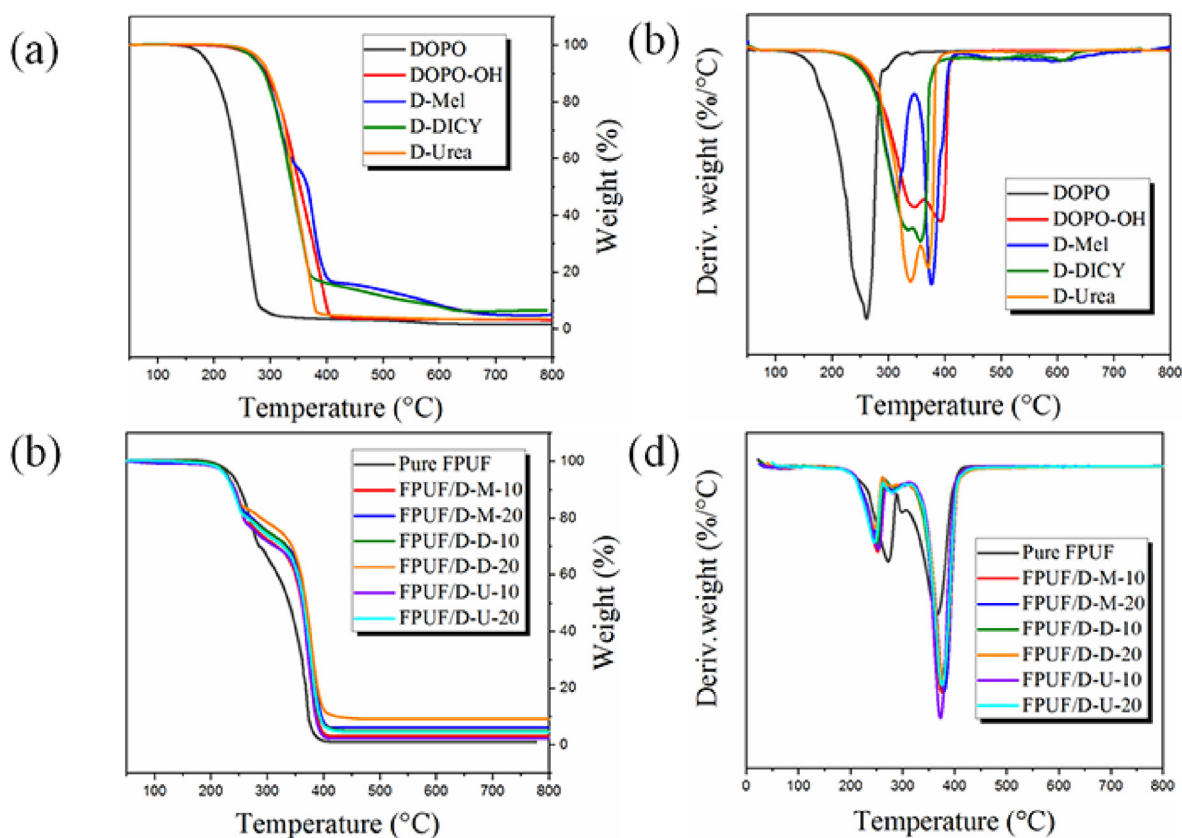
Mechanical properties and density of pure FPUF and DOPO derivatives-containing FPUF.

Sample	Tensile strength (kPa)	Elongation break (%)	50% compression set (%)	25% compression hardness (N)	Density (kg/m ³)
Pure FPUF	110 ± 8	300 ± 13	6.0 ± 0.19	95 ± 3	32 ± 1
FPUF/D-M-10	142 ± 6	258 ± 8	7.5 ± 0.25	127 ± 6	35 ± 1
FPUF/D-M-20	148 ± 8	267 ± 10	7.9 ± 0.31	136 ± 4	39 ± 2
FPUF/D-D-10	162 ± 4	251 ± 12	7.4 ± 0.15	126 ± 6	35 ± 1
FPUF/D-D-20	168 ± 5	260 ± 9	8.0 ± 0.20	141 ± 5	38 ± 1
FPUF/D-U-10	131 ± 5	282 ± 14	6.9 ± 0.27	115 ± 7	36 ± 2
FPUF/D-U-20	140 ± 8	295 ± 13	7.3 ± 0.08	120 ± 6	39 ± 1

Table 3

The characteristic TGA data of DOPO and its derivatives.

Sample	T _i (°C)	T _{max} (°C)	Char residue at T _{max} (%)	Char residue at 800 °C (%)
DOPO	186	261	31	2
DOPO-OH	274	391	23	3
D-Mel	273	374	38	5
D-DICY	274	357	38	7
D-Urea	272	350	40	4

T_i: Temperature at which the material decomposes to 5%.T_{max}: Temperature at maximum decomposition rate.**Fig. 7.** TGA and DTG curves of DOPO and its derivatives (a and b), pure FPUF and DOPO derivatives-containing FPUF (c and d).**Table 4**

The characteristic TGA data of pure FPUF and DOPO derivatives-containing FPUF.

Sample	T _i (°C)	T _{max} (°C)	Char residue at T _{max} (%)	Char residue at 800 °C (%)
Pure FPUF	238	365	24	1
FPUF/D-M-10	228	375	29	3
FPUF/D-M-20	228	380	31	6
FPUF/D-D-10	229	375	32	5
FPUF/D-D-20	228	378	36	9
FPUF/D-U-10	227	374	29	2
FPUF/D-U-20	226	376	33	5

summary, the addition of DOPO derivatives has little effect on the thermal decomposition temperature of FPUF and it can promote the formation of char residue.

3.4. Flame retardancy of FPUF

The LOI of the samples was tested by limiting oxygen index meter and the results are listed in Table 5. It can be seen that the LOI

of FPUF increases as the load of additives increase. Among them, D-DICY has the best flame retardancy. When the addition amount is 20phr, the LOI of FPUF reaches 24.5%. The vertical burning test is an important indicator for evaluating the flame retardancy of polymers. In this work, vertical burning test was carried out in accordance with the TB 117–2000 standard [38]. The digital photos of the vertical burning test of FPUF are shown in Fig. 8 and the relevant data are listed in Table 5. Pure FPUF burns quickly after ignition and

Table 5

The vertical burning and LOI test results of pure FPUF and DOPO derivatives-containing FPUF.

Sample	Pass/No (TB117-2000)	LOI (%)
Pure FPUF	No	17.5
FPUF/D-M-10	Pass	23.5
FPUF/D-M-20	Pass	24.0
FPUF/D-D-10	Pass	24.0
FPUF/D-D-20	Pass	24.5
FPUF/D-U-10	Pass	23.0
FPUF/D-U-20	Pass	23.5

the fire spreads rapidly. At the same time, the dripping of melt is very obvious. After the addition of the DOPO derivatives, the combustion of FPUF is suppressed and no flame spread, and the dripping phenomenon is significantly reduced. It is worth noting that all of the DOPO derivatives-containing FPUF can pass the vertical combustion test.

Cone calorimetry (CC) is a widely used method for investigating the combustion behavior of materials. In this work, the combustion performance of the samples was quantitatively analyzed by studying parameters such as time to ignition (TTI), peak heat release rate (pHRR), total heat release (THR), total smoke production (TSP) and average effective heat of combustion (Av-EHC) [39]. The HRR and THR curves of FPUF are shown in Fig. 9 and the corresponding data are listed in Table 6. The ignition time of pure FPUF is only about 2s,

the combustion is rapid and a large amount of heat is released after ignition. Its pHRR and THR values are 317.5 kW/m² and 24.2 MJ/m², respectively. With the addition of the DOPO derivatives, the TTI of FPUF is extended to more than 6s and the heat release is significantly reduced. The above results indicate that D-DICY has the best flame retardancy under the same load. When the addition amount of D-DICY was 20 phr, the pHRR and THR of FPUF decreased by 55.7% and 52.9%, respectively. However, the introduction of DOPO derivatives will increase the TSP of FPUF. This is due to the increase in the density of FPUF. On the other hand, this is also related to the decomposition of DOPO derivatives, which will release gas-phase products to play a flame retardant effect. Furthermore, the Av-EHC and the burn rate index (FIGRA) of FPUF have also been reduced. Av-EHC reflects the combustion degree of volatile gases, and a decrease in Av-EHC value indicates that the additives have gas phase flame retardant effect [40]. FIGRA is a derived parameter equal to the maximum value of HRR/time, reflecting the maximum combustion effect of the material as it burns [41]. This value decreased by 64.3% when 20 phr D-DICY was incorporated into FPUF. In summary, CC results show that the addition of DOPO derivatives can improve the flame retardancy of FPUF.

3.5. Flame retardant mechanism

The gaseous products of pure FPUF and DOPO derivatives-containing FPUF at the maximum decomposition rate were

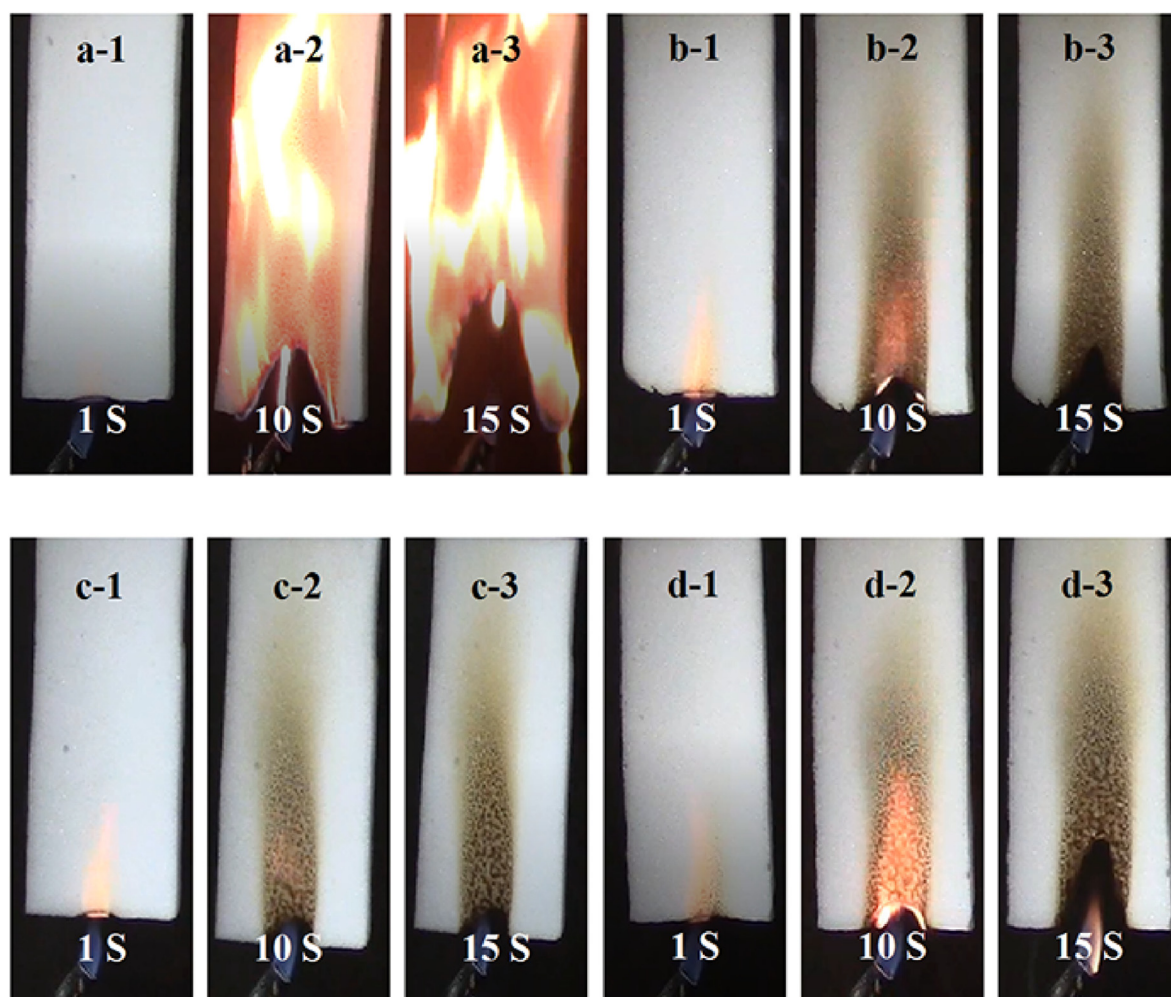


Fig. 8. Digital images of pure FPUF (a), FPUF/D-M-20 (b), FPUF/D-D-20 (c), FPUF/D-U-20 (d) during vertical burning.

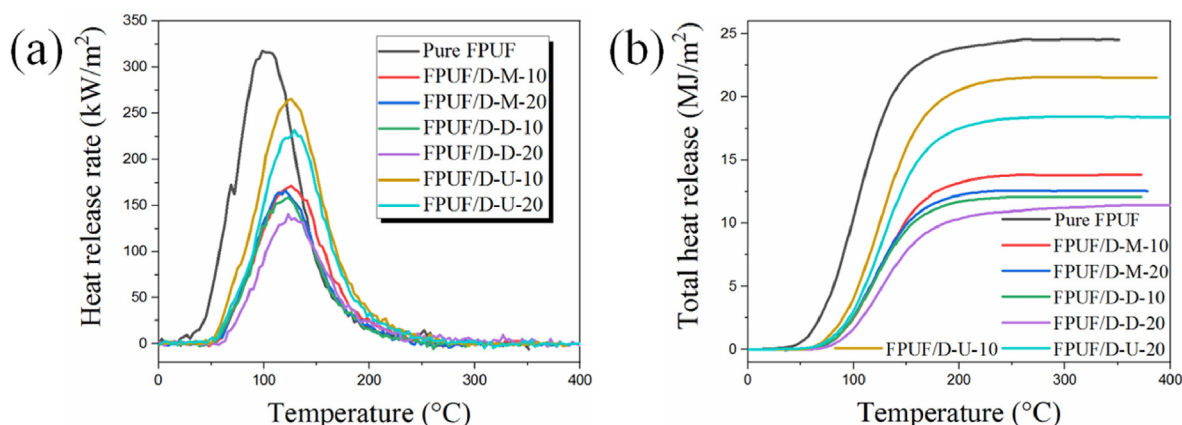


Fig. 9. HRR (a) and THR (b) curves of pure FPUF and DOPO derivatives-containing FPUF.

Table 6

Cone calorimetry data of pure FPUF and DOPO derivatives-containing FPUF.

Sample	TTI (s)	pHRR (kW/m ²)	THR (MJ/m ²)	TSP (m ²)	Av-EHC (MJ/kg)	FIGRA	Char residue (%)
Pure FPUF	2 ± 1	318 ± 17	24.2 ± 2.1	1.58 ± 0.10	24 ± 3	3.20 ± 0.13	2 ± 1
FPUF/D-M-10	6 ± 1	171 ± 10	13.8 ± 1.5	4.57 ± 0.14	11 ± 1	1.36 ± 0.08	6 ± 1
FPUF/D-M-20	7 ± 1	166 ± 8	12.5 ± 0.8	5.30 ± 0.25	12 ± 2	1.32 ± 0.05	9 ± 1
FPUF/D-D-10	7 ± 1	159 ± 13	12.1 ± 1.1	4.31 ± 0.18	10 ± 2	1.29 ± 0.03	7 ± 1
FPUF/D-D-20	7 ± 1	141 ± 9	11.4 ± 0.6	4.91 ± 0.13	9 ± 1	1.14 ± 0.06	10 ± 1
FPUF/D-U-10	6 ± 1	265 ± 14	21.5 ± 1.9	4.80 ± 0.14	18 ± 3	2.10 ± 0.04	4 ± 1
FPUF/D-U-20	6 ± 1	232 ± 11	18.4 ± 1.4	5.46 ± 0.31	16 ± 2	1.84 ± 0.11	7 ± 1

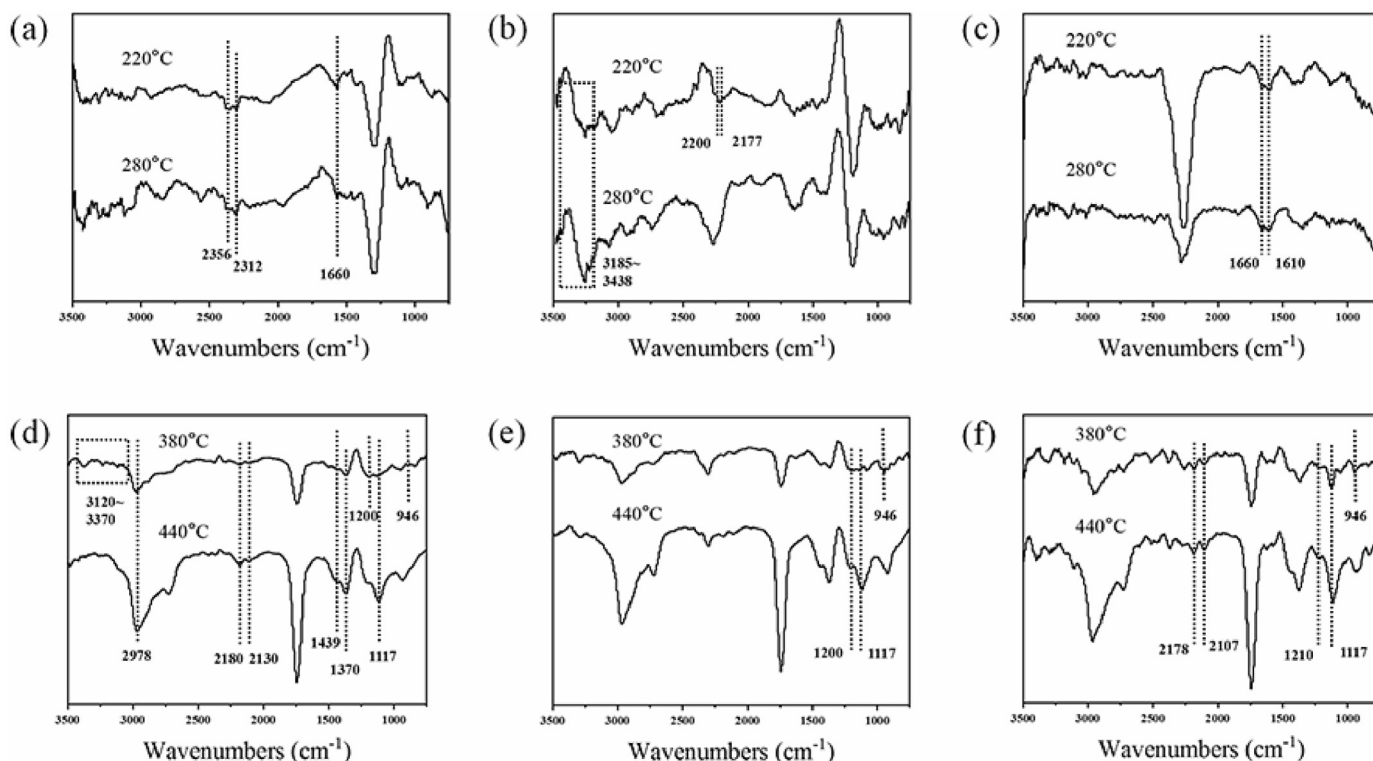


Fig. 10. FT-IR spectra at maximum weight loss rate of FPUF/D-M-20 (a and d), FPUF/D-D-20 (b and e), FPUF/D-U-20 (c and f).

analyzed by TG-IR. The FTIR spectrum of the volatile pyrolysis products of FPUF/D-M-20 at different temperature are shown in Fig. 10a and d. At 220 °C, the peak at 3387 cm⁻¹ is attributed to the asymmetrical stretching vibration of -NH₂ group. The absorption

peaks at 2356 and 2312 cm⁻¹ are due to the stretching vibration of CO₂. The peak at 1660 cm⁻¹ is attributed to the stretching vibration of C=N bond [25,26]. When the temperature reached 280 °C, no obvious new absorption peaks appeared. When the temperature

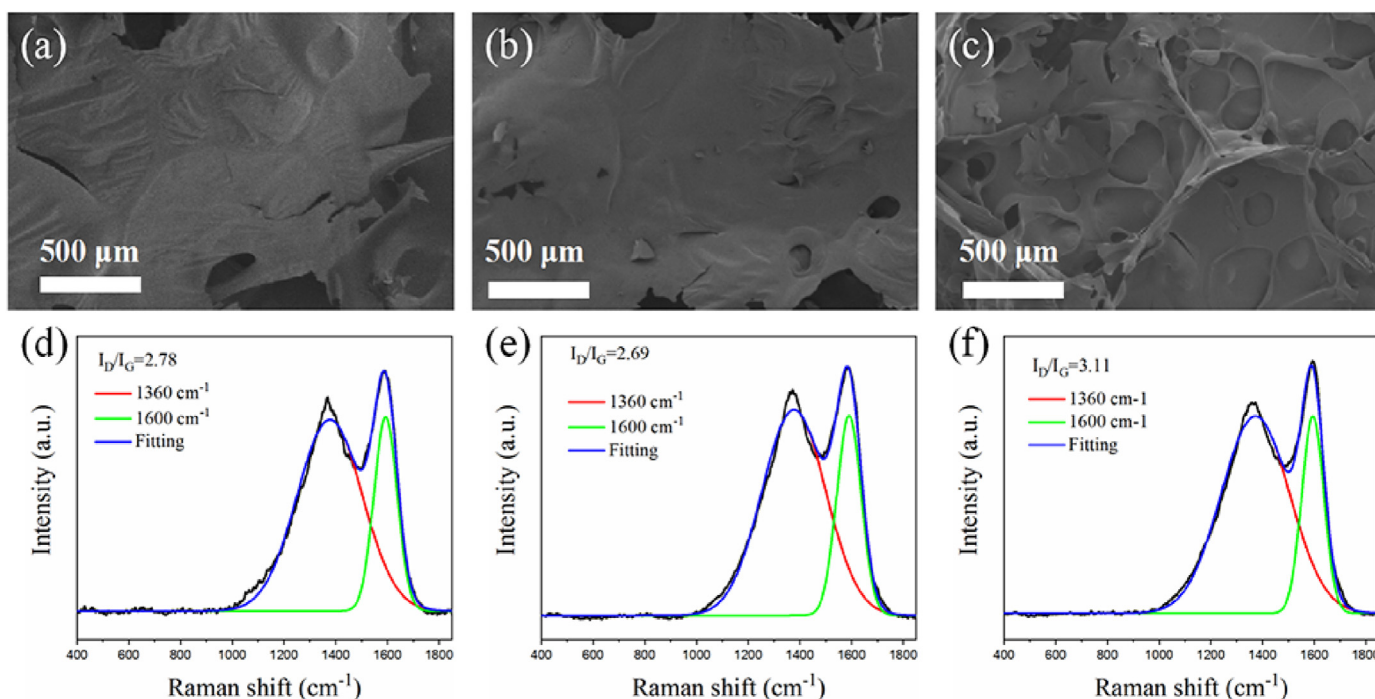


Fig. 11. The surface SEM images and Raman spectra of the char residues of FPUF/D-M-20 (a and d), FPUF/D-D-20 (b and e), FPUF/D-U-20 (c and f).

increased to 380 °C, the characteristic absorption peaks of -N-H group ($3120\text{--}3370\text{ cm}^{-1}$) and benzene (2978 and 1370 cm^{-1}) can be observed. The absorption peaks at 2180 and 2130 cm^{-1} are attributed to the stretching vibration of $\text{C}\equiv\text{N}$ bond. In addition, the peak at 1439 cm^{-1} corresponds to the stretching vibration of C-N bond. The absorption peak at 946 cm^{-1} represents -NH₃ group. The characteristic peaks at 1200 cm^{-1} and 1117 cm^{-1} are related to the stretching vibration of P=O and P-O bond [16]. As can be seen from Fig. 10b and e, FPUF/D-D-20 has characteristic absorption peaks of -NH group ($3185\text{--}3438\text{ cm}^{-1}$) and $\text{C}\equiv\text{N}$ bond (2200 and 2177 cm^{-1}) at 220 °C [27]. When the temperature reached 380 °C, the peak at 946 cm^{-1} represents the stretching vibration of -NH₃ group, and the absorption peaks at 1200 and 1117 cm^{-1} are due to the stretching vibration of P=O and P-O bond. From Fig. 10c and f, FPUF/D-U-20 has a characteristic absorption peak of the -C=N bond at 220 °C. And when the temperature reached 380 °C, the absorption peaks of $\text{C}\equiv\text{N}$ ($2178/2107\text{ cm}^{-1}$), -NH₃ (946 cm^{-1}), P=O (1210 cm^{-1}) and P-O (1117 cm^{-1}) appeared. The above results indicate that DOPO derivatives-containing FPUF decomposes with increasing temperature, and the pyrolysis products include phosphorus and nitrogen-containing compounds.

The SEM was used to analyze the char residue of FPUF. Because pure FPUF has almost no char residue, its SEM image is not taken. The images of char residue of DOPO derivatives-containing FPUF are displayed in Fig. 11. From Fig. 11a and b, a continuous carbon layer can be observed. However, in Fig. 11c, there are holes and cracks in the surface of carbon layer. In order to further study the characteristics of char residue, Raman spectroscopy was performed on the char residue [42]. The corresponding Raman spectra of FPUF are shown in Fig. 11. The D band at 1360 cm^{-1} and the G band at 1600 cm^{-1} correspond to carbon vibrations from disordered carbon-containing compounds and graphite-containing compounds, respectively. The integrated intensity ratio (I_D/I_G) of D and G bands is used to evaluate the degree of graphitization [43]. It can be seen that FPUF/D-M-20 and FPUF/D-D-20 have lower I_D/I_G than FPUF/D-U-20, indicating that D-Mel and D-DICY have better efficiency in improving the graphitization of FPUF.

Based on the above analysis, the possible flame retardant mechanism was proposed. Taking FPUF/D-D-20 as an example, D-DICY decomposes with increasing temperature, and it is broke down into DOPO-OH and dicyandiamide. As the temperature increases, DOPO-OH can produce gaseous phosphorus-containing products such as P· and PO·, which can quench highly active hydrogen and hydroxyl radicals in the flame, thereby interrupting the chain reaction of combustion. The non-flammable NH₃ produced by dicyandiamide can dilute flammable gases. On the other hand, phosphoric acid, polyphosphoric acid, etc. generated by DOPO-OH will cover the surface of the FPUF, which can reduce the thermal decomposition rate of the carbon skeleton and catalyze it to form a carbon layer network. Furthermore, D-DICY promotes the formation of char residue and improves the graphitization of them. The continuous and compact carbon layer can suppress the transfer of heat and the overflow of gases.

4. Conclusions

In this work, novel phosphorus-nitrogen-containing DOPO derivative salts were synthesized and applied to FPUF. The test results show that the structure of FPUF modified by DOPO derivative salts is maintained. The initial decomposition temperature of the foam is slightly reduced, the maximum decomposition rate temperature is increased, and the char formation performance is significantly improved. The density of foam increases and the tensile strength and compression hardness are enhanced. The flame retardancy of FPUF is improved and D-DICY has the best flame retardancy. When its addition amount is 20 phr, the LOI of FPUF can reach 24.5%. Based on the analysis of the gas phase and the condensed phase, the flame retardant mechanism was proposed. In the gas phase, DOPO derivatives can produce phosphorus-containing products such as P· and PO·, which can interrupt the combustion reaction by capturing highly active hydrogen and hydroxyl radicals in the flame. Furthermore, the non-combustible NH₃ can dilute the flammable gases. In the condensed phase, DOPO derivatives can

catalyze the formation of the carbon network and improve its graphitization degree. The dense and continuous carbon layer effectively prevents heat transfer and gas release during combustion. The synthesis steps in this work are simple, low cost, environmental friendly, and have broad prospects of practical application.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment.

CRediT authorship contribution statement

Shicong Ma: Formal analysis, Conceptualization, Writing - original draft. **Yuling Xiao:** Software, Validation. **Feng Zhou:** Software. **Bernhard Schartel:** Methodology. **Yin Yam Chan:** Investigation. **Oleg P. Korobeinichev:** Data curation. **Stanislav A. Trubachev:** Supervision. **Weizhao Hu:** Resources. **Chao Ma:** Visualization, Writing - review & editing. **Yuan Hu:** Supervision.

This work was financially supported by the National Natural Science Foundation of China (51761135113, 51874266, U1833113, 51911530127).

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4.2 Synthesis of ethyl (Diethoxymethyl)phosphinate derivatives and their flame retardancy in flexible polyurethane foam: structure-flame retardancy relationships

Feng Zhou, Chao Ma, Kang Zhang, Yin Yam Chan, Yuling Xiao, Bernhard Schartel, Manfred Doring, Bibo Wang, Weizhao Hu and Yuan Hu. *Polym Degrad Stabil.* **2021**, 188. Doi: 10.1016/j.polymdegradstab.2021.109557.

Status: This article was accepted and published.

<https://doi.org/10.1016/j.polymdegradstab.2021.109557>

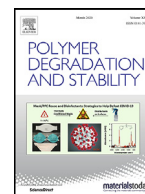
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- Feng Zhou
 - Investigation
 - Formal analysis
 - Writing – original draft
- Chao Ma
 - Validation
 - Writing – review & editing
- Kang Zhang
 - Data curation
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- Yuling Xiao
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- Manfred Doring
 - Conceptualization
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 - Project administration
- Yuan Hu
 - Funding acquisition

Abstract

Three novel liquid ethyl (diethoxymethyl)phosphinate derivatives (EDPs) were synthesized and incorporated into flexible polyurethane foams (FPUFs). The flame retardancy of FPUFs were evaluated

by limiting oxygen index (LOI), vertical burning and cone calorimetry tests, and the results indicated the structure-flame retardancy relationship of EDPs. Among these EDPs, P-(diethoxymethyl)-N-phenylphosphonamidate (EDPPA) exhibited the best flame retardant effect, methyl 3-((diethoxymethyl)(ethoxy)phosphoryl)propanoate (EDPMA) the second, and ethyl phenyl (diethoxymethyl)phosphonate (EDPPO) the worst. When the incorporation of EDPPA was 10 wt%, the FPUFs could self-extinguish and pass the vertical burning test. Meanwhile, the LOI value of FPUF-PA increased to 23.6% with 20 wt% loading of flame retardant. According to the investigation of volatiles during the thermal degradation of FPUFs and the morphologies of char residues after cone test, we inferred the possible flame retardant mechanism. The results indicated that EDPs could release phosphorus-containing compounds in the gas phase, which would generate phosphorus-containing radicals and play the role of radical scavenger. In the condensed phase, EDPs can promote the formation of dense, intact and thermal stably char layer on the surface of FPUFs. Moreover, we found that the structure influence on flame retardancy was attributed to the atoms linked to the central phosphorus. Our results indicate that these EDPs are promising flame retardants in FPUFs that can be applied to improve the flame retardancy of FPUFs in various practical applications.



Synthesis of Ethyl (Diethoxymethyl)phosphinate Derivatives and Their Flame Retardancy in Flexible Polyurethane Foam: Structure-flame Retardancy Relationships

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ARTICLE INFO

Article history:

Received 24 December 2020

Revised 5 March 2021

Accepted 12 March 2021

Available online 18 March 2021

Keywords:

Ethyl (diethoxymethyl)phosphinate derivatives

Flame retardant

Flexible polyurethane foam

Structure-flame retardancy relationship

ABSTRACT

Three novel liquid ethyl (diethoxymethyl)phosphinate derivatives (EDPs) were synthesized and incorporated into flexible polyurethane foams (FPUFs). The flame retardancy of FPUFs were evaluated by limiting oxygen index (LOI), vertical burning and cone calorimetry tests, and the results indicated the structure-flame retardancy relationship of EDPs. Among these EDPs, P-(diethoxymethyl)-N-phenylphosphonamidate (EDPPA) exhibited the best flame retardant effect, methyl 3-((diethoxymethyl)(ethoxy)phosphoryl)propanoate (EDPMA) the second, and ethyl phenyl (diethoxymethyl)phosphonate (EDPPO) the worst. When the incorporation of EDPPA was 10 wt%, the FPUFs could self-extinguish and pass the vertical burning test. Meanwhile, the LOI value of FPUF-PA increased to 23.6% with 20 wt% loading of flame retardant. According to the investigation of volatiles during the thermal degradation of FPUFs and the morphologies of char residues after cone test, we inferred the possible flame retardant mechanism. The results indicated that EDPs could release phosphorus-containing compounds in the gas phase, which would generate phosphorus-containing radicals and play the role of radical scavenger. In the condensed phase, EDPs can promote the formation of dense, intact and thermal stably char layer on the surface of FPUFs. Moreover, we found that the structure influence on flame retardancy was attributed to the atoms linked to the central phosphorus. Our results indicate that these EDPs are promising flame retardants in FPUFs that can be applied to improve the flame retardancy of FPUFs in various practical applications.

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1. Introduction

Flexible polyurethane foams (FPUFs) are polymeric materials that are synthesized from polyols and isocyanates. They are used widely in household for their excellent resilience and cushioning properties.[1,2] However, as polymeric materials with open-cell structure, they are easily ignited and highly flammable. In recent years, fire accidents frequently happen in the buildings and cause large damages because of the ignition of the cushioning materials in the furniture. [3–5] In order to improve the flame retardancy of FPUFs and eliminate the fire safety threats, researchers have developed many kinds of flame retardants and flame retard-

ing strategies for FPUFs. [6–11] Among the many types of flame retardants, organophosphorus compounds (like phosphonate, phosphate, phosphonamidate and phosphoramidate, etc) exhibit high flame retardant efficiency and good compatibility in the polymer matrix. [12–18] Moreover, there are no releasing of halogen-containing gases during the combustion, which means they are lower toxic and more environmental friendly as compared with halogenated flame retardants. [19] Over the past decade, many researches on this area have been reported. Rao et al. had synthesized a phosphorus-containing melamine salt (DPMMA) and found high flame-retarding efficiency in FPUFs. In their research, FPUFs that contained merely 5 php flame retardant exhibited self-extinguish in TB 117-2000 vertical burning. [11] Zhou et al. synthesized a novel liquid phosphonate (BDMPP) and compared its flame-retarding effect to the commercialized flame retardant dimethyl methylphosphonate (DMMP). Their investigation indi-

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cated that FPUFs-BD samples showed higher limiting oxygen index (LOI) values, vertical burning level and lower heat release at the same flame retardant loading because of the existence of (+3) valence phosphorus. [20] Based on the previous investigations, the flame retardant effects of organophosphorus can be concluded. Generally, the flame retardant effects are divided into two types: gas phase and condensed phase effects. The gas phase effect is attributed to the released phosphorus-contained species which can play the radical scavenging effects and thus promote the flame inhibition. [21–23] In the condensed phase, the decomposition products of organophosphorus flame retardants (like phosphoric and polyphosphoric acid) are able to form protective char layers on the surface of polymer matrix, which can hinder the transfer of heat, oxygen and combustible gas, and thus protect the inner polymer. [24–27]

In recent years, more attentions are concentrated on the influence of phosphorus-containing compounds' chemical structure on the flame retardancy of FPUFs. At the very beginning, Liang et al. [12] synthesized a series of dimethyl phosphite derivatives with systematic structure variations to investigate their structure-flame retardancy relationship on FPUFs. Their results of flame tests revealed that phosphonates and phosphoramidates performed better than the corresponding phosphates in improving the flame retardancy of FPUFs. Moreover, flame retardants that containing allyl show better flame retardancy than the corresponding propyl containing ones. Compared with the other one, phosphonates, phosphoramidates and allyl terminated flame retardants were more effective in generating phosphorus-containing radicals, thus exhibited higher flame retardancy in FPUFs. Basing on these results, Matthias Neisius et al. [28] focused on the structure influence of phosphoramidates on FPUFs' flame retardancy. As shown in the flame tests, dimethyl phosphoramidates presented higher flame retardancy than the phenyl ones, monoallyl derivatives were better than the other one in the same class phosphoramidates. Moreover, they had investigated the influence of the structure on the flame retardancy of 9,10-dihydro-9,10-oxa-10-phosphaphenanthrene-10-oxide (DOPO) based phosphoramidate. [29] In the fire tests, bis DOPO phosphoramidate/foam formulations show the highest flame retardant level as compared to the other foam composites. This results was attributed to the better thermal stability of bis DOPO phosphoramidate that it can prolong the effective gas phase flame retardant effect during the combustion. Chen et al. [30] had synthesized four melamine salts with different phosphorus valence, investigate their influence on the decomposition and flame retardancy of FPUFs. Among these four melamine salts, CMA and MHPA the had the +1 phosphorus valence, performed better flame retardant effect than MPOA (+3) and MPyP (+5). Furthermore, they found that with the increasing of the phosphorus valence, the char yield was increased while the phosphorus-containing compounds decreased in the gas phase.

Easily obtained from the industrialized and recyclable hypophosphorous acid (H_3PO_2), ethyl (diethoxymethyl)phosphinate (EDP) is a potential flame retardant intermediate. Through the reactions of P–H, numerous organophosphorus compounds can be synthesized. However, to the best of our knowledge, there are no reports on the flame retardancy of EDP and its derivatives (EDPs). Therefore, it is essential to investigate their flame retardancy and the corresponding structure-flame retardant properties relationships of EDPs. In this paper, a series of ethyl (diethoxymethyl)phosphinate derivatives (EDPs) were synthesized according to the Atherton-Todd or Michael addition reactions, and used into FPUFs. The aim of our work was to improve the flame retardancy of FPUFs and investigate EDPs' structure influence on flame retardancy. The flame retardancy of FPUF-EDPs composites were evaluated through LOI, vertical burning and cone calorimetry tests. Thermogravimetric analysis/infrared spectrometry was

applied to investigate the volatiles of these FPUFs during the thermal degradation. Scanning electron microscopy and Raman spectroscopy were used to characterized the morphology of char residues after cone calorimetry test. According to these investigations, we inferred the possible flame retardant mechanisms. The results indicated that the structure influence on flame retardancy was attributed to the atoms linked to the central phosphorus.

2. Experiment

2.1. Materials

Hypophosphorous acid aqueous solution (30.0–35.0%), triethyl orthoformate (TEO), phenylamine, phenol, methyl acrylate, triethylamine (TEA), chloroform, dichloromethane, dibutyltin dilaurate (DBTDL) and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Trifluoroacetic acid (TFA) was purchased from Shanghai Aladdin Biochemical Technology Co. Ltd., China. Polyether polyol 330 (hydroxyl value = 56 mg KOH/g, number average molecular weight = 3000 g/mol, average functionality = 3), triethylenediamine (A33, 33%), silicone surfactant and toluene diisocyanate (TDI 80/20, 4:1 mixture of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate) were kindly provided by Jiangsu Lvyuan New Material Co. Ltd., China. Distilled water was used as a chemical blowing agent and made by our laboratory. Hypophosphorous acid aqueous solution was distilled under vacuum at 30 °C to get the anhydrous hypophosphorous acid. The other chemicals were used as received.

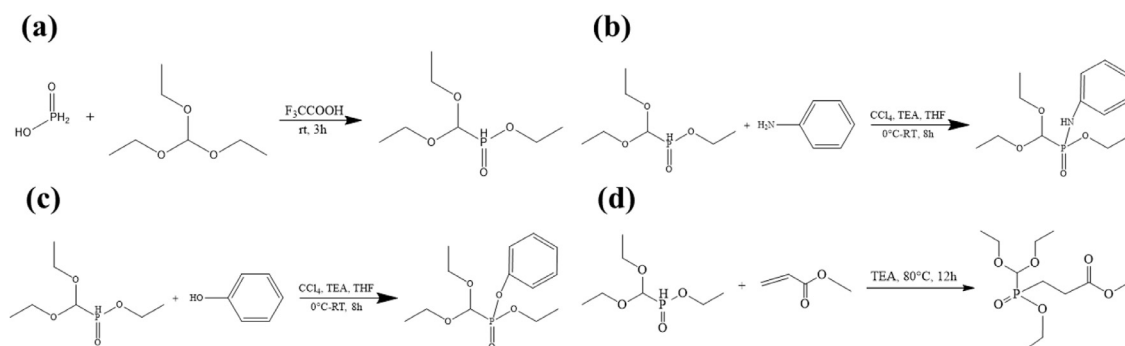
2.2. Synthesis of EDP

The synthesis of EDP had been reported by Cécile Fougère. [31] At room temperature, 0.02 mol TFA and given amount of anhydrous hypophosphorous acid (0.1 mol, 6.6 g) and TEO (0.2 mol, 29.6 g) were added into a 500 mL three-necked round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere. After 3 h stirring, the reaction mixture was concentrated by rotary evaporation and dissolved into chloroform, then washed by saturated aqueous NaHCO_3 and dried with magnesium sulfate. The solvent was removed by rotary evaporation and the final product was obtained and purified via reduced pressure distillation. The synthetic route was illustrated in Scheme 1 and nuclear magnetic resonance (NMR), fourier transform infrared (FTIR) spectra of product were shown in Fig. 1.

Analytical Data for EDP: colorless, transparent liquid. ^1H NMR (CDCl_3 , Fig. 1a–1) δ (ppm): 1.27 (6H, $\text{CHOCH}_2\text{CH}_3$), 1.39 (3H, POCH_2CH_3), 3.71–3.85 (4H, $\text{CHOCH}_2\text{CH}_3$), 4.23–4.24 (2H, POCH_2CH_3), 4.70 (1H, $\text{CHOCH}_2\text{CH}_3$), 6.90 (1H, P–H). ^{31}P NMR (CDCl_3 , Fig. 1a–2) δ (ppm): 27.82. FTIR (KBr, Fig. 1e): 2979, 2933, 2902 cm^{-1} ($-\text{CH}_2-$, $-\text{CH}_3$), 2385 cm^{-1} (P–H), 1230 cm^{-1} ($\text{P}=\text{O}$), 1165, 1114 cm^{-1} (C–O–C), 1062 cm^{-1} (P–O–C), 773 cm^{-1} (P–C).

2.2. Synthesis of EDPPA and EDPPPO

EDPPA and EDPPPO were synthesized through the Atherton-Todd reaction between EDP and phenylamine or phenol. Briefly, EDP and carbon tetrachloride (1.1 equiv.) were dissolved into dichloromethane in a 500 mL three-necked round-bottom flask equipped with a dripping funnel and magnetic stirrer. Subsequently, given amount of phenylamine or phenol and TEA (1.1 equiv.) were added dropwise into this flask during 1 h. The reaction temperature was controlled at 0–5°C, and the reaction solution was stirred at room temperature for 8 h. After the reaction was completed, the solution was filtrated and the filtrate was washed by hydrochloric acid solution (1 M), saturated aqueous NaHCO_3 solution and saturated aqueous NaCl solution. Then, the organic layer



Scheme 1. Synthetic routes of EDP (a), EDPPA (b), EDPPPO (c) and EDPMA (d).

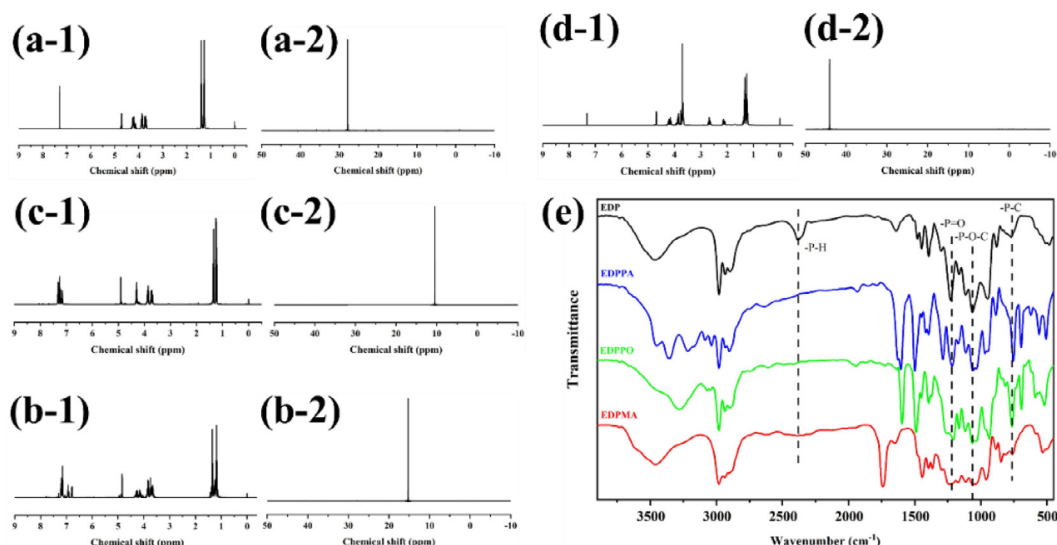


Fig. 1. NMR spectra of EDP (a), EDPPA (b), EDPPPO (c) and EDPMA (d), FT-IR spectrum (e).

was dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporator. The final product was obtained after drying at 60°C under reduced pressure. The synthetic routes were illustrated in Scheme 1 and the NMR, FTIR spectra of products were shown in Fig. 1.

Analytical Data for EDPPA: light brown, transparent liquid. 1H NMR ($CDCl_3$, Fig. 1b-1) δ (ppm): 1.19 (6H, $CHOCH_2CH_3$), 1.34 (3H, $POCH_2CH_3$), 3.65–3.86 (4H, $CHOCH_2CH_3$), 4.14–4.28 (2H, $POCH_2CH_3$), 4.83 (1H, $CHOCH_2CH_3$), 6.78 (1H, *N-H*), 6.92–7.22 (5H, *Ar-H*). ^{31}P NMR ($CDCl_3$, Fig. 1b-2) δ (ppm): 15.27. FTIR (KBr, Fig. 1e): 2981, 2933, 2900 cm^{-1} ($-CH_2-$, $-CH_3$), 3037, 3085 cm^{-1} (*Ar-H*), 3365 cm^{-1} (*N-H*), 1286 cm^{-1} (*C-N*), 1215 cm^{-1} ($P=O$), 1170, 1111 cm^{-1} ($C-O-C$), 1050 cm^{-1} ($P-O-C$), 887 cm^{-1} ($P-N$), 750 cm^{-1} ($P-C$).

Analytical Data for EDPPPO: colorless, transparent liquid. 1H NMR ($CDCl_3$, Fig. 1c-1) δ (ppm): 1.25 (6H, $CHOCH_2CH_3$), 1.34 (3H, $POCH_2CH_3$), 3.70–3.88 (4H, $CHOCH_2CH_3$), 4.30 (2H, $POCH_2CH_3$), 4.92 (1H, $CHOCH_2CH_3$), 7.15–7.33 (5H, *Ar-H*). ^{31}P NMR ($CDCl_3$, Fig. 1c-2) δ (ppm): 10.46. FTIR (KBr, Fig. 1e): 2983, 2931, 2898 cm^{-1} ($-CH_2-$, $-CH_3$), 3071, 3046 cm^{-1} (*Ar-H*), 1209 cm^{-1} ($P=O$), 1165, 1117 cm^{-1} ($C-O-C$), 1060 cm^{-1} ($P-O-C$), 934 cm^{-1} ($P-O-Ar$), 763 cm^{-1} ($P-C$).

2.3. Synthesis of EDPMA

EDPMA was synthesized from EDP and methyl acrylate according to the Michael addition reaction. Generally, EDP, methyl acry-

late (2.2 equiv.) and TEA (1.1 equiv.) were added into a 250 mL flask and stirred at 80°C for 12 h. After removing TEA and methyl acrylate through the rotary evaporator, the transparent, colorless, liquid final product was dried overnight under vacuum at 60°C. The synthetic route was illustrated in Scheme 1 and NMR, FTIR spectra of product were shown in Fig. 1.

Analytical Data for EDPMA: colorless, transparent liquid. 1H NMR ($CDCl_3$, Fig. 1d-1) δ (ppm): 1.26 (6H, $CHOCH_2CH_3$), 1.33 (3H, $POCH_2CH_3$), 2.13 (2H, PCH_2CH_2), 2.67 (2H, CH_2COOCH_3), 3.69 (4H, $CHOCH_2CH_3$), 3.84 (3H, CH_2COOCH_3), 4.20 (2H, $POCH_2CH_3$), 4.69 (1H, $CHOCH_2CH_3$). ^{31}P NMR ($CDCl_3$, Fig. 1d-2) δ (ppm): 44.06. FTIR (KBr, Fig. 1e): 2979, 2933, 2902 cm^{-1} ($-CH_2-$, $-CH_3$), 1740 cm^{-1} ($C=O$), 1229 cm^{-1} ($P=O$), 1170, 1114 cm^{-1} ($C-O-C$), 1051 cm^{-1} ($P-O-C$), 761 cm^{-1} ($P-C$).

2.4. Preparation of pure and flame retardants FPUFs

The FPUFs used in this paper were prepared through a one-pot free rising foaming process and the detailed formulations of these FPUFs were listed in Table S1. In a plastic cup, polyether polyols, flame retardants, DBTDL, A33, distilled water, and silicone surfactant were mixed using vigorous mechanical, and stirring for 1 min. After adding given amount of TDI ($NCO/OH = 1.05$), the mixture was vigorously stirred for 5 s, then was poured into an aluminum mold to pre-polymerization. The FPUFs were obtained after further cured at 80°C for 24 h.

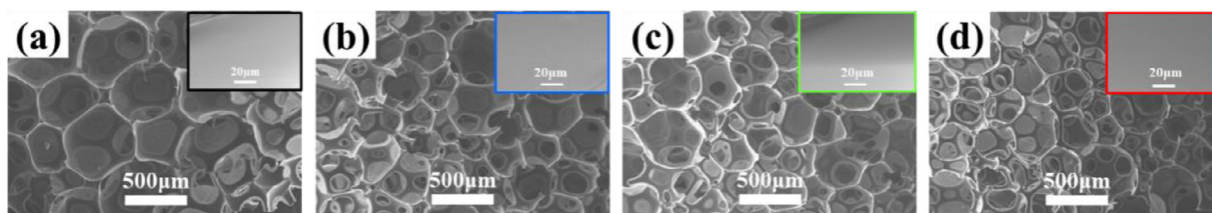


Fig. 2. SEM images of pure FPUF (a), FPUF-20PA (b), FPUF-20PO (c) and FPUF-20MA (d).

2.5. Characterization

Fourier transform infrared (FTIR) spectra of EDP and its derivatives were obtained from a Nicolet 6700 spectrometer (Nicolet Instrument Company, U.S.). Nuclear magnetic resonance (NMR) was performed on a Bruker AV400 NMR spectrometer (400MHz) using deuterated chloroform (CDCl_3). The densities of these FPUFs were measured manually according to ISO 845 standard, and the values were summarized in Table S1. The dimension of test sample was $100 \times 100 \times 25 \text{ mm}^3$. Scanning electron microscopy (SEM) photographs were recorded on a FEI Sirion 200 scanning electron microscope at an acceleration voltage of 10 kV. Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere using a Q5000 thermal analyzer (TA Co., U.S.). The foam sample was cut into small pieces and put in the pan, with a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 600°C . Limiting oxygen index (LOI) was obtained from a HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ISO 4589-1:1996. The dimension of the test samples was $150 \times 10 \times 10 \text{ mm}^3$. Vertical burn test was performed on a CFZ-2 type instrument (Jiangning Analysis Instrument Co., China) based on California technical bulletin 117 (TB 117-2000), the dimension of the test samples was $12 \times 3 \times 0.5 \text{ inch}^3$. Cone calorimetry test was carried out on a cone calorimeter according to ISO Standard 5660-1. The heat flux was $25 \text{ kW}/\text{m}^2$ and the samples were of dimension $100 \times 100 \times 25 \text{ mm}^3$. Raman spectra were measured on a LabRAM-HR Confocal Raman Microprobe (JobinYvon Instruments, France) in the wave number range of 2000 to 500 cm^{-1} .

3. Results and discussion

3.1. Microstructure of FPUFs

The microstructure of FPUFs was investigated using SEM, and the SEM images were presented in Fig. 2. As shown in Fig. 2a, pure FPUF exhibited an open-cell cellular structure with uniform pore size. In addition, the surface of the pores was smooth and homogeneous under high magnification. After incorporated with EDPs, the microstructures of the modified FPUFs were not changed (Fig. 2b–d). All EDPs modified foams maintained similar cellular structure and uniform pore sizes as compared with pure foam. Moreover, no wrinkles could be observed on the surface of pores which indicated the good compatibility of these liquid EDPs and FPUFs. Nevertheless, the pore sizes of modified samples were decreased, which might be attributed to the effect of EDPs on the activity of foaming catalysts. The density of pure FPUF was measured as $34.4 \text{ kg}/\text{m}^3$. After flame retardant modification, the densities of FPUFs were increased. The densities of FPUF-10FR and FPUF-20FR samples were increased to about $38 \text{ kg}/\text{m}^3$ and $40 \text{ kg}/\text{m}^3$, respectively. This was because of the decrease of pore sizes that the FPUFs became more denser as compared with pure foam. The investigation of microstructure indicated that these EDPs were compatible with FPUFs and would not affect the microstructure of FPUFs.

3.2. Thermal degradation of FPUFs

Thermogravimetric analysis (TGA) under nitrogen atmosphere was conducted to investigate the thermal degradation of FPUFs. The resultant curves of TGA and differential thermogravimetry (DTG) were presented in Fig. 3 and related key parameters like the initial decomposition temperature ($T_{5\%}$), the maximum weight loss rate (R_{max}), the temperature at R_{max} (T_{max}) and the char yield after thermal decomposition (CY) were summarized in Table 1. The thermal degradation of pure and EDPs incorporated FPUFs was similar and could be divided in two steps. The first weight loss stage was attributed to the thermal decomposition of urethane bond and the second one belonged to the thermal decomposition of the remaining soft segments. For pure FPUF, the initial decomposition temperature was 250°C and it showed two maximum weight loss rate at 280°C and 365°C . After incorporated with EDPs, the $T_{5\%}$ and $T_{\text{max}1}$ values of modified FPUFs were decreased indicating that the flame retardant FPUFs were less thermal stable than pure FPUF. This phenomenon was attributed to the lower thermal stability of these flame retardants that the thermal decomposition products of EDPs may react with the urethane bond, promoting the decomposition of polyurethane matrix. (TGA curves of EDPs were shown in Fig. S2) In addition, among these modified samples, the $T_{5\%}$ values of FPUF-MA were lower than the others. This was because that aromatic ring was more thermal stable than alkyl chain. Considering $T_{\text{max}2}$, the values of modified FPUFs shifted to higher temperatures. However, the increase was not obvious. When the thermal decomposition was finished at 600°C , there was almost no CY for pure FPUF. In contrast, all modified FPUFs presented higher CY, which also increased with the increasing of flame retardant amount. The improvement of $T_{\text{max}2}$ and CY demonstrated that the flame retardant FPUFs were more thermal stable than pure FPUF at the second thermal degradation stage. Based on the TGA results, it might be suggested that EDPs predominantly decomposed at the first weight loss stage and the decomposition products of EDPs could improve the char yield.

3.3. Flame retardancy of FPUFs

The flame retardancy of FPUFs were evaluated by LOI, vertical burning, UL-94 horizontal burning and cone calorimetry tests. LOI represents the minimum oxygen content that needed for combustion. Normally, materials with higher LOI are hard to combust. As listed in Table 2, the LOI value of pure FPUF was 17.5%. After incorporated with EDPs, higher LOI values were obtained for modified foams and the LOI values increased slowly with the increasing of flame retardant addition. Among these modified foams, under the same flame retardant addition, FPUF-PA exhibited the highest LOI values and the values of foam composites were in the order: FPUF-PA > FPUF-MA > FPUF-PO. Moreover, vertical burning tests of FPUFs were conducted to investigate the flame spreading according to TB117-2000. The digital photos of FPUFs at 5s, 10s, 12s and 15s during the vertical burning tests were presented in Fig. 4. For pure foam (Fig. 4a), it was easy to ignite and burned fast and completely after ignition. When EDPs were incorporated, the flame

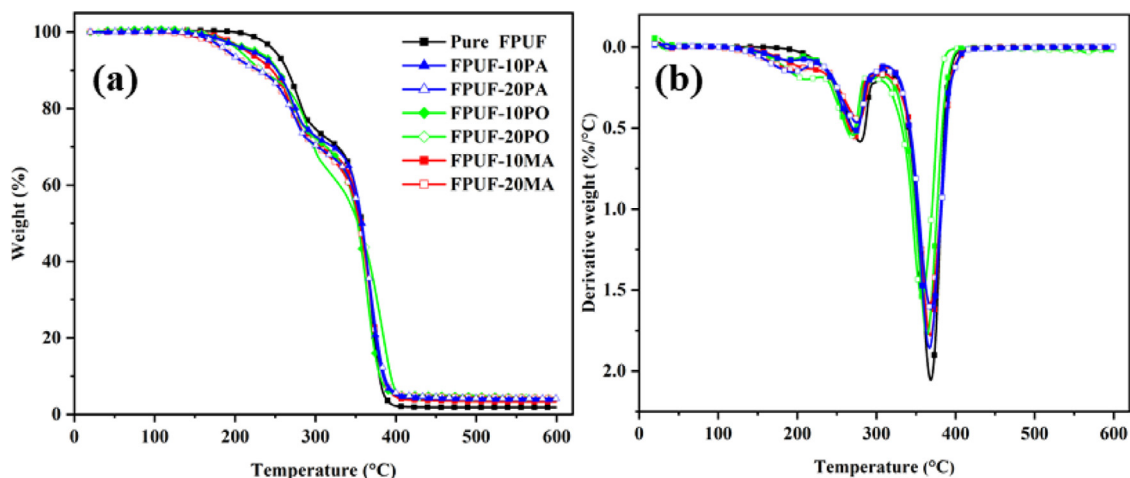


Fig. 3. TGA (a) and DTG (b) curves of FPUFs.

Table 1
TGA results of FPUFs.

Sample	$T_{5\%}$ (°C)	T_{max1} (°C)	R_{max1} (%/°C)	T_{max2} (°C)	R_{max2} (%/°C)	CY (%)
Pure FPUF	250	280	0.583	365	2.05	1.8
FPUF-10PA	219	274	0.516	366	1.86	3.7
FPUF-20PA	192	275	0.466	368	1.62	4.1
FPUF-10PO	226	270	0.543	363	1.76	4.1
FPUF-20PO	206	268	0.551	361	1.54	4.4
FPUF-10MA	214	273	0.554	368	1.78	3.3
FPUF-20MA	190	276	0.448	368	1.59	3.8

Table 2
Data of cone calorimetry tests of pure FPUF, FPUF-PA, FPUF-PO and FPUF-MA.

Sample	Pure FPUF	FPUF- 10PA	FPUF- 20PA	FPUF-10PO	FPUF-20PO	FPUF-10MA	FPUF- 20MA
TTI (s)	2 ± 0	4 ± 2	4 ± 1	4 ± 1	3 ± 1	2 ± 1	3 ± 0
t_p (s)	75 ± 3	93 ± 3	99 ± 2	81 ± 5	90 ± 3	84 ± 3	93 ± 1
PHRR (kW/m ²)	340 ± 10	282 ± 5	298 ± 9	311 ± 5	322 ± 11	291 ± 8	304 ± 10
FIGRA	4.53 ± 0.05	3.03 ± 0.03	3.01 ± 0.04	3.84 ± 0.02	3.58 ± 0.01	3.46 ± 0.04	3.27 ± 0.06
THR (MJ/m ²)	22.8 ± 0.5	20.2 ± 0.7	20.6 ± 0.8	21.1 ± 0.7	21.7 ± 1.0	20.4 ± 0.3	20.9 ± 0.6
THR/TML (MJ•m ⁻² •g ⁻¹)	2.69 ± 0.02	2.19 ± 0.05	2.12 ± 0.07	2.34 ± 0.02	2.33 ± 0.05	2.20 ± 0.07	2.18 ± 0.04
TSP (m ²)	1.33 ± 0.06	2.03 ± 0.07	2.32 ± 0.04	1.81 ± 0.05	2.19 ± 0.05	1.88 ± 0.03	2.28 ± 0.07
CY (%)	1.4 ± 0.4	3.2 ± 0.5	3.7 ± 0.3	3.4 ± 0.2	3.9 ± 0.3	2.8 ± 0.1	3.4 ± 0.1
LOI (%)	17.5 ± 0.1	21.4 ± 0.1	23.6 ± 0.3	20.9 ± 0.2	22.1 ± 0.3	21.2 ± 0.4	22.5 ± 0.2
Vertical burning (Pass or Fail)	Fail	Pass	Pass	Fail	Pass	Fail	Pass
UL94-HB	No	HF2	HF1	HF2	HF1	HF2	HF1

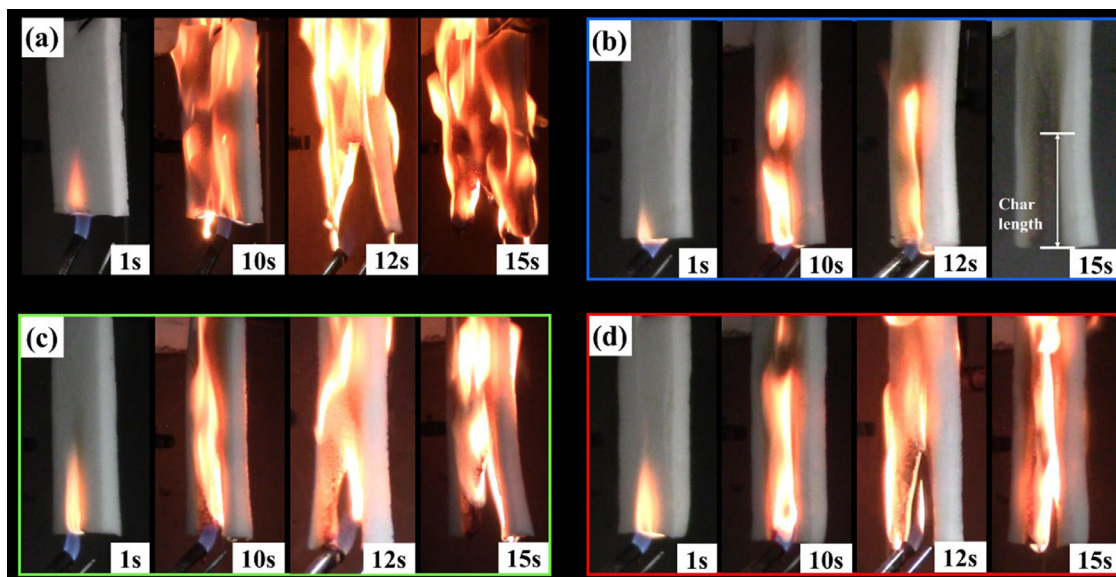


Fig. 4. Digital photos of pure FPUF (a), FPUF-10PA (b), FPUF-10PO (c) and FPUF-10MA (d) during vertical burning.

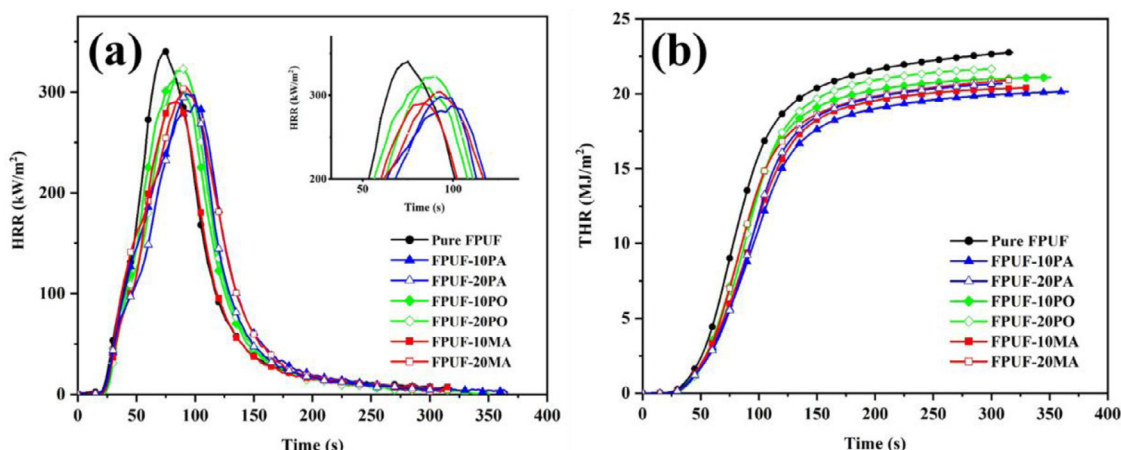


Fig. 5. PHRR (a) and THR (b) curves of FPUFs.

propagation became slower as compared with pure FPUF. Besides, there were fewer melting droplets for the modified FPUFs. With 10 wt% loading of flame retardant, only EDPPA modified FPUF can pass the vertical burning test and exhibited self-extinguish behavior (Fig. 4b). As shown in these pictures, the flame zone become smaller during vertical burning test. After combustion, the charred region did not reach the clamp which indicated good flame retardancy of the EDPPA. When the addition increased to 20 wt%, all flame retardant FPUFs can pass the vertical burning (Fig. S1). Besides, in UL 94-HB tests, FPUFs can reach HF-2 level with 10 wt% flame retardant, and HF-1 with 20 wt% flame retardant. The results of LOI, vertical burning and horizontal burning tests indicated that FPUF-PA showed the best flame retardancy while the flame retardancy of FPUF-PO was the worst at the same flame retardant amount. This phenomenon was attributed to the structure influence on the flame retardancy of EDPs. The detailed flame retardant mechanisms of these EDPs would be discussed in the following sections.

Cone calorimetry test is now recognized as the best method to investigate the combustion properties of materials. In order to investigate the combustion properties of FPUFs and further evaluate their flame retardancy, cone calorimetry test with a heat flux of 25 kW/m² was conducted according to ISO 5660-1. The time to ignition (TTI), the peak heat release rate (PHRR), the time to PHRR (t-PHRR), the total heat release (THR), the total smoke production (TSP), the char yield (CY), the fire growth rate (FIGRA) and the total heat release per total mass loss (THR/TML) were obtained from cone calorimetry test measurements and values were summarized in Table 2. Besides, HRR and THR curves versus temperature were presented in Fig. 5. In cone calorimetry test, pure FPUF ignited and burned fast. The values of its TTI and t-PHRR were only 2 s and 72 s, respectively. After incorporated with EDPs, the TTI and t-PHRR values were increased, which meant the ignition and combustion of FPUFs became slower as compared with pure FPUF. Moreover, FIGRA of EDPs modified FPUFs were lower than pure FPUF too. FIGRA is defined as the PHRR/t-PHRR, lower FIGRA represents prolonged time to the maximum heat release. [32] Therefore, the decrease of FIGRA could also indicated the flame was slowing down. PHRR and THR are key parameters in cone calorimetry test that low PHRR and THR values indicate good flame retardancy of materials. For pure FPUF, it exhibited one heat release peak in Fig. 5, its PHRR and THR values were measured as 340 kW/m² and 22.8 MJ/m², respectively. After flame retardant modification, the PHRR and THR values of FPUFs became lower. Nevertheless, PHRR and THR values of FPUFs bounced as more EDPs was incorporated. This bounce was attributed to the increasing of foams' densities

that more flammable ingredients were involved into the combustion. [33,34] In addition, it's could be obviously noticed that FPUF-10PA presented the lowest PHRR and THR values among the FPUF-10FR samples, with a decrease of 17.1% and 11.4% respectively as compared with pure FPUF; FPUF-10MA the second and FPUF-10PO worst. When 20 wt% EDPs were incorporated, the decreasing trend was the same. This results further indicated the structure influence on flame retardant effect of these EDPs.

THR/TML indicates the effective combustion heat releasing from the volatiles, and its reduction is attributed to the gas phase flame retardant effects. [35] As seen in Table 2, the THR/TML value of pure FPUF was 2.69 MJ·m⁻²·g⁻¹ and this value decreased after EDPs was incorporated. Moreover, among the EDPs modified FPUFs, the decrease of THR/TML were in the order: FPUF-PA > FPUF-MA > FPUF-PO, which reflected the corresponding increasing in the gas phase flame retardant effect of EDPs. Besides, the increasing of TSP values could also indicate the gas phase flame retardant effect of EDPs, which presented the same growth trend with that of THR/TML. The condensed phase flame retardant effect is attributed to the protective char residues that high CY would indicate high flame retardant effect. In cone calorimetry test, the CY values of flame retardant modified FPUFs were increased as compared with pure sample. The value of FPUF-10PA, FPUF-20PA, FPUF-10PO, FPUF-20PO, FPUF-10MA and FPUF-20MA was 3.2%, 3.7%, 3.4%, 3.9%, 2.8% and 3.4%, respectively. However, these increase were limited due to the open-cell structure of FPUFs. Moreover, the increasing of CY was corresponded with that in the TGA results.

Based on the above results and discussions, it could be concluded that these as designed EDPs was able to improve the flame retardancy of FPUFs and the flame retardancy of these EDPs in FPUF decreases in the order: EDPPA > EDPPPO > EDPMA.

3.4. Flame retardant mechanism of FPUFs

Generally, the char residues after combustion, and volatiles during the thermal pyrolysis can reflect the flame retardant mechanism of materials. SEM photographs, digital photos and Raman spectra of the char residues after cone calorimetry tests were illustrated in Fig. 6. It was intuitively seen in Fig. 6a that there were almost no char residues for pure FPUF, while the modified samples exhibited more char residues as compared with pure FPUF. Besides, the char residues of FPUF-PO and FPUF-PA were more intact and denser than that of FPUF-MA, as illustrated in Fig. 6b. These results suggested that the combustion products of FPUF-PO and FPUF-PA can form dense and intact char layer to isolate the heat and oxygen transfer and protect the inner foam. In addition, Raman spectroscopy was applied to evaluate the thermal stability of the char

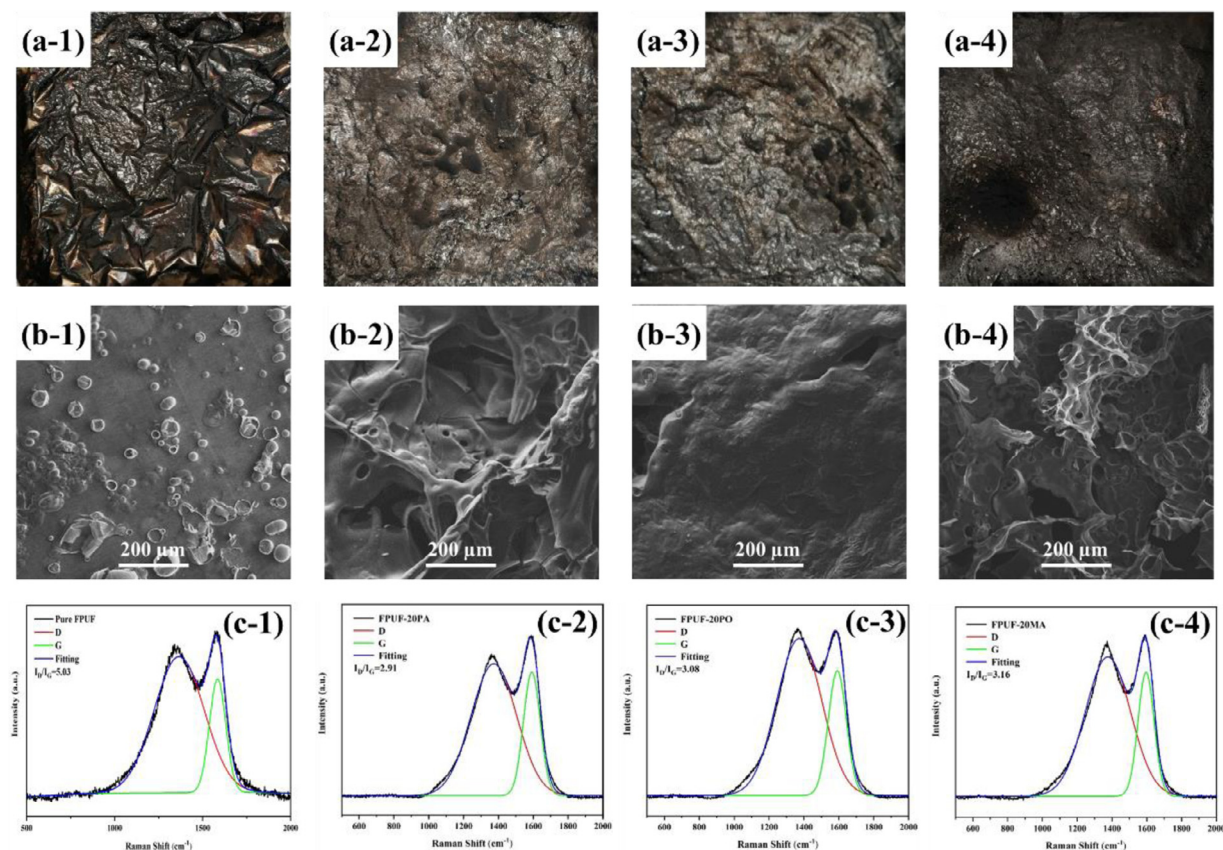


Fig. 6. Digital photos, SEM images and the corresponding Raman spectra of char residues after cone calorimetry tests. (a, pure FPUF; b, FPUF-20PA; c, FPUF-20PO; d, FPUF-20MA).

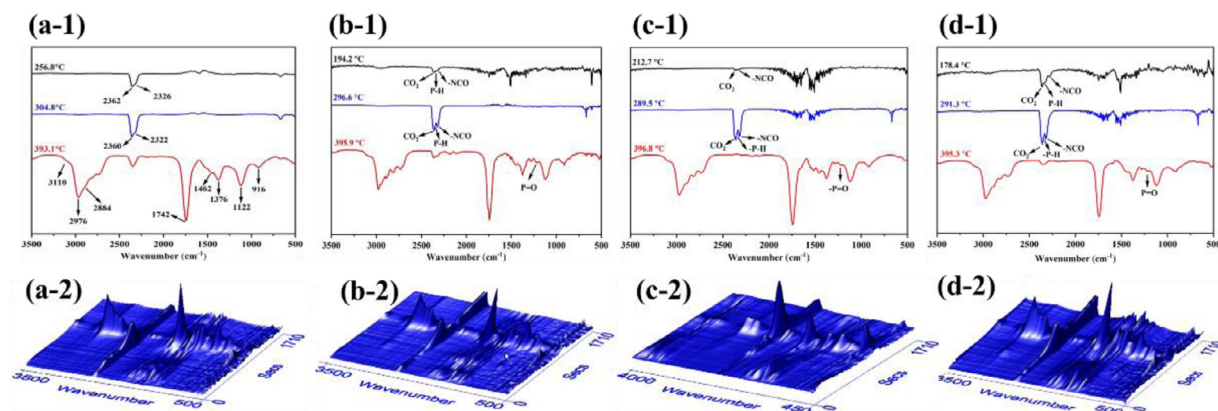


Fig. 7. FTIR spectra of volatiles at different temperature and the corresponding 3D absorbing curves of FPUFs. (a, pure FPUF; b, FPUF-20PA; c, FPUF-20PO; d, FPUF-20MA)

2884 cm^{-1}), C=O (1742 cm^{-1}), N=N (1376 cm^{-1}), C–O (916 cm^{-1}) and NH_3 (1122 cm^{-1}) were observed. [39,40] After incorporating EDPs, phosphorus-containing compounds were detected in the pyrolysis products of FPUFs. As marked in Fig. 7b–c, the identical peaks at 2346 cm^{-1} and 1216 cm^{-1} were because of the vibration of P–H and P=O, indicating the releasing of phosphine and its derivatives. [41,42] During the combustion, these phosphorus-containing compounds could generate phosphorus-containing radicals and play the role of radical scavenger in the gas phase. [36,43] In addition, it was obviously seen that no peaks of the phosphorus-containing compounds were founded in IR spectrum of FPUF-PO $T_{5\%}$ (Fig. 7c). This phenomenon was attributed to the reason that the bond energy of P–O is higher than P–C and P–N, which means EDPPA and EDPMA are easier to pyrolysis and generate phosphorus-containing compounds than EDPO. Thus, the gas phase flame retardancy of FPUFs was attributed to the ability to generate phosphorus-containing radicals during the combustion. Meanwhile, because of more phosphorus-containing radicals existed in the gas phase, FPUF-PA and FPUF-MA exhibited better flame retardancy than FPUF-MA.

4. Conclusions

Three novel EDPs with similar structure were successfully synthesized from hypophosphorous acid and incorporated into FPUFs. The result of SEM revealed that these EDPs were compatible with FPUFs and would not affect the structure. In TGA tests, the modified FPUFs presented lower thermal stability as compared with pure FPUF. Nevertheless, they showed better flame retardancy in the LOI, vertical burning and cone calorimetry tests. Besides, it was clearly seen that EDPPA exhibited the best flame retardant effect in FPUFs. With 10 wt% EDPPA, the modified FPUF can pass the vertical burning and show high LOI value of 23.6%. In addition, FPUF-10PA showed the lowest PHRR and THR values among these FPUFs, with a decrease of 17.1% and 11.4% respectively as compared with pure FPUF. This phenomenon was because of the structure influence on flame retardancy that FPUF-PA possessed the ability to form denser, more intact, protective char layers and more radical scavengers as compared with the other two FPUF-EDPs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Feng Zhou: Investigation, Formal analysis, Writing - original draft. **Chao Ma:** Validation, Writing - review & editing. **Kang Zhang:** Data curation. **Yin yam Chan:** Visualization. **Yuling Xiao:** Software. **Bernhard Schartel:** Methodology. **Manfred Doring:** Conceptualization. **Bibo Wang:** Resources. **Weizhao Hu:** Project administration. **Yuan Hu:** Funding acquisition.

Acknowledgments

The work was financially supported by the National Natural Science Foundation of China (51803204, 51761135113, U1833113 and 51874266) and Fundamental Research Funds for the Central Universities (WK2320000043).

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4.3 A liquid phosphorous flame retardant combined with expandable graphite or melamine in flexible polyurethane foam

Yin Yam Chan, Chao Ma, Feng Zhou, Yuan Hu and Bernhard Schartel. *Polym Advan Technol.* **2022**, 33, 326-339. Doi: 10.1002/pat.5519.

Status: This article was accepted and published. <https://doi.org/10.1002/pat.5519>

First author contribution:

- Validation
- Methodology
- Investigation
- Data curation
- Writing – Original draft, review and editing
- Visualization
- Project administration

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 - Project administration

- Funding acquisition

Abstract

A systematic series of flexible polyurethane foams (FPUF) with different concentrations of flame retardants, bis([dimethoxyphosphoryl]methyl) phenyl phosphate (BDMPP), and melamine (MA) or expandable graphite (EG) was prepared. The mechanical properties of the FPUFs were evaluated by a universal testing machine. The pyrolysis behaviors and the evolved gas analysis were done by thermogravimetric analysis (TGA) and TGA coupled with Fourier-transform infrared (TG-FTIR), respectively. The fire behaviors were studied by limiting oxygen index (LOI), UL 94 test for horizontal burning of cellular materials (UL 94 HBF), and cone calorimeter measurement. Scanning electronic microscopy (SEM) was used to examine the cellular structure's morphology and the postfire char residue of the FPUFs. LOI and UL 94 HBF tests of all the flame retarded samples show improved flame retardancy. BDMPP plays an essential role in the gas phase because it significantly reduces the effective heat of combustion (EHC). This study highlights the synergistic effect caused by the combination of BDMPP and EG. The measured char yield from TGA is greater than the sum of individual effects. No dripping phenomenon occurs during burning for FPUF-BDMPP-EGs, as demonstrated by the result of the UL 94 HBF test. EG performs excellently on smoke suppression during burning, as evident in the result of the cone calorimeter test. MA reduces the peak heat release rate (pHRR) significantly. The synergistic effect of the combination of BDMPP and EG as well as MA offers an approach to enhance flame retardancy and smoke suppression.

RESEARCH ARTICLE

A liquid phosphorous flame retardant combined with expandable graphite or melamine in flexible polyurethane foam

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Funding information

Deutsche Forschungsgemeinschaft, Grant/Award Number: Scha 730/19-1; National Natural Science Foundation of China, Grant/Award Number: 51761135113

Abstract

A systematic series of flexible polyurethane foams (FPUF) with different concentrations of flame retardants, bis([dimethoxyphosphoryl]methyl) phenyl phosphate (BDMPP), and melamine (MA) or expandable graphite (EG) was prepared. The mechanical properties of the FPUFs were evaluated by a universal testing machine. The pyrolysis behaviors and the evolved gas analysis were done by thermogravimetric analysis (TGA) and TGA coupled with Fourier-transform infrared (TG-FTIR), respectively. The fire behaviors were studied by limiting oxygen index (LOI), UL 94 test for horizontal burning of cellular materials (UL 94 HBF), and cone calorimeter measurement. Scanning electronic microscopy (SEM) was used to examine the cellular structure's morphology and the postfire char residue of the FPUFs. LOI and UL 94 HBF tests of all the flame retarded samples show improved flame retardancy. BDMPP plays an essential role in the gas phase because it significantly reduces the effective heat of combustion (EHC). This study highlights the synergistic effect caused by the combination of BDMPP and EG. The measured char yield from TGA is greater than the sum of individual effects. No dripping phenomenon occurs during burning for FPUF-BDMPP-EGs, as demonstrated by the result of the UL 94 HBF test. EG performs excellently on smoke suppression during burning, as evident in the result of the cone calorimeter test. MA reduces the peak heat release rate (pHRR) significantly. The synergistic effect of the combination of BDMPP and EG as well as MA offers an approach to enhance flame retardancy and smoke suppression.

KEYWORDS

bis([dimethoxyphosphoryl]methyl) phenyl phosphate, expandable graphite, flexible polyurethane foam, melamine, phosphorous flame retardant

1 | INTRODUCTION

Generally, polyurethanes (PU) are a class of copolymers composed of soft and hard segments. Usually, the soft segment is a polyester or a polyether polyol, whereas the hard segment is composed of isocyanate and maybe chain extender if needed.¹The soft segment determines elasticity, while the hard segment provides strength and rigidity. PU

with desired physical and mechanical properties can be produced by altering the ratio of the soft segment to the hard segment. For the past several decades, PU has been used frequently because of its wide range of applications in products such as foams, elastomers, adhesives, paints, and coatings. The PU foams are usually classified into rigid, semi-rigid, and flexible types, depending primarily on the density and degree of openness of the cells. Closed-cell rigid PU foam is used mainly for

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thermal insulation in buildings and refrigerators. Open-cell flexible PU foam (FPUF) is used as a cushion material in furniture, vehicles, and packaging. It is easy to ignite PU foams readily by a small flame source, and they burn quickly with a high rate of heat release because of their cellular structure, low density, and high hydrocarbon content.^{2–5} To reduce the possibility of fire, commercial additive-type flame retardants available on the market are simply physically mixed with the polymer matrix. Metal hydroxides, halogenated compounds, phosphorous compounds, melamine cyanurate, and intumescent products are commonly used as flame retardants in polymers.⁶ The concerns regarding health and environmental problems caused by halogenated flame retardants aroused interest among scientists in developing non-halogenated flame retardants. Interestingly, incorporating more than one type of flame retardant into the polymer matrix may bring a synergistic effect to flame retardancy.^{7,8} A synergistic effect means that the overall flame retardancy is even better than the superposition of the individual component's effects. Wilke et al. studied the synergetic effect between phosphorus and expandable graphite (EG) in thermoplastic styrene-ethylene-butylene-styrene elastomers.⁹ Rao et al. found that EG and phosphorus contributed to the compactness of char residue in FPUF.¹⁰ This is due to the gluing effect on the fluffy expanded graphite exerted by the phosphorous compound. They concluded that the intensity of synergism, which provides better flame retardancy to the material, increased significantly when the proper ratio of EG to phosphorus was applied. Feng et al. explored the synergistic effect between phosphorus and EG as well.¹¹ They showed that the system remarkably increased residual char yield and intensely reduced the fire parameters compared to the one using a single flame retardant. Synergistic action is apparent in the polymer matrix with phosphorus and nitrogen compounds. Yuan et al. synthesized phosphorous and melamine-derived polyol for rigid polyurethane foam and found out that the appropriate ratio between these components greatly improved the material's fire performance.¹² Phosphorus-nitrogen synergism in cotton cellulose was a focus of the work by Gaan and his coworkers.¹³ They proposed that the formation of a protective layer during the burning process was an observable effective synergism between phosphorus and nitrogen. The voluminous protective layer acted as a shield to prevent further burning of the underlying materials. By taking advantage of synergism, a smaller quantity of flame retardants can be used to maintain the physical and mechanical properties of the material. Among different phosphorous flame retardants, dimethyl methylphosphonate (DMMP) is an effective flame retardant because it contains a rather high content of phosphorus (25 wt%) compared to other phosphorous flame retardants, such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, triphenyl phosphate, triethyl phosphate, and aluminum diethylphosphinate. In this work, a liquid phosphorous flame retardant, bis([dimethoxyphosphoryl]methyl) phenyl phosphate (BDMPP), was combined with two commercial flame retardants, melamine (MA) and EG in FPUF. Zhou et al. proposed and compared BDMPP with dimethyl methylphosphonate (DMMP) in terms of fire properties; they found that BDMPP is more advantageous to flame retardancy than DMMP.¹⁴ BDMPP still contains a very high phosphorus content (22 wt%). BDMPP contains two kinds of phosphorus, phosphonate, and phosphate, since it is synthesized from dimethyl (hydroxymethyl)

phosphonate and phenyl dichlorophosphate. The presence of aromatic rings in BDMPP contributed to a better charring effect and an increased char yield in the condensed phase during burning. The molecular weight of BDMPP is higher than that of DMMP. Hence, BDMPP provided superior retainability to inhibit migration and volatilization. The current work focusses on the flame retardancy and fire performance of FPUF incorporated with BDMPP, MA, and EG.

2 | EXPERIMENTAL

2.1 | Materials

The chemicals used in the foaming formulation are described in Table 1. The materials listed in Table 1, except deionized water, were provided by Jiangsu Lvyuan New Material Co., Ltd. (Jiangsu, China).

For the flame retardants, EG flakes with an expansion ratio of 150–200 and particle size of 30–50 μm were supplied by Qingdao Xingyuan Colloidal Graphite Co., Ltd. (Qingdao, China). MA was purchased from Anhui Jinhe Chemical Co., Ltd (Shanghai, China). BDMPP was prepared by the State Key Laboratory of Fire Science, the University of Science and Technology of China, following the procedures described in Reference 14. The attention of readers interested in corresponding information on BDMPP is also turned to the original paper published on its synthesis.¹⁴

A set of foam samples were prepared at the State Key Laboratory of Fire Science, University of Science and Technology of China. Three additive-type flame retardants were used in the FPUF. One of the flame retardants is a liquid phosphorous flame retardant, shown in Figure 1, called bis([dimethoxyphosphoryl]methyl) phenyl phosphate

TABLE 1 Foaming formulation of flexible polyurethane foam

	Material	Weight (g)
Component A	Polyether polyol (330, hydroxyl value = 56 mg KOH/g, number average molecular weight = 3000 g/mol, average functionality = 3)	62.5
	Grafted polyether polyol (2045, prepared by the in situ polymerization of acrylonitrile and styrene in a polyether polyol, hydroxyl value = 20 mg KOH/g, number average molecular weight = 8400 g/mol, functionality = 3)	20.83
	Silicone oil	0.92
	Stannous octoate	0.15
	Triethylenediamine (A33, 33%)	0.23
	Dichloromethane	2.92
	Deionized water	2.67
Component B	Toluene diisocyanate (TDI 80/20, 80:20 mixture of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate)	38.33

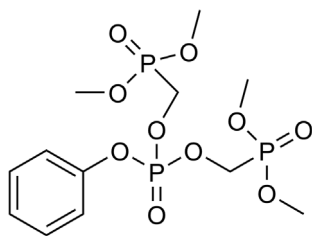


FIGURE 1 Bis([dimethoxyphosphoryl]methyl) phenyl phosphate (BDMPP)

(BDMPP). The rest are all commercial flame retardants, MA and EG. Each sample, except the reference sample FPUF, contains 20-phr of the polyether polyol and the grafted polyether polyol blended with a sole flame retardant or adual flame retardant. Table 2 shows the type and amount of flame retardants used in each sample. The additive flame retardants were weighted based on parts per hundred of the sum of polyether polyol and grafted polyether polyol.

2.2 | Sample preparation

The preparation of FPUF was conducted by mixing component A and component B using the one-pot method. The foams were prepared at 60°C for 20 min in a temperature controlled closed mold 200 × 200 × 100 mm (length×width×thickness) in size. First, component A was stirred uniformly in a disposable polypropylene cup by a high-speed stirrer for 3 min. Afterward, component B was mixed with the blended component A for few seconds under a high stirring rate. Then the mixture was discharged into the mold. The foam was cured for 24 h in an oven at 80°C to complete the polymerization.

2.3 | Measurements and characterization

2.3.1 | Morphological characterization

The micrographs of the foams and their char residues were examined using a scanning electron microscope (SEM) Zeiss EVO 10 (Oberkochen, Germany). The acceleration voltage was set to 10 kV. The specimens were sputter-coated with 15 nm of gold to reduce the chances of electrostatic charging. Only the foam structure at the surface, the direct interface with the mold, shows a skin accompanied with a thin layer of smaller cell size and higher density. We prepared and investigated only specimens cut out from the inner homogenous part of the foams.

2.3.2 | Physical and mechanical properties measurements

The apparent density of the specimen was measured according to ISO 845. A Universal Testing Machine Zwick Z010 (Ulm, Germany) was used to evaluate the tensile strength, elongation at break, and compression

TABLE 2 Content of flame retardants in the samples

Sample	Flame retardants (in phr ^a)
FPUF	—
FPUF-20BDMPP	20-phr BDMPP
FPUF-20MA	20-phr MA
FPUF-20EG	20-phr EG
FPUF-5BDMPP-15MA	5-phr BDMPP and 15-phr MA
FPUF-10BDMPP-10MA	10-phr BDMPP and 10-phr MA
FPUF-15BDMPP-5MA	15-phr BDMPP and 5-phr MA
FPUF-5BDMPP-15EG	5-phr BDMPP and 15-phr EG
FPUF-10BDMPP-10EG	10-phr BDMPP and 10-phr EG
FPUF-15BDMPP-5EG	15-phr BDMPP and 5-phr EG

^aphr, Parts per hundred of the sum of polyether polyol and grafted polyether polyol.

strength. A load cell with 500 N was used, the speed of the power-actuated grip was 500 mm/min for the tensile test. The strain rate was 100 mm/min for the compression test. The tensile strength and elongation at break were measured using specimens with a thickness of 10 mm cut as test piece type 1A following ISO 1798, while the compressive strength was measured according to ISO 3386-1. The specimen size for determining the compression was 40 × 30 × 10 mm (length×width×thickness). 3 cycles of compression were performed for the compression test. Four and three test specimens were measured for each material in the tensile test and the compression test, respectively.

2.3.3 | Pyrolysis: Mass loss and evolved gases

Thermogravimetric analysis (TGA) records the change in the mass of a sample as a function of time under a nitrogen atmosphere using a TG 209 F1 Iris from Netzsch Instruments (Selb, Germany), thereby determining the thermal decomposition behavior of the samples. The alumina crucible with 10 mg of the powdered sample was then put on the thermo-microbalance of the TGA device. The samples were subjected to a heating program under a constant nitrogen gas flow of 30 ml/min at a steady heating rate of 10 K/min. Simultaneously, TGA coupled with Fourier transform infrared spectroscopy (FTIR), Brucker Tensor 27 FT-IR (Ettlingen, Germany) analyzes the gaseous pyrolysis products evolved from the specimens in the furnace.

2.3.4 | Fire behavior

Before the measurements, all test specimens were stored at 23°C and 50% relative humidity for a minimum of 48 h. The limiting oxygen index (LOI) of the specimens 150 × 10 × 10 mm (length×width×thickness) in size was determined at room temperature according to ISO 4589-2. The fire behavior was analyzed using a cone calorimeter from Fire Testing Technology Limited (West Sussex, United Kingdom), and the test was carried out in accordance with ISO 5660. The specimen for the

cone calorimeter is $100 \times 100 \times 50$ mm (length $\times$ width $\times$ thickness) in size. The specimen placed in an aluminum foil container was exposed in the horizontal orientation to a radiative heat flux of 25 kW m^{-2} with a distance of 25 mm between the cone heater and the surface of the specimen. All materials showed an impressive repeatability and thus were only measured twice in the cone calorimeter. UL 94 HBF is used to measure the burning rate and evaluate the tendency of the materials to either extinguish or spread the flame when the specimen has been ignited. It was performed to determine the horizontal burning characteristics following ISO 9772 with a specimen size of $150 \times 50 \times 10$ mm (length $\times$ width $\times$ thickness). The number of specimens for LOI and UL 94 were according to the standards.

3 | RESULTS AND DISCUSSION

3.1 | Morphological characterization and mechanical properties measurements

The morphology is a critical factor that influences the physical and mechanical properties of FPUF. A scanning electron microscope

(SEM) was used to observe the morphology of foams, and the SEM images are displayed in Figure 2. All foams show a semi-open cell structure. The FPUF in Figure 2A has smoother edges on the blow-holes, uniform cell size, and even cell distribution. Generally, high loading of additive-type flame retardants must be incorporated into the polymer matrix for better flame retardancy. Therefore, the high content of additive-type flame retardants is often detrimental to the mechanical properties, as they function mainly as a nucleating agent. The SEM images show the influence of flame retardants on cellular structures. FPUF-20BDMPP, and FPUF-20MA in Figure 2B,C, respectively, show a similar structure with cells slightly larger than in FPUF. The SEM images of FPUF-20EG and FPUF-BDMPP-EGs show less continuous and less regular spherical cell structure. This phenomenon was attributed to nucleation triggered by EG particles in the polymer matrix.^{15–16} EG is a kind of solid particle that affects bubble nucleation and bubble growth in the foaming process, thereby damaging the foam's structure to some extent. Especially for FPUF-10BDMPP-10EG shown in Figure 2I, the struts are somewhat thicker, and the cellular structure is somewhat less complete than the others.

Density is a major parameter affecting foam flexibility and support. The apparent density of the flame retardant samples shown in Table 3

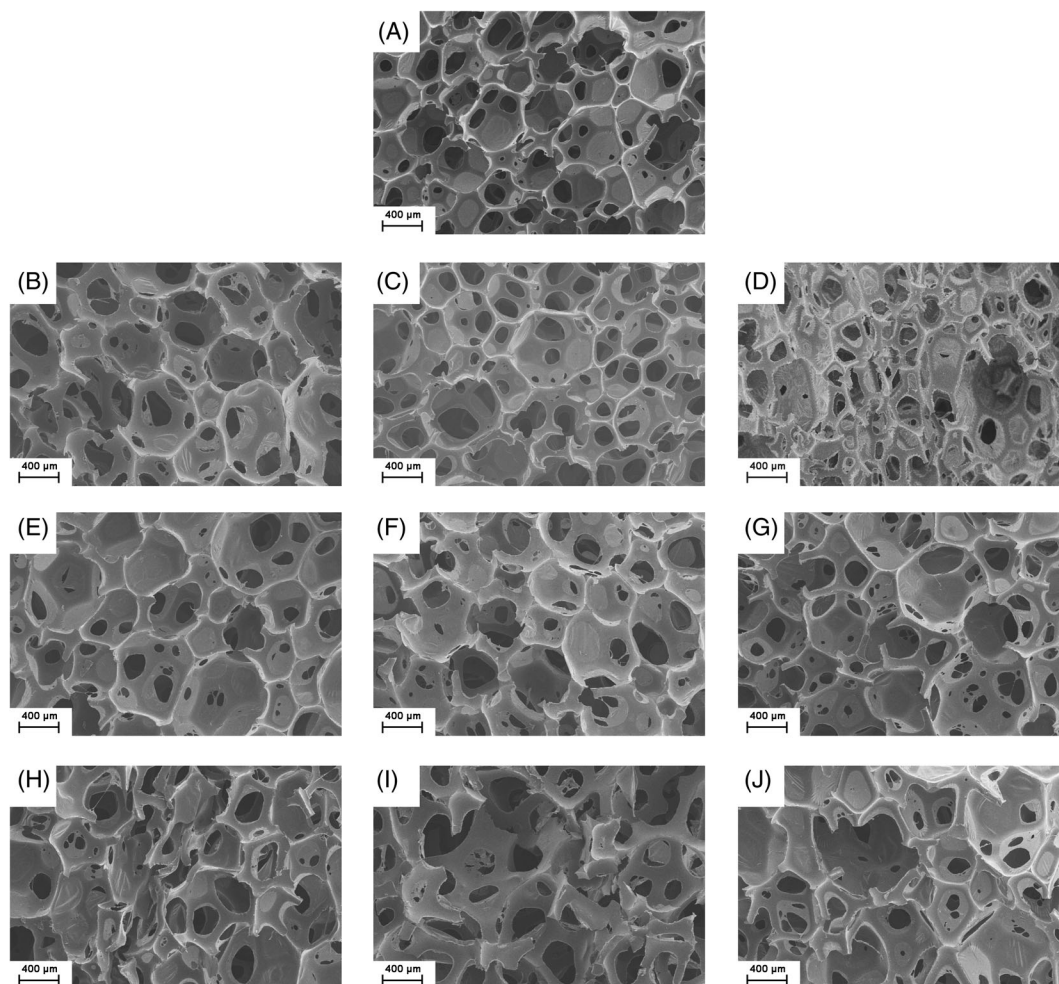


FIGURE 2 SEM images of (A) FPUF, (B) FPUF-20BDMPP, (C) FPUF-20MA, (D) FPUF-20EG, (E) FPUF-5BDMPP-15MA, (F) FPUF-10BDMPP-10MA, (G) FPUF-15BDMPP-5MA, (H) FPUF-5BDMPP-15EG, (I) FPUF-10BDMPP-10EG, (J) FPUF-15BDMPP-5EG

TABLE 3 Mechanical test results of the samples

Sample	Tensile strength (kPa)	Elongation at break (%)	Compression stress value at 40% compression (CV ₄₀) (kPa)	Apparent density (kg m ⁻³)
FPUF	126 ± 13	138 ± 9	6.61 ± 0.13	34.2 ± 0.4
FPUF-20BDMPP	140 ± 16	140 ± 16	6.37 ± 0.21	40.1 ± 2.2
FPUF-20MA	102 ± 13	91 ± 15	6.34 ± 0.12	34.4 ± 0.7
FPUF-20EG	156 ± 9	111 ± 11	6.08 ± 0.20	35.9 ± 2.3
FPUF-5BDMPP-15MA	94 ± 11	87 ± 16	6.67 ± 0.87	37.9 ± 2.3
FPUF-10BDMPP-10MA	93 ± 10	96 ± 11	5.30 ± 0.29	40.2 ± 0.5
FPUF-15BDMPP-5MA	54 ± 9	104 ± 14	1.99 ± 0.19	33.8 ± 0.7
FPUF-5BDMPP-15EG	139 ± 4	151 ± 4	5.98 ± 0.75	38.9 ± 3.4
FPUF-10BDMPP-10EG	112 ± 4	145 ± 8	4.22 ± 0.09	42.0 ± 8.8
FPUF-15BDMPP-5EG	54 ± 14	83 ± 17	2.84 ± 0.53	33.7 ± 0.9

ranges from 33.7 to 42 kg m⁻³, which is comparable to the FPUF. FPUF-20BDMPP exhibits the highest density among the FPUFs with other single flame retardants. For the FPUFs containing two flame retardants, FPUF-10BDMPP-10EG shows the highest density. FPUF-15BDMPP-5MA and FPUF-15BDMPP-5EG show the lowest density. Additive flame retardants often show an adverse effect on the density of foams. Here in this study, no significant change occurred in the density of the foams.

The mechanical properties of FPUFs were evaluated by measuring their tensile strength, elongation at break, and compression. The data are listed in Table 3. Apart from foam density, the additives themselves influence the mechanical properties. The value for the tensile strength of FPUF-20EG is the highest of all the samples, which means the EG improved the tensile strength of FPUF. This effect of EG is also obvious in FPUF-5BDMPP-15EG and FPUF-10BDMPP-10EG. Among the FPUFs with 20-phr of a single flame retardant, FPUF-20MA has the lowest tensile strength and elongation at break, but still has good mechanical properties. The melamine particles weakened the structure by stiffening the cellular network.¹⁷ This effect of MA can also be observed in FPUF-5BDMPP-15MA and FPUF-10BDMPP-10MA. For the FPUFs with the combination of two flame retardants, the incorporation of 15-phr BDMPP with either 5-phr MA or 5-phr EG in FPUF significantly reduces tensile strength and compression stress/strain characteristic at 40% compression (CV₄₀) because of the lower density and detrimental effects to the mechanical properties caused by the two flame retardants. Apart from FPUF-15BDMPP-5MA and FPUF-15BDMPP-5EG, all the other seven foams showed very similar mechanical properties compared to FPUF. Thus, the mechanical properties of the foam depend on the amount and the type of flame retardant added.

3.2 | Pyrolysis: Mass loss

The thermal decomposition behavior of the FPUFs was investigated. The pyrolysis of organic content typically generates volatile products

and leaves mostly carbonaceous char as residue. TGA measured the mass loss of the FPUFs during the pyrolysis process under a nitrogen atmosphere. Figure 3 shows the mass and the first derivative of mass loss (DTG) curves, and Table 4 records the selected data. $T_{5\%}$ and $T_{\max}$ are the temperatures where 5-wt% mass loss and maximum mass loss occurred, respectively. All FPUFs went through two distinguishable decomposition steps based on the chemical structure of the FPUF.¹⁸ There is no additional separated minor decomposition step happening at lower temperatures, an early decomposition or release of BDMPP were ruled out. The first weight loss is related to the urethane bond's cleavage, while the second step is attributed to the decomposition of the hydrocarbon chains.^{19,20} FPUF-20BDMPP shows the lowest $T_{5\%}$ at approximately 220°C, which is due to the interaction between polyurethane decomposition and the phosphorous compounds of BDMPP decomposition.^{2,21} Among the FPUFs incorporated with a sole retardant, 8.2 and 7.5-wt% of char yield were measured for FPUF-20BDMPP and FPUF-20EG, respectively, while there was no significant degree of charring for FPUF-20MA. It is evident that BDMPP and EG worked in the condensed phase, while MA did not. Phosphorous compounds enhanced carbonization, while EG yielded intumescence and remained in the crucible because EG cannot evaporate during thermal decomposition.^{22,23} The amount of char residue of all FPUF-BDMPP-EGs is greater than that of either FPUF-20BDMPP or FPUF-20EG. The synergistic effect caused by the combination of BDMPP and EG was attributed to the phosphorous flame retardant, which generates char-forming catalysts, increasing the char yield during thermal decomposition.^{10,24} FPUF-20EG shifted the first and second decomposition steps towards the highest temperature ($T_{\max} \#1 = 313^\circ\text{C}$ and $T_{\max} \#2 = 383^\circ\text{C}$) among all the samples, which indicates that 20-phr EG enhanced the thermal stability of the system.

3.3 | Pyrolysis: Evolved gas analysis

The evolved gaseous products during thermal decomposition under nitrogen atmosphere were determined using TG-FTIR. The TG-FTIR were performed to characterize how the single flame retardant work,

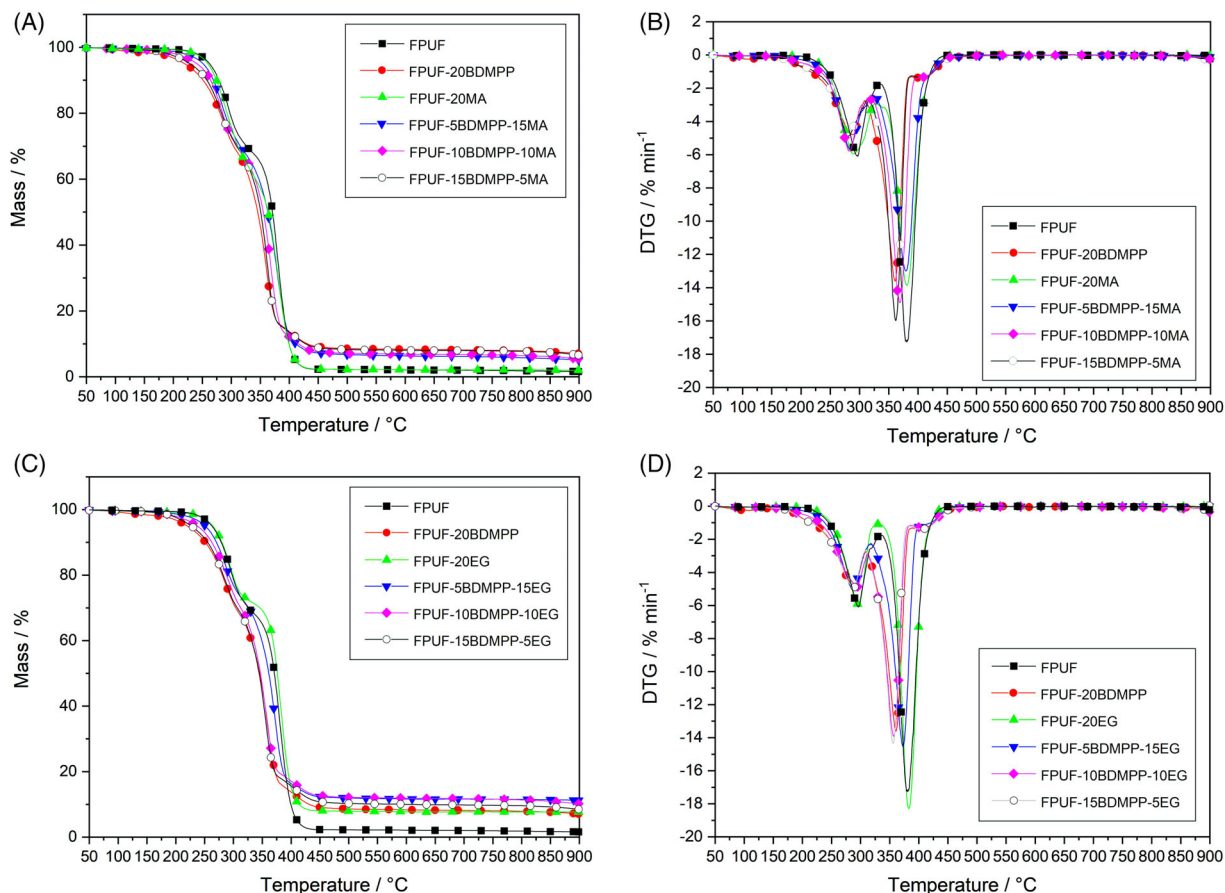


FIGURE 3 Thermogravimetry-(A) mass curves and (B) DTG curves of FPUF-BDMPP-MAs; (C) mass curves and (D) DTG curves of FPUF-BDMPP-EGs

TABLE 4 Selected thermogravimetry results obtained from the mass and DTG curves of FPUFs

Material	$T_{5\%}$ (°C)	$T_{\max}$ #1 (°C)	$T_{\max}$ #2 (°C)	Mass change #1 (wt%)	Mass change #2 (wt%)	Residue at 700°C (wt%)
FPUF	263	297	380	31.2	65.7	1.6
FPUF-20BDMPP	220	288	360	29.3	60.5	8.2
FPUF-20MA	260	290	381	34.7	62.7	2.0
FPUF-20EG	265	313	383	27.4	64.4	7.5
FPUF-5BDMPP-15MA	252	284	379	32.5	62.2	5.7
FPUF-10BDMPP-10MA	242	282	369	31.6	61.0	6.9
FPUF-15BDMPP-5MA	229	281	362	30.2	60.8	7.9
FPUF-5BDMPP-15EG	251	287	372	27.1	60.4	11.8
FPUF-10BDMPP-10EG	238	295	356	29.3	59.2	11.6
FPUF-15BDMPP-5EG	228	289	356	29.3	59.9	9.9

Abbreviations: $T_{5\%}$, the temperature at 5% mass loss; $T_{\max}$ #1, the first maximum mass loss rate; $T_{\max}$ #2, The second maximum mass loss rate.

particular which one is releasing phosphorus in the gas phase. Apart from that, the limited change in TG curves yields evolved gas analysis being of minor importance for understanding the fire behavior. As shown in Figure 4A, some characteristic bands were detected during the pyrolysis process. The noisy signals in the ranges of 2150–1250 and 4000–3400 cm^{-1} are related to the water vapor produced during thermal decomposition. The peaks of CO_2 (2360 and 670 cm^{-1}) were

observed.²⁵ The peak at 2276 cm^{-1} is attributed to the stretching vibration of $\text{N}=\text{C}=\text{O}$. From about 340°C, the transmittance intensity at 2276 cm^{-1} of $-\text{NCO}$ disappeared. This indicates that $\text{N}=\text{C}=\text{O}$ is the main product generated in the first stage of decomposition.^{26,27} The broad peaks at 3000–2850 cm^{-1} at 340 to 440°C are attributed to hydrocarbons.²⁸ Therefore, the major products in the second stage are hydrocarbons. The peaks at 1734 and 1363 cm^{-1} correspond to

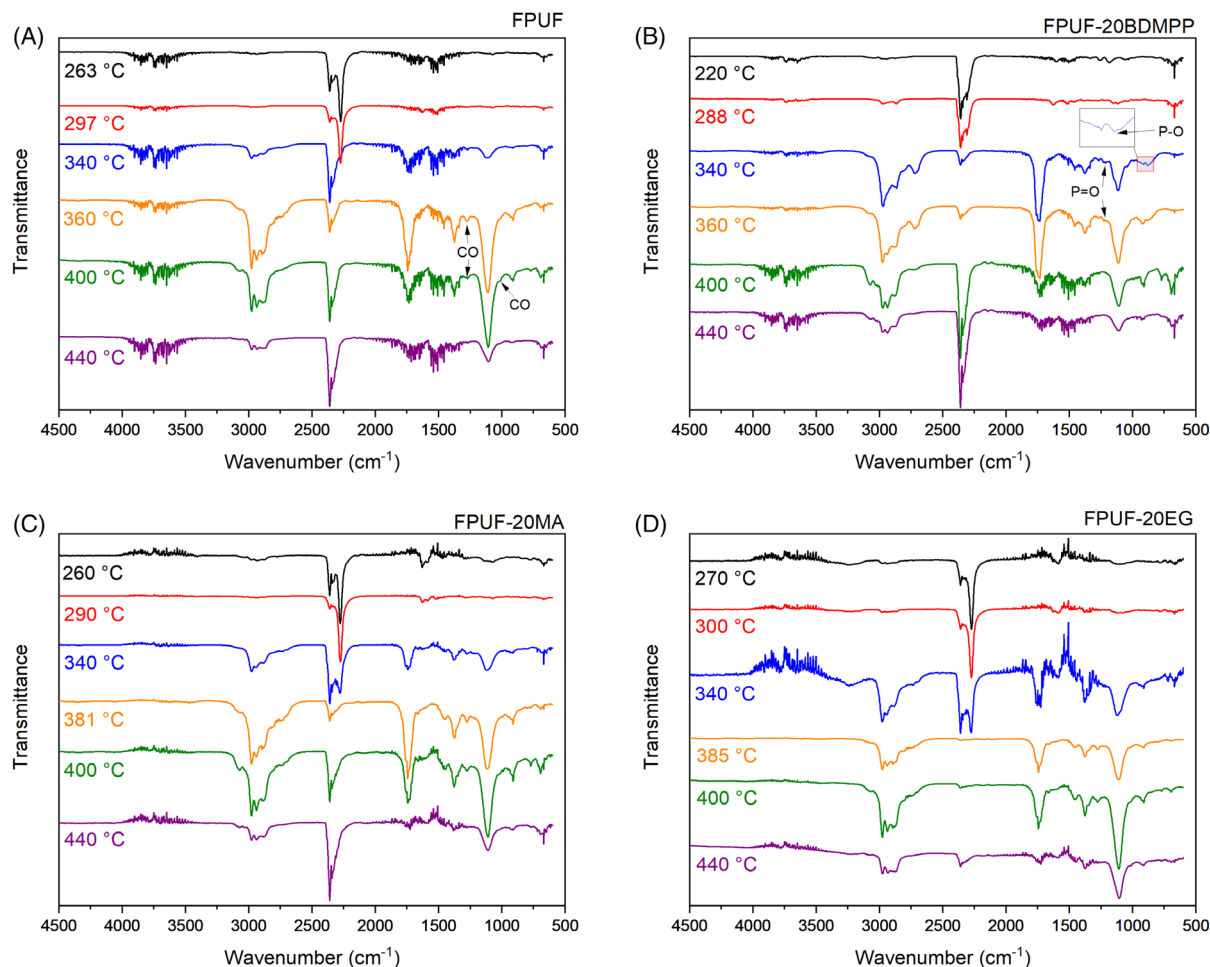


FIGURE 4 TG-FTIR spectra of the gas phase in the thermal degradation of (A) FPUF, (B) FPUF-20BDMPP, (C) FPUF-20MA, and (D) FPUF-20EG at different pyrolysis temperatures

the stretching vibration of the carbonyl compound.²⁸ The peaks at 1272 and 1110 cm^{-1} are attributed to C—O stretching. Figure 4B shows that the peaks at 1218 and 880 cm^{-1} are attributed to P=O and P—O, respectively.²⁶ The phosphorous moieties are released mainly during the second stage of decomposition. As a result, the fragments composed of phosphorus in the gas phase provide a radical quenching effect during combustion. As shown in Figure 4C, the peak at 1660 cm^{-1} is attributed to the triazine ring of melamine.²⁹ The nitrogen from MA produced by combustion acts as an inert diluent, diluting the fuel gases. There are smaller peaks in Figure 4D at 2400–2300 cm^{-1} and 670 cm^{-1} related to CO_2 in the range from 383 to 400 °C. This is probably due to the presence of EG, which may produce more stable char residue to change the CO_2 release. In conclusion, the results agree with the decomposition pathway of FPUF described in the literature.³⁰

3.4 | Fire behavior: Reaction to the small flame

The limiting oxygen index (LOI) is a measure of the minimum percentage of oxygen in a mixture of oxygen and nitrogen gases required to

support the combustion of materials in a candle-like setup. Table 5 lists the LOI value of the samples. All the FPUFs with flame retardants show improvement in the LOI values. The improvements are somewhat limited prospecting for further development. Nevertheless, considering that foams were investigated and there is no significant difference in morphology and density the increase in LOI is assessed to be meaningful. When 20-phr BDMPP, MA, or EG was added to FPUF, the LOI values increase, and their values are very similar: 20.0, 20.4, and 20.8 vol%, respectively. However, FPUFs with a single flame retardant exhibit typical LOI values of foams, limiting flame retardancy to FPUF. The LOI value of FPUFs containing different proportions of BDMPP and MA remains the same as those with single flame retardants. Nevertheless, it is notable that FPUF-5BDMPP-15EG achieved the highest LOI value among all the samples. With an increase of 3.6 to 22.2 vol%. FPUF-10BDMPP-10EG shows the second highest LOI value, 21.8 vol%. The higher EG content in FPUF-BDMPP-EGs provides the polymer with better fire protection, as observed in this case. Therefore, the optimal ratio of BDMPP to EG in FPUF-BDMPP-EGs that produces the greatest synergy is 1: 3.³¹

The results in Table 6 show that all the modified samples exhibit different degrees of improvement to flame retardancy in the UL

94 HBF test as compared to FPUF. FPUF burned entirely with the fastest burning rate and significant dripping behavior. The burning rate of all the foams with 20-phr of either a single or dual flame retardant(s) decreased compared to that of FPUF (120 mm/min). The EG contributed effectively to slowing down the burning rate. Due to the formation of a dense carbon layer, all samples with EG completely stopped the melt dripping. The expanded graphite served as a carrier to retain the polymer melt. Compared to FPUF-20EG, FPUF-5BDMPP-15EG exhibited a lower burning rate and exhibited self-extinguishing behavior, even though less EG was added. This is because the synergistic effect was exerted by BDMPP and EG. The gluing effect of BDMPP strengthened the integrality and continuity of the EG char layer.^{32,33} The burning rate of FPUF-5BDMPP-15MA was lower than that of FPUF-20BDMPP and FPUF-20MA. This indicates that 5-phr of BDMPP with either 15-phr of EG or 15-phr MA in the FPUF is enough to yield a remarkable synergistic effect in flame retardancy.

3.5 | Fire behavior: Cone calorimeter

A cone calorimeter is used to evaluate a comprehensive set of fire properties such as time of ignition (t_{ig}), peak heat release rate (PHRR),

total heat release (THR), average effective heat of combustion (EHC), residue, total smoke released (TSR) and the maximum average rate of heat emission (MARHE) in the fire scenarios of developing fires. Heat release rate (HRR) and THR curves of FPUF-BDMPP-MAs and FPUF-BDMPP-EGs are displayed in Figure 5. The measured data are presented in Table 7.

Typically, the HRR curve of FPUF consists of the two peaks associated with two-step decomposition, which is concluded from the result of TGA in accordance with the literature.^{34,35} The first decomposition step corresponds to the breaking of the urethane bond in PU, while the soft segment dominates the second step. The HRR curve of FPUF shows two peaks of heat release rate, where the second peak (pHRR at 503 kW m^{-2}) is higher than that of the first peak (pHRR at 294 kW m^{-2}). The t_{ig} is usually very short because of the low heat conductivity of FPUFs. At the first peak, the material was ignited, and the cellular structure started to collapse, thus producing volatile and liquid fragments. These liquid fragments produced more heat by oxidation and quickly developed a feedback loop. Subsequently, this feedback loop at the second peak with a high HRR formed a pool fire, and the sample burned intensively. After that, as the fuel was consumed, HRR dropped rapidly until the flame went out.^{36,37} Figure 5 (A1) shows that the HRR curves of the FPUFs with flame retardant(s) are similar to those of FPUF, with two explicit HRR peaks and the second peak higher than the first.

The EHC monitored in the cone calorimeter is a product of the effective heat of combustion of the volatiles and the combustion efficiency of the flame. The fuel dilution, reducing the effective heat of combustion of the volatiles, and flame inhibition, reducing mainly the combustion efficiency in the flame, reduce the EHC. Therefore, EHC is an important parameter to measure the activity of flame retardants in the gas phase. A reduction in EHC is observed for all flame retarded samples in Table 7, indicating that all flame retardants exerted different degrees of flame retardant effects in the gas phase. Among the FPUFs containing a single flame retardant, the best result in terms of EHC was achieved by FPUF-20BDMPP (22 MJ kg^{-1}). The EHC of FPUF-20BDMPP reduces by more than 14% when compared to the that of FPUF. This showed that the BDMPP plays an important role as a flame retardant through flame inhibition in the gas phase.³⁸ As

TABLE 5 LOI measurement

Sample	LOI/vol%
FPUF	18.6 ± 0.2
FPUF-20BDMPP	20.0 ± 0.2
FPUF-20MA	20.4 ± 0.1
FPUF-20EG	20.8 ± 0.2
FPUF-5BDMPP-15MA	20.0 ± 0.2
FPUF-10BDMPP-10MA	20.2 ± 0.1
FPUF-15BDMPP-5MA	20.6 ± 0.1
FPUF-5BDMPP-15EG	22.2 ± 0.2
FPUF-10BDMPP-10EG	21.8 ± 0.2
FPUF-15BDMPP-5EG	20.6 ± 0.1

TABLE 6 Result of UL 94 horizontal burning tests

Material	Burning time (s)	Distance burned (mm)	Burning drops	Burning rate (mm/min)
FPUF	50	100	Yes	120
FPUF-20BDMPP	63	100	Yes	95
FPUF-20MA	108	100	Yes	56
FPUF-20EG	46	15	No	20
FPUF-5BDMPP-15MA	131	100	Yes	46
FPUF-10BDMPP-10MA	69	100	Yes	87
FPUF-15BDMPP-5MA	70	100	Yes	86
FPUF-5BDMPP-15EG	34	5	No	9
FPUF-10BDMPP-10EG	205	100	No	29
FPUF-15BDMPP-5EG	72	100	No	83

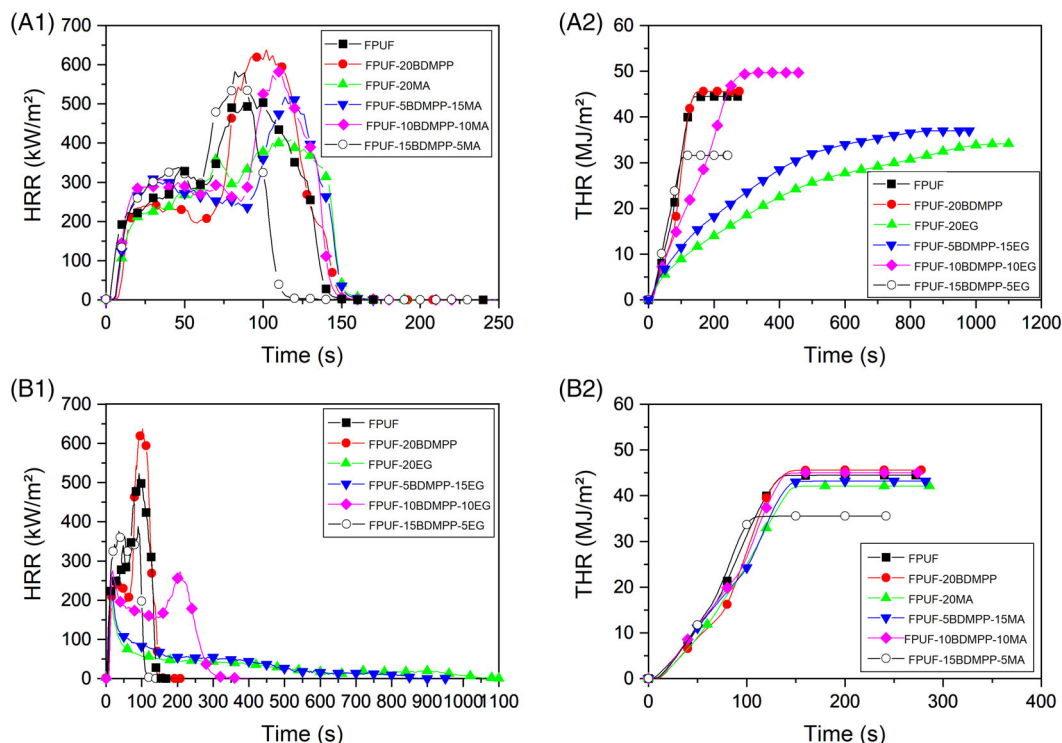


FIGURE 5 (A1) Heat release rate and (A2) total heat release rate of FPUF-BDMPP-MAs; (B1) heat release rate and (B2) total heat release rate of FPUF-BDMPP-EGs

TABLE 7 Table of cone calorimeter results

Sample	t_{ig} /s $\pm$ 1 s	PHRR /kW m ⁻²	THR /MJ m ⁻²	TML/g	Av. EHC/MJ kg ⁻¹	Residue/ wt%	TSR /m ² m ⁻²	MARHE/ kW m ⁻²
FPUF	6	503 $\pm$ 20	43.3 $\pm$ 0.1	16.9 $\pm$ 0.4	25.6 $\pm$ 0.6	0 $\pm$ 0.3	392 $\pm$ 4	320 $\pm$ 13
FPUF-20BDMPP	7	586 $\pm$ 52	42.3 $\pm$ 0.8	19.2 $\pm$ 0.8	22.0 $\pm$ 0.5	2.9 $\pm$ 1.9	946 $\pm$ 132	325 $\pm$ 7
FPUF-20MA	4	391 $\pm$ 20	40.3 $\pm$ 0.9	16.6 $\pm$ 0.2	24.3 $\pm$ 0.3	2.2 $\pm$ 0.8	299 $\pm$ 2	276 $\pm$ 11
FPUF-20EG	5	183 $\pm$ 19	16.2 $\pm$ 4.5	6.8 $\pm$ 1.7	23.6 $\pm$ 0.6	63.1 $\pm$ 7.7	52 $\pm$ 26	109 $\pm$ 10
FPUF-5BDMPP-15MA	5	523 $\pm$ 5	41.8 $\pm$ 0.9	18.2 $\pm$ 0.2	23.0 $\pm$ 0.1	4.6 $\pm$ 0.1	641 $\pm$ 22	310 $\pm$ 13
FPUF-10BDMPP-10MA	5	564 $\pm$ 18	43.1 $\pm$ 0.8	18.8 $\pm$ 0.2	22.9 $\pm$ 0.2	5.3 $\pm$ 0.4	757 $\pm$ 8	314 $\pm$ 8
FPUF-15BDMPP-5MA	4	559 $\pm$ 24	35.6 $\pm$ 0.4	16.1 $\pm$ 0.4	22.1 $\pm$ 0.3	4.7 $\pm$ 0.4	789 $\pm$ 36	328 $\pm$ 9
FPUF-5BDMPP-15EG	4	213 $\pm$ 27	22.4 $\pm$ 5.8	10.3 $\pm$ 2.0	21.4 $\pm$ 1.4	47.4 $\pm$ 4.7	204 $\pm$ 73	130 $\pm$ 17
FPUF-10BDMPP-10EG	5	252 $\pm$ 23	40.4 $\pm$ 8.0	18.3 $\pm$ 3.6	22.0 $\pm$ 0.1	12.3 $\pm$ 1.8	987 $\pm$ 291	173 $\pm$ 15
FPUF-15BDMPP-5EG	4	346 $\pm$ 42	31.6 $\pm$ 0.7	15.7 $\pm$ 0.2	20.1 $\pm$ 0.2	3.8 $\pm$ 1.5	998 $\pm$ 37	280 $\pm$ 28

Abbreviations: av, average; EHC, effective heat of combustion; MARHE, maximum average rate heat emission; PHRR, peak heat release rate; t_{ig} , time to ignition; THR, total heat release; TML, total mass loss; TSR, total smoke release.

concluded from the evolved gas analysis, radical scavenging occurred because phosphorus was released from BDMPP.³⁹ The presence of EG also showed a significant reduction in EHC. We hypothesize three contributions that could explain this phenomenon. EG created a protection layer, which caused incomplete pyrolysis in the second stage of burning. The second stage of burning generally corresponds mainly to the second step of pyrolysis. In PU the second stage of burning is usually characterized by a higher EHC.¹⁸ Reducing the contribution of the second stage of burning results in a reduced contribution of the second decomposition step to the pyrolysis products, and thus

reduces EHC. The second reason is the strongly increased charring in FPUF-20EG, which means that mainly graphitized carbon is stored with a higher effective heat of combustion than the PU. Thus, in the case of PU, increased charring goes along with emitting volatiles with a lower EHC than PU.³⁸ The last minor reason is that EG is treated with sulfuric acid as an intercalation reagent. During burning, the oxidation reaction of H₂SO₄ releases inert gases such as CO₂, SO₂, and H₂O, which dilute the combustible gas.^{16,40,41} Compared to other flame retardants, MA only shows a small effect on EHC through some fuel dilution. The FPUFs with the combination of BDMPP and EG,

especially FPUF-15BDMPP-5EG (20.1 MJ kg⁻¹), exhibit significant reduction in EHC values. The EHC of FPUF-15BDMPP-5EG reduced more than 21% compared with that of FPUF. As can be seen from this phenomenon, there was a synergistic effect between BDMPP and EG in the gas phase.

The pHRR of FPUF-20MA was reduced by 22% because MA acts as a heat sink to increase the heat capacity of the system and limits the increase in surface temperature of FPUF. Hence, MA reduces the generation rate of volatile fuel and decreases the pHRR effectively.⁴² Considering Figure 5(A2), the burning time and THR of FPUF-15BDMPP-5MA are reduced significantly compared to those of either

FPUF-20BDMPP or FPUF-20MA. Therefore, a synergistic effect was observed between 15-phr BDMPP and 5-phr MA in FPUF.

Even with the low loadings of EG presented in the system, the shape of the HRR curve was clearly changed. The addition of higher EG content led to a profound reduction in the PHRR, as the peaks became significantly smaller, with the curves much flatter. EG provides for significant charring, leading to the formation of a thermal insulating barrier which slows down the transfer of heat and mass within the pyrolysis zone for further decomposition in the condensed phase. The expanded graphite increases the thickness of the char layer to prolong the time of burning. This can be explained in detail with the cone calorimeter data

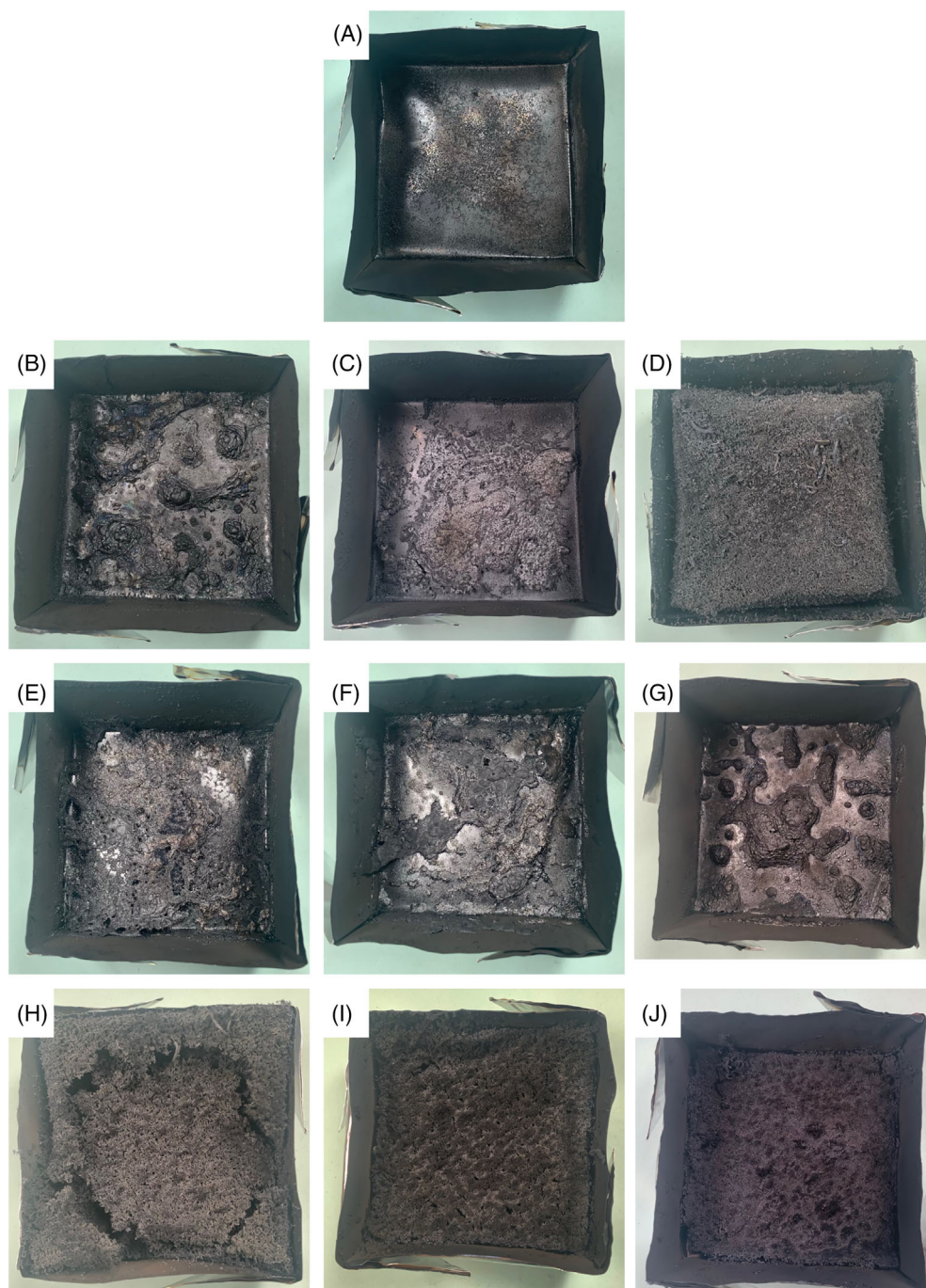


FIGURE 6 Fire residue images of (A) FPUF, (B) FPUF-20BDMPP, (C) FPUF-20MA, (D) FPUF-20EG, (E) FPUF-5BDMPP-15MA, (F) FPUF-10BDMPP-10MA, (G) FPUF-15BDMPP-5MA, (H) FPUF-5BDMPP-15EG, (I) FPUF-10BDMPP-10EG, (J) FPUF-15BDMPP-5EG

and the fire behavior of FPUF-20EG. At the beginning of the curve, the polymer matrix was under heat exposure, and thus the HRR increased swiftly. After the first sharp peak, the HRR dropped quickly because the EG expanded under heat, and acted as an excellent protective layer to save the material underneath.

THR is a measure of the entire amount of heat energy evolved during the burning time of the material. The THR decreased drastically from 43.3 MJ m^{-2} for the non-flame retarded foam to 16.2 MJ m^{-2} for FPUF-20EG. The reduced value indicates that the expanded graphite formed protective layer, providing an excellent shielding

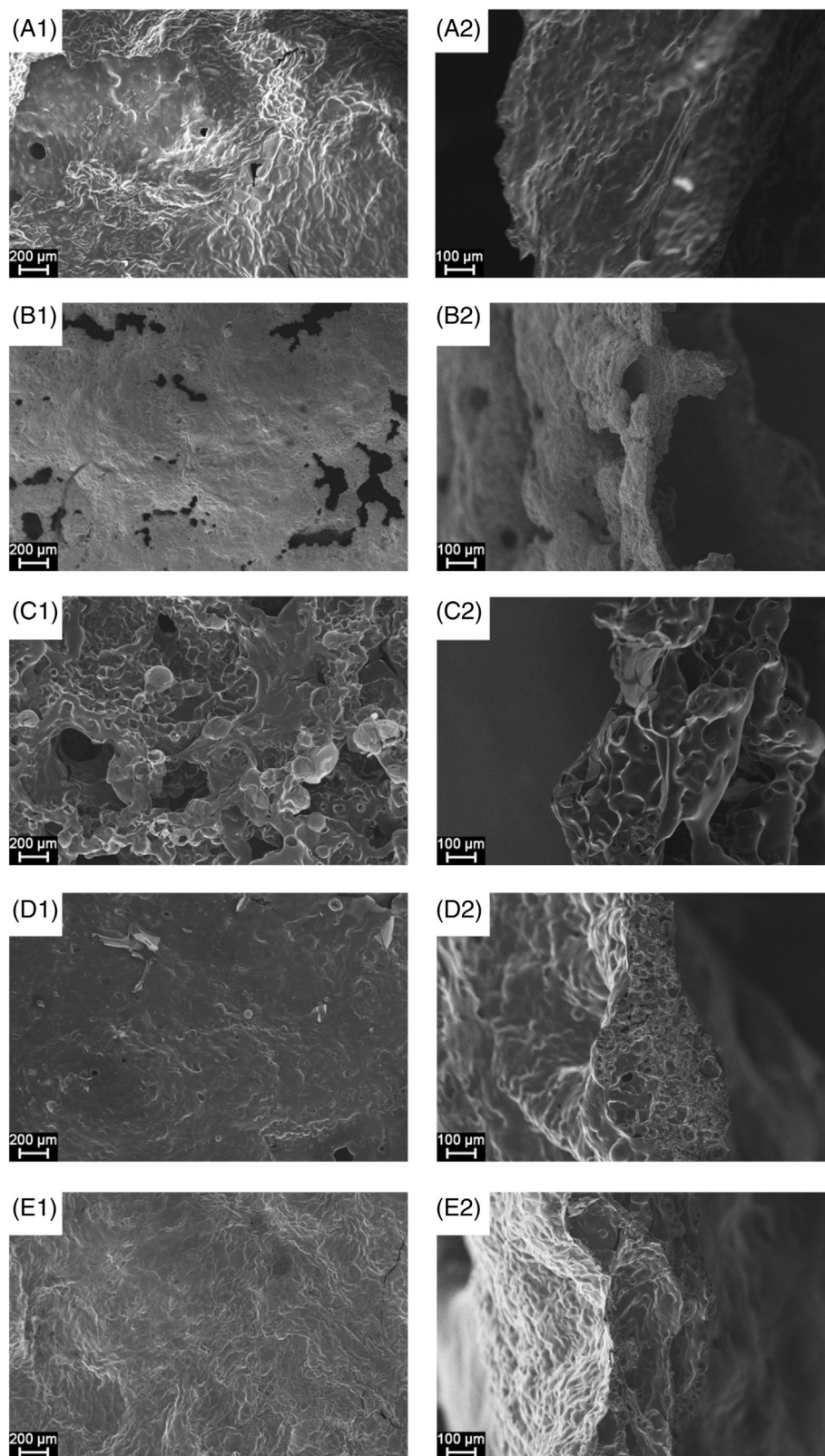


FIGURE 7 (A1) Surface and (A2) side view of FPUF-20BDMPP; (B1) surface and (B2) side view of FPUF-20MA; (C1) surface and (C2) side view of FPUF-5BDMPP-15MA; (D1) surface and (D2) side view of FPUF-10BDMPP-10MA; (E1) surface and (E2) side view of FPUF-15BDMPP-5MA

effect to the material underneath and leading to incomplete combustion. As combined with the results from the EHC and the yield of residue, the charring effect of EG in the condensed phase caused the major reduction in THR.

MARHE is one of the fire hazard indices of developing fires under a real-scale fire scenario. This is used to determine the combustibility of a material. The MARHE value of FPUF-20EG is reduced remarkably, to almost onethird that of the non-flame retarded foam. The FPUF-BDMPP-MAs show no changes in MARHE, but the FPUF-BDMPP-EGs lowered the value significantly. Based on the results for MARHE, EG is apparently an effective additive to reduce the MARHE.

The TSR of FPUF-20BDMPP is $946 \text{ m}^2 \text{ m}^{-2}$, which indicates that BDMPP generates a large amount of smoke. This value is nearly 2.5 times that of FPUF. FPUF-20MA and FPUF-20EG greatly suppressed the smoke. Melamine acts as an inert diluent in the gas phase to reduce smoke emission.⁴³ D. Price et al. showed a chemical interaction between the melamine and the isocyanate at temperatures over 250°C through the reaction between $-\text{NH}_2$ and $-\text{NCO}$. This interaction suppressed the smoke produced from isocyanate.⁴² The great charring ability of EG produced a compact carbonaceous char that could limit the release of aromatic hydrocarbons to form smoke from the condensed phase into the gas phase.

3.6 | Fire residues

Figure 6 shows the images for the char residue of FUPFs after cone calorimeter measurement. FPUF in Figure 6A was consumed completely after burning and almost no residue remained. Figure 6B, C, E, F, G display a thin layer of fragile inorganic residue that remained in the aluminum foil tray. The micrographs of the FPUFs with EG (Figure 6D, H, I, J) show that the char layer formed during burning provided a thermal insulation barrier to protect the inner polymer matrix and to prevent further decomposition. According to Figure 6H, I, J, the integrity of expanded graphite residue was retained due to the presence of a sufficient amount of BDMPP.⁴⁴ The gluing effect by the phosphorous compound reinforced the integrity and continuity of the char layers, resulting in an enhanced barrier formed in the condensed phase.^{32,45}

Figure 7 shows SEM images of the fire residue of FPUF-BDMPP20, FPUF-20MA, FPUF-5BDMPP-15MA, FPUF-10BDMPP-10MA, and FPUF-15BDMPP-5MA. FPUF-20BDMPP produced an intact and dense char residue which acted as a protective layer to the materials underneath during burning. FPUF-20MA resulted in a thin, layered residue with more holes on the surface. When 5-phr of MA from FPUF-20MA was replaced with 5-phr BDMPP, fire residue changed significantly on the surface and in the crosssection. Interestingly, FPUF-5BDMPP-15MA has a bumpy surface with a random size of holes and bubbles. Both FPUF-10BDMPP-10MA and FPUF-15BDMPP-5MA show a closed char surface. FPUF-10BDMPP-10MA exhibits a layer of tiny, compacted bubbles in its crosssection, while FPUF-15BDMPP-5MA consists of multiple layers with small bubbles and holes. The layered structure exhibited excellent protection against

fire during burning.⁴⁶ Hence, the THR of FPUF-15BDMPP-5MA was significantly reduced.

4 | CONCLUSIONS

In this work, a set of flame retarded FPUF samples was prepared to understand the interaction between BDMPP and MA/EG. In each flame retarded sample, the total amount of additives was 20 phr. From the result of LOI and UL 94 HBF tests, all flame retarded samples showed reduced flammability and a lower burning rate. In the systems with a single flame retardant, both 20-phr BDMPP and 20-phr EG enhanced flame retardancy in the gas phase. 20-phr MA and 20-phr EG reduced the pHRR significantly. EG is a great smoke suppressant, according to the result of TSR from the cone calorimeter. FPUF-20EG produced only 13% of the amount of smoke released by FPUF. FPUF-20BDMPP and FPUF-20EG exhibited high char yield after a pyrolysis process. As to the systems with dual flame retardants, the overall flame retardancy of FPUF-BDMPP-EGs was better than that of FPUF-BDMPP-MAs. The synergistic effect between BDMPP and EG, mainly due to BDMPP contributing gluing effect to expanded graphite, improved the char yield and stopped dripping. Among FPUF-BDMPP-EGs, FPUF-5BDMPP-15EG showed the best flame retardancy properties according to the LOI value and the burning rate in UL 94 HBF. Self-extinguishing behavior was also observed for FPUF-5BDMPP-15EG from the UL 94 HBF test.

In summary, the thermal pyrolysis and fire performance indicate that the combination of BDMPP and EG actively improves the fire behavior of PFUF by synergistic effects in the gas and condensed phases.

ACKNOWLEDGEMENTS

The authors appreciate the contribution of the mechanical tests from D. Schulze. This project was financed by the DFG (Deutsche Forschungsgemeinschaft) (SCHA 730/19-1) and the NSFC (National Natural Science Foundation of China) (51761135113).

Open access funding enabled and organized by Projekt DEAL.

CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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How to cite this article: Chan YY, Ma C, Zhou F, Hu Y, Scharrel B. A liquid phosphorous flame retardant combined with expandable graphite or melamine in flexible polyurethane foam. *Polym Adv Technol.* 2021;1-14. doi:10.1002/pat.5519

4.4 Flame retardant flexible polyurethane foams based on phosphorous soybean-oil polyol and expandable graphite

Yin Yam Chan, Chao Ma, Feng Zhou, Yuan Hu and Bernhard Schartel. *Polym Degrad Stabil.* **2021**, 191.

Doi: 10.1016/j.polymdegradstab.2021.109656.

Status: This article was accepted and published. <https://doi.org/10.1016/j.polymdegradstab.2021.109656>

First author contribution:

- Conceptualization
- Methodology
- Validation
- Investigation
- Data curation
- Writing – Original draft, review and editing
- Visualization
- Project administration

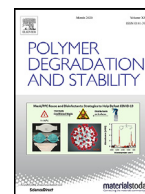
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Abstract

A phosphorous soybean-oil-based polyol was derived via epoxidation and ring opening reaction as an alternative to petrochemical-based polyol for the synthesis of flexible polyurethane foams (FPUFs). 5-wt.% and 10-wt.% of expandable graphite (EG) were added to further improve flame retardancy. The mechanical properties (tensile strength and compression stress) of the foams were investigated. Thermogravimetric analysis (TGA) coupled with Fourier-transform infrared (FTIR) were conducted to evaluate the pyrolysis; limiting oxygen index (LOI), UL 94 and cone calorimeter were performed to analyze the fire performance of the foams; smoke density chamber was used to investigate the smoke released during burning. When 10-wt.% of EG was used, the flame retardancy of the foams was much enhanced due to the synergistic effect between phosphorus and EG. The char yield was three times higher (54-wt.%). The fire load MARHE approached 100kWm^{-2} , half of the value expected for a superposition. The combination of phosphorous polyols and EG is proposed as strategy for future flame retarded PFUFs.



Flame retardant flexible polyurethane foams based on phosphorous soybean-oil polyol and expandable graphite

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ARTICLE INFO

Article history:

Received 10 March 2021

Revised 11 June 2021

Accepted 14 June 2021

Available online 18 June 2021

Keywords:

Phosphorous soybean-oil-based polyol

Flexible polyurethane foam

Expandable graphite

Flame retardancy

Smoke measurement

ABSTRACT

A phosphorous soybean-oil-based polyol was derived via epoxidation and ring opening reaction as an alternative to petrochemical-based polyol for the synthesis of flexible polyurethane foams (FPUFs). 5-wt.% and 10-wt.% of expandable graphite (EG) were added to further improve flame retardancy. The mechanical properties (tensile strength and compression stress) of the foams were investigated. Thermogravimetric analysis (TGA) coupled with Fourier-transform infrared (FTIR) were conducted to evaluate the pyrolysis; limiting oxygen index (LOI), UL 94 and cone calorimeter were performed to analyze the fire performance of the foams; smoke density chamber was used to investigate the smoke released during burning. When 10-wt.% of EG was used, the flame retardancy of the foams was much enhanced due to the synergistic effect between phosphorus and EG. The char yield was three times higher (54-wt.%). The fire load MARHE approached 100 kWm⁻², half of the value expected for a superposition. The combination of phosphorous polyols and EG is proposed as strategy for future flame retarded FPUFs.

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1. Introduction

Polyurethane (PU) presents in different parts of our daily life due to its versatility. The production of flexible polyurethane foam (FPUF) is the largest sector of the worldwide PU market, and the investigation showed that demand for it continues to increase [1]. FPUF is usually used in upholstered furniture, mattresses, packaging, and all kind of seats in transportation, because of its excellent properties such as its light weight and high resilience [2]. Most of the FPUFs available on the market are produced from petroleum derivatives. However, petroleum is a non-renewable resource. To reduce the consumption of petroleum, scientists and the public are shifting their attention toward using alternative raw materials. One of the appropriate approaches is to use vegetable oil as a substitute in PU production.

Petroleum-derived polyols and diisocyanates are usually the main constituents of FPUF for building crosslinked networks. Generally speaking, petrochemical polyols for FPUF production have a functionality of 3 and a molecular weight between 3000 and 6000, with a hydroxyl value (OH value) of 56 - 28 mg KOH/g [3]. The hydroxyl functional groups react with diisocyanates to form urethane bonds in PU. If there is water used as a blowing agent, di-

isocyanates react with the water to generate urea linkages in the foam. A certain similarity in chemical structure can be found between vegetable oils and petrochemical polyols. Vegetable oils are composed of triglycerides, which contain a glycerol with three long carbon chains of fatty acid. Several methods of synthesizing of bio-based polyols have been reported in the literature; the polyols derived from vegetable oil such as soybean oil [4–6], palm oil [7,8], castor oil [9] and rapeseed oil [10] could potentially replace the petrochemical ones completely or in part. Hence, modified vegetable oils with the appropriate functionality, molecular weight and OH value might be a good substitute for producing FPUF.

As compared to other kinds of vegetable oil, soybean oil dominates the market in vegetable oil production [11], has competitively low costs [12], and could serve as a raw material for bio-based industrial products [13]. Soybean oil consists of fatty acids which can easily be modified into polyol. These fatty acids are naturally unsaturated and are reactive to form oxirane rings by epoxidation. The hydroxyl groups are introduced by a ring-opening reaction of epoxidized soybean oil. However, soybean-oil-based polyol has its disadvantages, including a low molecular weight which affects the mechanical properties, and the absence of primary hydroxyl groups which results in a slow curing process. Apart from their sustainability advantages over ingredients from limited non-renewable resources, using bio-based polyols usually shows benefits for biodegradability and tensile strength [3,14].

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FPUFs catch fire easily, mostly because of their low-density open-cell structure, which boosts fire growth velocity and can cause detriment to human lives and the economy. Therefore, it is important to enhance their fire retardancy to reduce the occurrence of tragedies [15]. Flame retardants can be generally categorized into two types: reactive type and addition type. Reactive type flame retardants form covalent bonds with the polymer chain. Additive type flame retardant can simply be mixed physically with polymeric materials. Reactive type flame retardants typically show better compatibility with polymers and often better mechanical properties [16–18]. The combination of two or more types of flame retardant in the polymer may provide synergistic effects, making overall flame retardancy higher than the sum of the effects of the single flame retardants [19,20]. Yuan et al. synthesized rigid PU foam by using phosphorous polyol and nitrogenous polyol [21]. The combination of phosphorous and nitrogenous flame retardants in the polymer yields a synergistic effect [22]. This effect improved the thermal stability and flame retardancy of the rigid PU foam. Wilke et al. analyzed the synergy between phosphorus flame retardant and EG in a styrene-ethylene-butylene-styrene elastomer system. They concluded that the phosphorus content influences the degree of volume expansion of graphite layer by gluing fluffy residue together [23–26].

The aim of this work was to synthesize flame retarded bio-based FPUF by replacing petrochemical polyol with phosphorous bio-based polyol. Dimethyl phosphonate was used as a phosphorous source to graft on the backbone of soybean oil because the epoxy groups on epoxidized soybean oil are in the secondary position. The P-H group of dimethyl phosphonate has high reactivity to attack the epoxy groups to undergo ring opening reaction [27,28]. Phosphorus promotes carbonization and inhibits combustion [29,30]. Soybean oil was chemically modified into phosphorus-grafted polyol, which then partially substituted the petrochemical polyol in the formulation of FPUF. The formulation was modified and optimized to produce a flame retarded bio-based FPUF with physical and mechanical properties that are acceptable in comparison to the reference FPUF. Furthermore, EG, which was added to the polymer matrix physically, contributed to flame retardancy and smoke suppression. During burning, loose “worm-like” char layers, developed rapidly by graphite expansion, shielded the material from heat transfer to the inner matrix and reduced the components' rates of decomposition [30–33]. The morphologies, mechanical properties, pyrolysis, fire behaviors and smoke properties were studied.

2. Experimental

2.1. Materials

Soybean oil (99%) and dimethyl phosphonate (98%) were purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Hydrogen peroxide 30% aqueous solution ($\geq 30.0\%$), ethyl acetate ($\geq 99.5\%$) and anhydrous sodium sulfate ($\geq 99\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Anhydrous formic acid ($\geq 98.5\%$) was produced by Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Polyether polyol (330, hydroxyl value = 56 mg KOH/g, number average molecular weight = 3000 g/mol, average functionality = 3), graft polyether polyol (2045, prepared by the in situ polymerization of acrylonitrile and styrene in a polyether polyol, hydroxyl value = 20 mg KOH/g, number average molecular weight = 8400 g/mol, average functionality = 3), stannous octoate, triethylenediamine (A33, 33%), dichloromethane, silicone surfactant and toluene diisocyanate (TDI 80/20, 80:20 mixture of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate) were supplied by Jiangsu Lvyan New Material Co., Ltd., (Jiangsu, China). Deion-

ized water and dichloromethane were used as a chemical blowing agent and physical blowing agent in the foaming process respectively. EG with an expansion ratio of 150 – 200 was supplied by Qingdao Xingyuan Colloidal Graphite Co., Ltd. (Qingdao, China). All the chemicals were used without further purification.

2.2. Preparation of phosphorous soybean-oil-based polyol

2.2.1. Epoxidation of soybean oil

250 g of soybean oil and 15.2 g of anhydrous formic acid were poured into a 500 ml round bottomed flask, which was equipped with a magnetic stirrer and a pressure equalizing dropping funnel filled with 45.1 g of 30% hydrogen peroxide. Under continuous stirring, the system was heated up to 55 °C in the oil bath. With agitation, hydrogen peroxide was then gradually added drop by drop. After all of the hydrogen peroxide had been added, the reaction was maintained at 65 °C for a further 6 h. After cooling, the reaction mixture was dissolved in ethyl acetate and washed several times with deionized water from a separation funnel. The remaining water in the mixture was removed by adding the excess amount of anhydrous sodium sulfate. This sodium sulfate was then filtered out through suction filtration. The ethyl acetate was removed using a rotatory evaporator when the temperature reached 75 °C. The washed product was stored in a vacuum oven overnight at 70 °C. The synthetic route is illustrated in Fig. 1.

2.2.2. Opening of oxirane rings in epoxidized soybean oil

150 g of epoxidized soybean oil and 65.7 g of dimethyl phosphonate (DMP) were poured into a 500 ml round bottomed flask which was equipped with a magnetic stirrer. The reaction was maintained under stirring for 6 h at 80 °C. After cooling, the mixture was dissolved in ethyl acetate and washed several times with deionized water from a separation funnel. The ethyl acetate was removed using a rotatory evaporator at 75 °C. The washed product was stored in a vacuum oven overnight at 70 °C. The synthetic route is illustrated in Fig. 2. The OH value of the synthesized polyol is 90 mg KOH/g and its viscosity is favorable for foaming. The product is a mixture because it is not possible to confirm that all of the phosphorus groups attached to specific locations on the carbon chain.

2.3. Preparation of flexible polyurethane foams

The FPUFs were prepared using a one pot method, and formed inside a closed mold 200 mm × 200 mm × 100 mm in size (length × width × thickness) set to a controlled temperature of 60 °C for 20 min. The composition of soybean-oil-based flexible polyurethane foams is tabulated in Table 1. The additives consisted of 0.92 g of silicon oil, 0.15 g of stannous oil, 0.23 g of A-33, 2.91 g dichloromethane and 3.2 g deionized water. First component A (the synthesized soybean-oil-based polyol, polyether polyol, graft polyether polyol and the additives) was stirred in a disposable plastic cup using a high-speed stirrer at a uniform rate for 3 min. Then the weighted component B (TDI) was added to the stirred component A and blended under high speed in 5 s. The mixture was poured into the mold during the subsequent expansion. Afterward the foam was cured in an oven at 80 °C for 24 h to complete the polymerization. The obtained foams were designated as FPUF20, FPUF40, FPUF60 and FPUF80, respectively, designating the percentage of polyether polyol replaced by phosphorous soybean-oil-based polyol. It was our goal to increase the intrinsic flame retardancy as well as the amount of renewable starting material of flame retarded FPUF; nevertheless these materials contains reactive phosphorus flame retardants in terms of California AB 2998. The FPUFs with an additional 5-wt.% or 10-wt.% of EG were prepared in the same way. The only difference was that the weighted

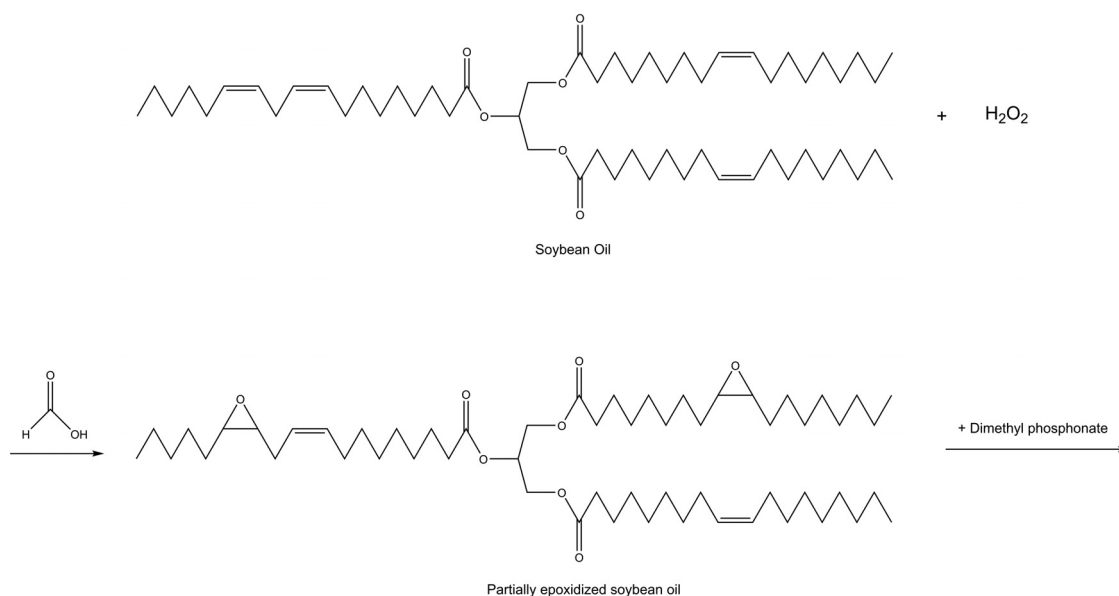


Fig. 1. Synthesis of partially epoxidized soybean oil.

Table 1
Composition of soybean-oil-based flexible polyurethane foams.

	Synthesized polyol (g)	Polyether polyol (g)	Graft polyether polyol (g)	Additives (g)	TDI (g)	EG (g)
FPUF	0	62.5	20.83	7.41	38.33	0
FPUF20	12.5	50	20.83	7.41	38.33	0
FPUF40	25	37.5	20.83	7.41	38.33	0
FPUF60	37.5	25	20.83	7.41	38.33	0
FPUF80	50	12.5	20.83	7.41	38.33	0
FPUF-5EG	0	62.5	20.83	7.41	38.33	6.43
FPUF20-5EG	12.5	50	20.83	7.41	38.33	6.43
FPUF40-5EG	25	37.5	20.83	7.41	38.33	6.43
FPUF60-5EG	37.5	25	20.83	7.41	38.33	6.43
FPUF80-5EG	50	12.5	20.83	7.41	38.33	6.43
FPUF-10EG	0	62.5	20.83	7.41	38.33	12.85
FPUF20-10EG	12.5	50	20.83	7.41	38.33	12.85
FPUF40-10EG	25	37.5	20.83	7.41	38.33	12.85
FPUF60-10EG	37.5	25	20.83	7.41	38.33	12.85
FPUF80-10EG	50	12.5	20.83	7.41	38.33	12.85

amount of EG listed in Table 1 was first incorporated homogeneously into the component A through high-speed stirring for 3 min before foaming.

2.4. Measurements

2.4.1. Characterization of phosphorous soybean-oil-based polyol

Nuclear magnetic resonance (NMR) spectroscopy analysis was used to determine the molecular structure, the chemical content, and the purity of chemicals. ^1H and ^{31}P NMR spectra were recorded by Bruker AVANCE AV 400 (Fällanden, Switzerland) using deuterated chloroform CDCl_3 as the solvent.

2.4.2. Morphological characterization

The morphologies of the foams and their char obtained from the fire test were studied by scanning electron microscopy (SEM). The specimens were sputter coated with a 15 nm of gold to avoid electrostatic charging during examination. The electron high tension (EHT) value was set to 10 kV. The images were obtained from Zeiss EVO 10 (Oberkochen, Germany).

2.4.3. Foam mechanical and physical properties measurements

The apparent density of the samples was measured in accordance with the ISO 845 standard. For mechanical tests, tensile

strength and elongation at break of the foams were determined using a Universal Testing Machine Zwick Z010 (Ulm, Germany) following ISO 1798. The compressive strength was measured according to ISO 3386-1.

2.4.4. Thermal properties

Thermogravimetric analysis (TGA) measures the change in the mass of a sample over time as a function of temperature in an inert atmosphere. TG 209 F1 Iris from Netzsch Instruments (Selb, Germany) was used as a heating source to measure the thermal degradation behavior of FPUF. The samples were grinded to a fine powder using CryoMill from Retsch (Haan, Germany) before testing. 10 mg of powdered sample was weighed and placed in the aluminum oxide crucible before it was put in the furnace. The sample was then heated up from 40 °C to 950 °C under nitrogen at a heating rate of 10 K/min. TGA coupled with Fourier transform infrared spectroscopy (FTIR), Bruker Tensor 27 FT-IR (Ettlingen, Germany), allowed the gaseous reaction products produced in the TGA chamber to be investigated simultaneously.

2.4.5. Fire behavior measurements

All the specimens for fire behavior measurements were conditioned at 23 °C and 50% relative humidity for at least 48 h before

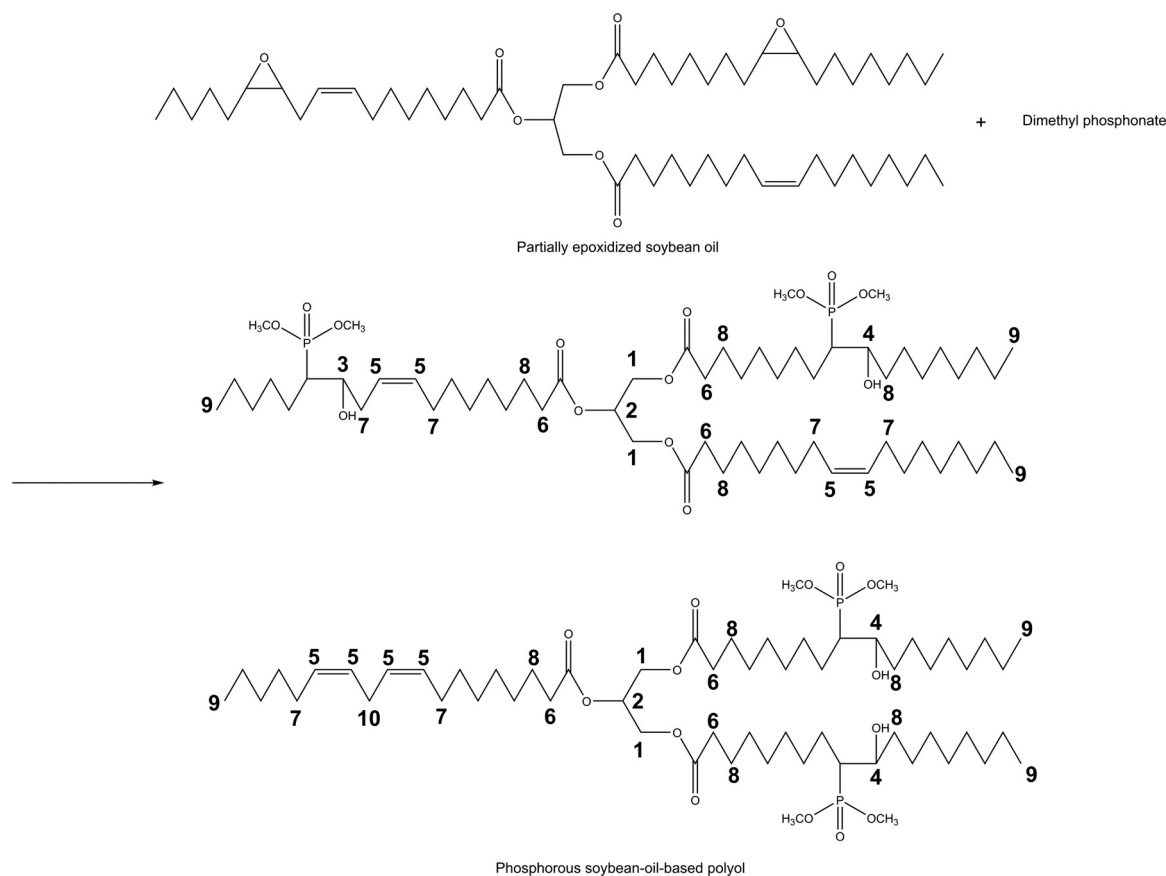


Fig. 2. Synthesis of phosphorous soybean-oil-based polyols.

measuring. Limiting oxygen index (LOI) was determined at ambient temperature according to ISO 4589-2, and the size of the specimens was 150 mm × 10 mm × 10 mm (length × width × thickness). The measurement was done by combusting a specimen with a mixture of a certain concentration of oxygen and nitrogen and then reducing the percentage of oxygen until a critical level was reached. The burning behavior was characterized by cone calorimeter manufactured by Fire Testing Technology Limited, United Kingdom. The test was performed following the ISO 5660 standard. A specimen with the dimensions of 100 mm × 100 mm × 50 mm (length × width × thickness) was placed in an aluminum foil tray and exposed horizontally to an external heat flux of 25 kW m⁻² located 25 mm away from the cone heater. Considering the low phosphorus content in the foams, the rather typical low heat flux for the development of foams was chosen. The foams should burn not too intense to get meaningful comparisons. All samples were run twice; a third measurement was done if any key result deviated by more than 10%. The graphs use the data from the single measurement with the most representative data, the tables summarize the averaged results; the uncertainty is estimated using the observed deviation from the averaged value. UL 94 HBF tests were conducted according to ISO 9772. The measurement determines the tendency of the materials to either extinguish or spread the flame once the specimen has been ignited. A specimen 150 mm × 50 mm × 10 mm in size (length × width × thickness) was used for this test.

2.4.6. Smoke and toxic gas measurements

The smoke density chamber (SDC) from Fire Testing Technology Limited, United Kingdom, contains a sealed test chamber with

photometric equipment. It measured the specific optical density of smoke generated by samples and determined the content of smoke. The measurement was done according to the ISO 5659 standard with a specimen size of 75 mm × 75 mm × 25 mm (length × width × thickness), exposing the specimens to an external heat flux of 25 kW m⁻². The FTIR-spectrometer coupled with the smoke density chamber provided the qualitative and quantitative data on the composition of gases in the smoke. The FTIR-spectrometer was calibrated according to the standard ISO 19702.

3. Results and discussion

3.1. Characterization of phosphorous soybean-oil-based polyol

To confirm the synthesis of the soybean-oil-based polyol, the chemical structure was characterized by ¹H NMR and ³¹P NMR spectroscopy. ³¹P NMR was used to determine the presence of phosphorus in the synthesized polyol. Fig. 3a and b show the ¹H and ³¹P NMR spectra of dimethyl phosphonate and soybean-oil-based polyol. It was mentioned above that the product was a mixture. Thus, two polyol molecules labelled with numbers are shown in Fig. 2 for a better explanation of the peaks in the ¹H NMR spectrum of phosphorous soybean-oil-based polyol in Fig. 3a, which depicts different types of hydrogen in the synthesized polyol and their corresponding signals. In Fig. 3a, a signal at about 3.4 ppm refers to the hydrogen generated from epoxy ring opening. The peak at 5.34 ppm corresponds to a carbon double bond, RCH=CHR. It indicates that a peak at 2.04 ppm belongs to the hydroxyl group formed from epoxy ring opening. The highest signal at 1.25 ppm is attributed to the hydrogen atoms which bond with the rest

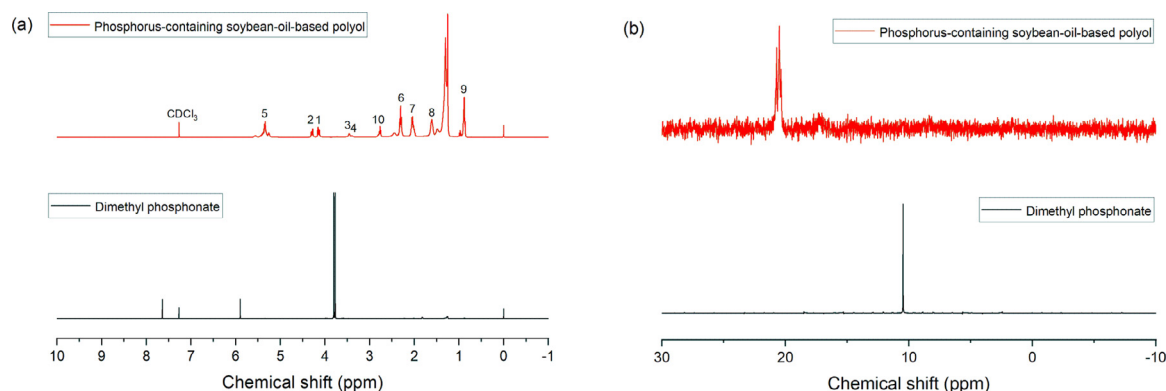


Fig. 3. (a) ^1H and (b) ^{31}P NMR spectra of dimethyl phosphonate and phosphorous soybean-oil-based polyol.

Table 2.

Apparent density and mechanical test results.

	Apparent density (kg m^{-3})	Tensile strength (kPa)	Elongation at break (%)	Compression stress at 40% compression (kPa)	Compression stress at 65% compression (kPa)
FPUF	34.77 ± 1.79	116 ± 10.69	86.36 ± 8.16	3.82 ± 0.11	8.51 ± 0.42
FPUF20	29.13 ± 1.64	143.3 ± 6.21	148.2 ± 6.01	4.75 ± 0.39	10.54 ± 1.48
FPUF40	31.28 ± 2.08	133.7 ± 4.55	133.1 ± 1.65	6.68 ± 0.35	15.17 ± 1.43
FPUF60	34.90 ± 1.97	99.6 ± 16.21	88.96 ± 15.22	4.82 ± 0.27	12.41 ± 1.54
FPUF80	31.45 ± 0.56	86.53 ± 7.88	69.37 ± 7.31	4.57 ± 0.24	12.89 ± 1.21
FPUF-5EG	32.41 ± 1.51	114.2 ± 6.61	92.02 ± 7.98	6.32 ± 0.49	14.27 ± 1.64
FPUF20-5EG	31.75 ± 1.37	113.7 ± 20.66	118.1 ± 22.79	4.82 ± 0.19	11.51 ± 0.80
FPUF40-5EG	30.03 ± 1.28	101.7 ± 7.27	120.4 ± 10.42	4.27 ± 0.11	10.09 ± 0.33
FPUF60-5EG	32.95 ± 1.22	96.74 ± 7.18	102.4 ± 7.59	5.41 ± 0.22	14.51 ± 0.66
FPUF80-5EG	37.50 ± 1.81	52.21 ± 4.69	48.74 ± 2.27	4.31 ± 0.14	13.52 ± 0.57
FPUF-10EG	40.33 ± 3.73	133.2 ± 8.34	120.9 ± 14.31	6.83 ± 0.16	18.94 ± 0.64
FPUF20-10EG	31.05 ± 0.45	84.23 ± 10.66	84.71 ± 9.39	4.74 ± 0.27	11.72 ± 1.54
FPUF40-10EG	37.48 ± 1.52	98.79 ± 22.09	82.18 ± 16.26	7.20 ± 0.16	18.42 ± 0.62
FPUF60-10EG	36.98 ± 2.44	101.5 ± 11.37	84.38 ± 5.44	6.15 ± 0.26	18.92 ± 1.72
FPUF80-10EG	40.83 ± 1.47	55.15 ± 2.87	39.31 ± 0.85	6.59 ± 1.23	32.44 ± 8.94

of the carbon on the glycerol backbones. In Fig. 3b, the single peak for phosphorus at 10.46 ppm in dimethyl phosphonate shifted to 20.5 ppm in phosphorous soybean-oil-based polyol. The signal at 20.5 ppm corresponding to phosphate group indicated that dimethyl phosphonate reacted successfully with epoxy groups of epoxidized soybean oil to produce phosphorous soybean-oil-based polyol.

3.2. Foam morphologies

The apparent density and the cell structure, which are shown in Table 2 and Fig. 4, are important information to evaluate the physical properties of FPUF. All the FPUFs showed similar apparent density of around $30\text{--}40 \text{ kg m}^{-3}$. The cell size and cell size distribution are comparable for FPUF, FPUF20, FPUF40, FPUF-5EG, FPUF20-5EG, FPUF40-5EG, FPUF-10EG, FPUF20-10EG, and FPUF40-10EG. For higher contents of soybean-oil-based polyol, the cell sizes tended to increase, what is more the cellular structure was affected by the cell nucleation and cell growth during foaming. The SEM images in Fig. 4 reveal that more defects and a less regular cell structure were formed with increasing amounts of substitution of synthesized polyol. The structure becomes spongier; the increased porosity is expected to increase the air flow through the foam also reducing foam recovery due the pneumatic effect. The addition of EG up to 10-wt.% is characterized by remaining integrity throughout the entire cell structure.

3.3. Mechanical properties

According to Table 2, the compression stress increases due to the increasing amount of EG in FPUFs. The presence of EG gen-

erally increased the apparent density. The compression stress is highly related to the density of the samples. The foams with higher density showed the higher compression stress. As a result, EG enhances supporting properties.

Considering the samples without EG, the tensile strength and the elongation at break of FPUF20 and FPUF40 are higher than those of FPUF. Hydrogen bonds between segments in urethane groups are one of the factors affecting the mechanical properties. The molecular weight of the synthesized bio-based polyol (1256 g/mol) is lower than that of its petrochemical counterpart. Typically, the low molecular weight polyol with higher hydroxyl value induces more reactions between isocyanates and hydroxyl groups, so that more urethane and urea linkages are formed. This causes a greater number of hydrogen bonds and thus higher tensile strength [34]. The synthesized polyol contained dangling carbon chains which acted as a plasticizer, but also reduced the crosslink density [3]. Petrochemical polyols are polyether triols with hydroxyls at the terminal position, whereas the synthesized polyol has only secondary hydroxyl groups. Furthermore, the molecular weight of synthesized polyol is lower than that of the petrochemical one. After reacting with isocyanate, the length of the soft segment between the branching points of synthesized polyol is shorter than that in petrochemical polyol. Therefore, with a low content of the synthesized polyol, the elongation at break was enhanced, as the dangling carbon chains acted as a plasticizer. When the amount of synthesized polyol was further increased, the dangling carbon chains further reduced the crosslink density, and the shorter soft segments reduced the flexibility of the polymer. Meanwhile, the crosslinking density increases with the amount of synthesized polyol due to higher OH number. According to the results from SEM images, at higher content of polyol leading the foam

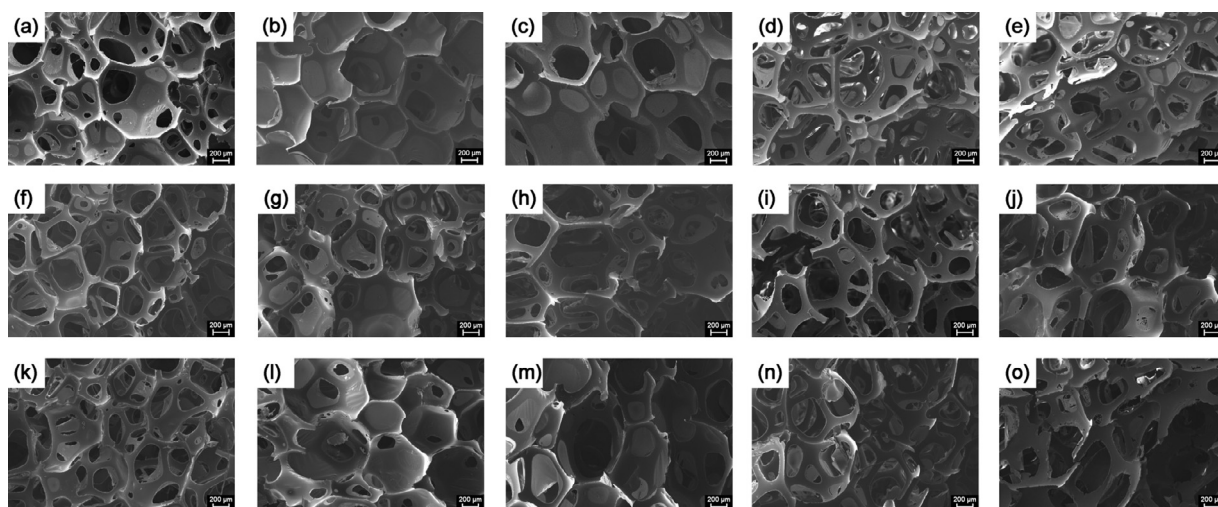


Fig. 4. SEM images of (a) FPUF, (b) FPUF20, (c) FPUF40, (d) FPUF60, (e) FPUF80, (f) FPUF-5EG, (g) FPUF20-5EG, (h) FPUF40-5EG, (i) FPUF60-5EG, (j) FPUF80-5EG, (k) FPUF-10EG, (l) FPUF20-10EG, (m) FPUF40-10EG, (n) FPUF60-10EG, (o) FPUF80-10EG.

Table 3

Selected results obtained from TG and DTG curves of the samples.

Material	T _{5%} °C	T _{max1} °C	T _{max2} °C	Difference between T _{max1} and T _{max2} °C	Residue at 700 °C %	Mass change 1 %	Mass change 2 %
FPUF	264.6	293.9	379.6	85.7	2.6	−30.5	−66.7
FPUF20	263.2	292.6	391.8	99.2	1.9	−28.3	−69.3
FPUF40	259.0	292.2	394.9	102.7	2.5	−27.6	−69.4
FPUF60	261.4	289.4	400.5	111.2	3.0	−26.4	−70.4
FPUF80	259.0	287.1	400.1	113.0	3.4	−24.9	−71.2
FPUF-5EG	263.1	296.1	380.1	84.0	4.0	−30.2	−65.3
FPUF20-5EG	263.6	295.0	392.7	97.8	3.3	−27.7	−68.6
FPUF40-5EG	262.9	293.0	398.7	105.7	5.5	−27.7	−66.5
FPUF60-5EG	261.5	290.9	400.8	110.0	7.0	−25.4	−66.9
FPUF80-5EG	263.4	293.7	402.0	108.3	6.3	−27.1	−66.2
FPUF-10EG	261.2	292.9	380.7	87.8	9.5	−28.1	−61.8
FPUF20-10EG	259.0	292.4	394.2	101.9	9.9	−26.1	−63.3
FPUF40-10EG	258.7	292.8	398.2	105.4	7.7	−27.9	−64.0
FPUF60-10EG	261.9	293.0	404.0	111.1	10.8	−25.6	−63.1
FPUF80-10EG	260.4	289.8	405.2	115.4	9.9	−25.2	−64.5

*T_{5%}: The onset temperature at 5% mass loss.

#T_{max1}: The first maximum thermal decomposition rate; T_{max2}: The second maximum thermal decomposition rate.

structure defects will most likely cause the observed decrease in mechanical properties. As a result, the tensile strength decreased after a further increase in the amount of synthesized polyol. The trend for the mechanical properties of FPUF-5EGs is similar to that of FPUFs without EG, but the mechanical properties of FPUF-5EGs are generally inferior to those of FPUFs without EG. The incorporation of EG into FPUF causes inferior mechanical properties as the EG deteriorates cellular structure of the foams. The results for FPUF-10EGs indicated that the higher loading of EG and the synthesized polyol compromised the performance in terms of tensile strength and elongation at break.

3.4. Pyrolysis

3.4.1. Thermogravimetry analysis

The mass loss of the FPUFs during pyrolysis under nitrogen was measured by thermogravimetry (TGA), and the selected characteristic data are recorded in Table 3. The thermal decomposition behaviors of the FPUFs were investigated. All samples went through a two-stage decomposition and, accordingly, there are two peaks in the DTG curve (the first derivative of the TGA curve) in the range from 200 to 500 °C. Generally, the first weight loss was attributed to the rupture of the polyurethane bond and thus it is accompanied with the release of TDI-derived products, while

the second stage was attributed mainly to the decomposition of the hydrocarbon chains of the polyol [35–38]. As illustrated in Fig. 5a1–a3, the decomposition of the first stage of all samples showed quite similar behavior. The incorporation of synthesized polyol and EG both increased the thermal stability of the second stage of decomposition. The FPUFs with higher content of synthesized polyol and EG shifted to the right in the second stage of the TGA curve, which means that the soft segments with higher phosphorus content started to decompose at higher temperatures. It indicates that the thermal stability of FPUFs containing synthesized polyol is higher than that of FPUF. This may be because the phosphorus increased the residue in the first decomposition step of FPUFs containing synthesized polyol, since phosphorous flame retardants generate char, forming a catalyst and thus increasing char yield during decomposition. The higher the synthesized polyol content, the greater the thermal stability. It was observed that the FPUFs with EG but without any synthesized polyol generally started to degrade at lower temperatures in the second stage, at around 380 °C. This indicates that they have lower thermal stability at the second stage of the decomposition. In contrast to the rest of the samples, they started to degrade between 391.8 °C and 405.1 °C in the second stage.

According to the DTG curves in Fig. 5b1–b3, the second peaks of DTG shifted to higher temperatures with higher content of syn-

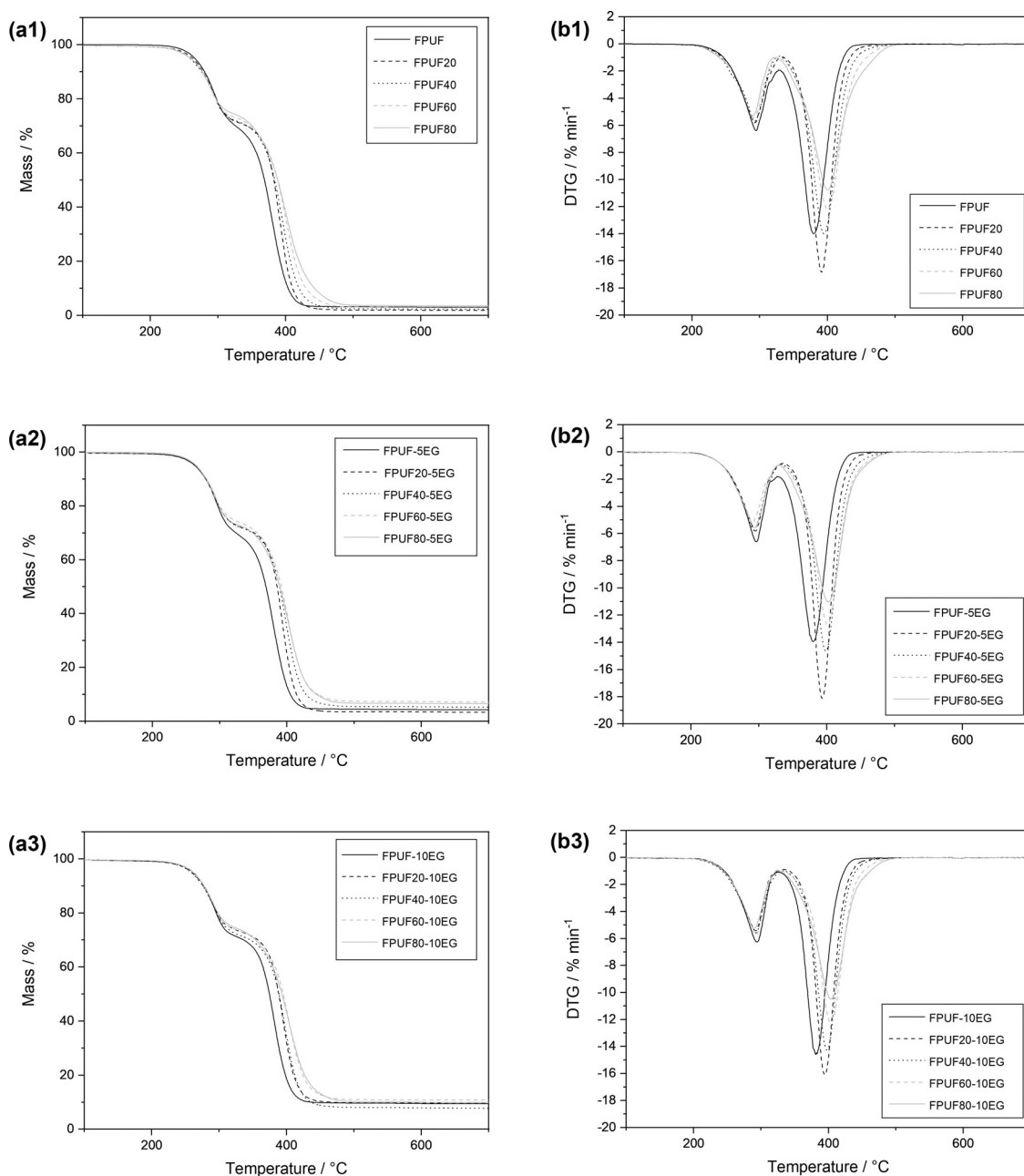


Fig. 5. TG curves of (a1) FPUFs, (a2) FPUF-5EGs and (a3) FPUF-10EGs; DTG curves of (b1) FPUFs, (b2) FPUF-5EGs and (b3) FPUF-10EGs.

thesized polyol. The separation between the first and second peaks was greater when the FPUFs contained higher phosphorus content.

3.4.2. Evolved gas analysis

To investigate the pyrolysis components of FPUFs evolved in the gas phase, the volatile products produced during thermal decomposition were evaluated using TG-FTIR. The TG-FTIR spectra of FPUF are similar to that of FPUF80. Common peaks are exhibited for both FPUF and FPUF80. The spectrum in Fig. 6a shows sharp absorption peaks at 2361 cm^{-1} and 2278 cm^{-1} at $294\text{ }^{\circ}\text{C}$, indicating the vibration absorption of CO_2 and $-\text{NCO}$ groups, respectively. At $340\text{ }^{\circ}\text{C}$, the absorption peaks at 2978 cm^{-1} , 2933 cm^{-1} and 2890 cm^{-1} show the stretching vibrations of $-\text{CH}_2$ and $-\text{CH}_3$. Moreover, the absorption peaks at 1744 cm^{-1} , 1100 cm^{-1} and 914 cm^{-1} represent $\text{C}=\text{O}$, $\text{C}-\text{O}$ and NH_3 , respectively. Although the peaks are not obvious, at $259\text{ }^{\circ}\text{C}$ Fig. 6b shows absorption peaks at 2320 cm^{-1} and $900\text{ }^{\circ}\text{C}$, which were attributed to the $\text{P}-\text{H}$ bond. A

peak at 1205 cm^{-1} corresponds to the stretching vibration of $\text{P}=\text{O}$. The phosphorous compounds were released as a gaseous product from the beginning of the thermal decomposition ($259\text{ }^{\circ}\text{C}$ - $398\text{ }^{\circ}\text{C}$).

3.4. Flame retardancy

3.4.1. Limiting oxygen value (LOI)

The results of LOI are listed in Table 4. Referring to the group of samples without EG, the LOI value of FPUF was only 18.8 vol.-%, whereas that of FPUF20 increased to 20.7 vol.-%. The LOI value of FPUF40 reached 21 vol.-%, which is the highest value among this group of samples. The phosphorus content in the synthesized polyol enhanced the flame retardancy. When 60-wt.% and 80-wt.% of the polyether polyol were replaced with the synthesized polyol in the polymer matrix, the results showed a trend of decreased LOI values (19.3 vol.-% and 19.2 vol.-% for FPUF60 and FPUF80, re-

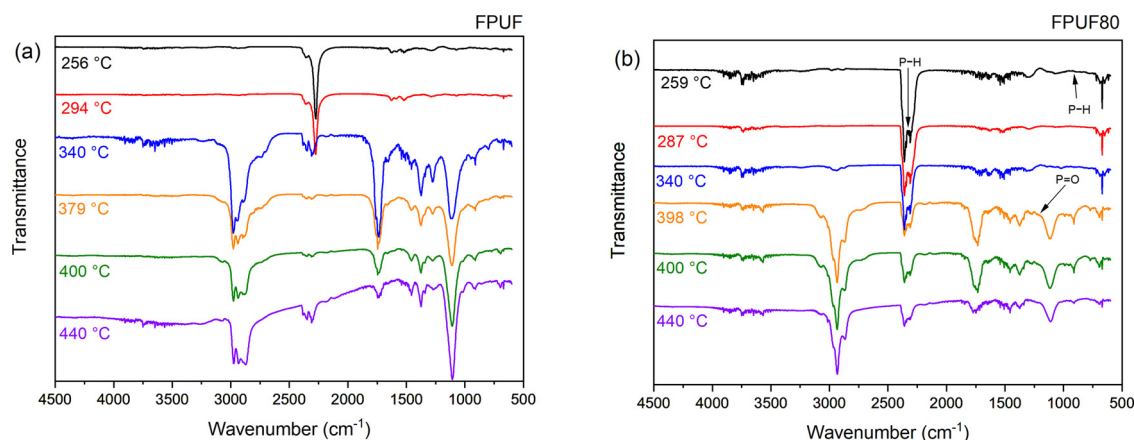


Fig. 6. TG-FTIR spectra of the gas phase in the thermal degradation of (a) FPUF and (b) FPUF80 at different pyrolysis temperatures.

Table 4
LOI results.

Sample	LOI (vol.-%)
FPUF	18.8 ± 0.1
FPUF20	20.7 ± 0.3
FPUF40	21 ± 0.1
FPUF60	19.3 ± 0.3
FPUF80	19.2 ± 0.2
FPUF-5EG	19.2 ± 0.2
FPUF20-5EG	19.8 ± 0.2
FPUF40-5EG	19.8 ± 0.2
FPUF60-5EG	20.2 ± 0.2
FPUF80-5EG	20.4 ± 0.2
FPUF-10EG	19.8 ± 0.2
FPUF20-10EG	21.2 ± 0.2
FPUF40-10EG	21.8 ± 0.2
FPUF60-10EG	21.6 ± 0.2
FPUF80-10EG	21.6 ± 0.2

spectively). This phenomenon can be explained by the existence of open-ended dangling aliphatic chains from the synthesized polyol. The larger amount of these dangling chains was brought into the polymer matrix when a higher content of synthesized polyol was used. These dangling hydrocarbon chains served as a good combustion fuel. Therefore, the fire behavior was weakened despite the higher phosphorus content in FPUF60 and FPUF80.

Moreover, 5-wt.% of EG was added as an additive type flame retardant. During burning of the FPUF, the EG flakes expanded and developed a “worm-like” structure that limited the heat and mass transfer from the polymer to the heat source [30]. EG provided additional flame retardancy to the system and the LOI value increased with increasing amounts of phosphorous soybean-oil-based polyol.

As a rule, the higher the loading of EG added, the higher the LOI value. The FPUFs with 10-wt.% EG exhibited better fire performance (with LOI values of up to 21.8 vol.-%) than the ones with 5-wt.% EG added (with LOI values of up to 20.4 vol.-%).

3.5.2. UL94 horizontal burning test

The horizontal burning characteristics of the samples were measured by UL 94 HBF test. The test was performed under the defined conditions with the specimens placed horizontally on a support gauze, with the specified gas flow rate and line pressure for the flame. Self-extinguishing and dripping behaviors were taken into consideration for the test. The results are listed in Table 5.

The samples with EG exhibited anti-dripping behavior because they all showed no sign of releasing burning drops that could ignite the cotton underneath. The FPUF with a higher loading of EG

showed a lower burning rate. The burned distance of the samples with 10-wt.% EG were reduced remarkably to 5 mm. Hence, FPUF-10EGs showed self-extinguishing behavior. The samples containing synthesized polyol and 10-wt.% EG exhibited better flame retardancy in the test. The burning rate of these samples was reduced to 8 mm/min.

3.5.3. Fire behavior: cone calorimeter

The cone calorimeter is used to evaluate the fire performance in fire scenarios of developing fires. Several parameters such as peak heat release rate (PHRR), time of ignition (t_{ig}), total heat release (THR), effective heat of combustion (EHC), total smoke released (TSR), char yield at flameout and the maximum average rate of heat emission (MARHE) are summarized in Table 6. Fig. 7a–c show the HRR curves of FPUFs without EG, with 5-wt.% of EG added, and with 10-wt.% of EG added, respectively. Fig. 8a–c display the heat release rates of selected FPUFs with different weight percentages of EG added. The char residue of the FPUFs, the relationship between the percentage of residue and the phosphorus content in residue, and the total heat release of FPUFs are plotted in Fig. 9a–c, respectively. Fig. 9b is taken from [39].

In general, FPUF collapsed rapidly during the first stage of burning and subsequently a liquid pool fire developed [23,40]. The values of t_{ig} recorded in Table 6 did not show any significant change when the content of EG and the synthesized polyol was varied, probably due to the uncertainty. According to Fig. 7a, FPUF exhibits two peaks of heat release rate (HRR). The second peak (pHRR at 492 kW m⁻²) is higher than the first (pHRR at 330 kW m⁻²). In the first peak, the material was ignited and the cellular structure started to collapse. The pool fire formed in the second peak and it mainly dominated the burning process. It also promoted the decomposition by establishing a feedback loop to the substance starting to burn and may have enhanced the flame spread to adjacent materials. To a certain extent, the phenomenon is associated with the two step decomposition of polyurethane (PU) that was observed in thermogravimetric analysis (TGA). The first decomposition step corresponds to the breaking of the urethane bonds accompanied by the release of TDI-derived products, whereas the second step is dominated by the decomposition of the hydrocarbon chains of polyol. The HRR curve of the remaining FPUFs without EG is similar to FPUF, with quite a similar shape and burning time. However, the HRR curve of the remaining FPUFs without EG does not show an obvious first pHRR. The HRR of the first stage of these FPUFs remained at around 200 kW m⁻² and then climbed up to a pHRR at 600–700 kW m⁻² in the second stage of burning. The pHRR of the remaining FPUFs without EG is higher than that of FPUF. The incorporation of synthesized polyol into the FPUF caused

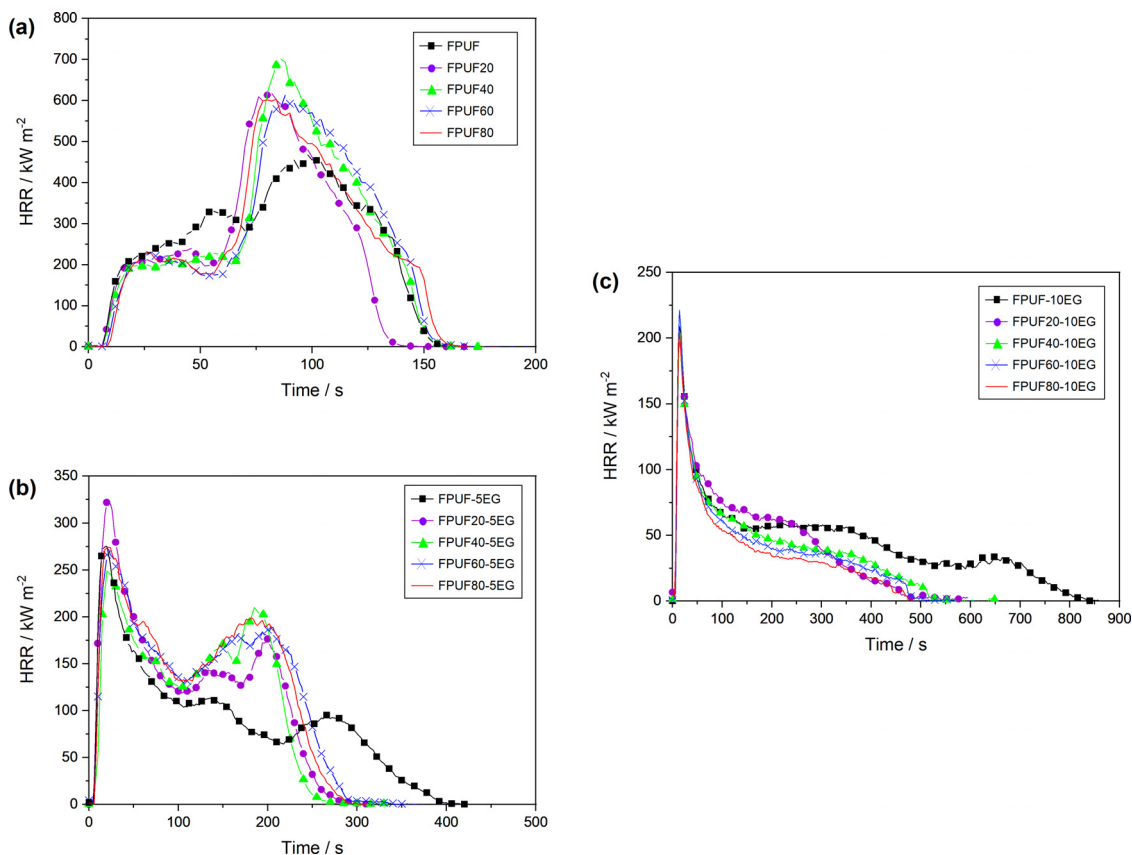


Fig. 7. Heat release rates of FPUFs with different replacement percentages of phosphorous soybean-oil-based polyol and (a) without expandable graphite added, (b) with 5-wt.% expandable graphite added, (c) with 10-wt.% expandable graphite added.

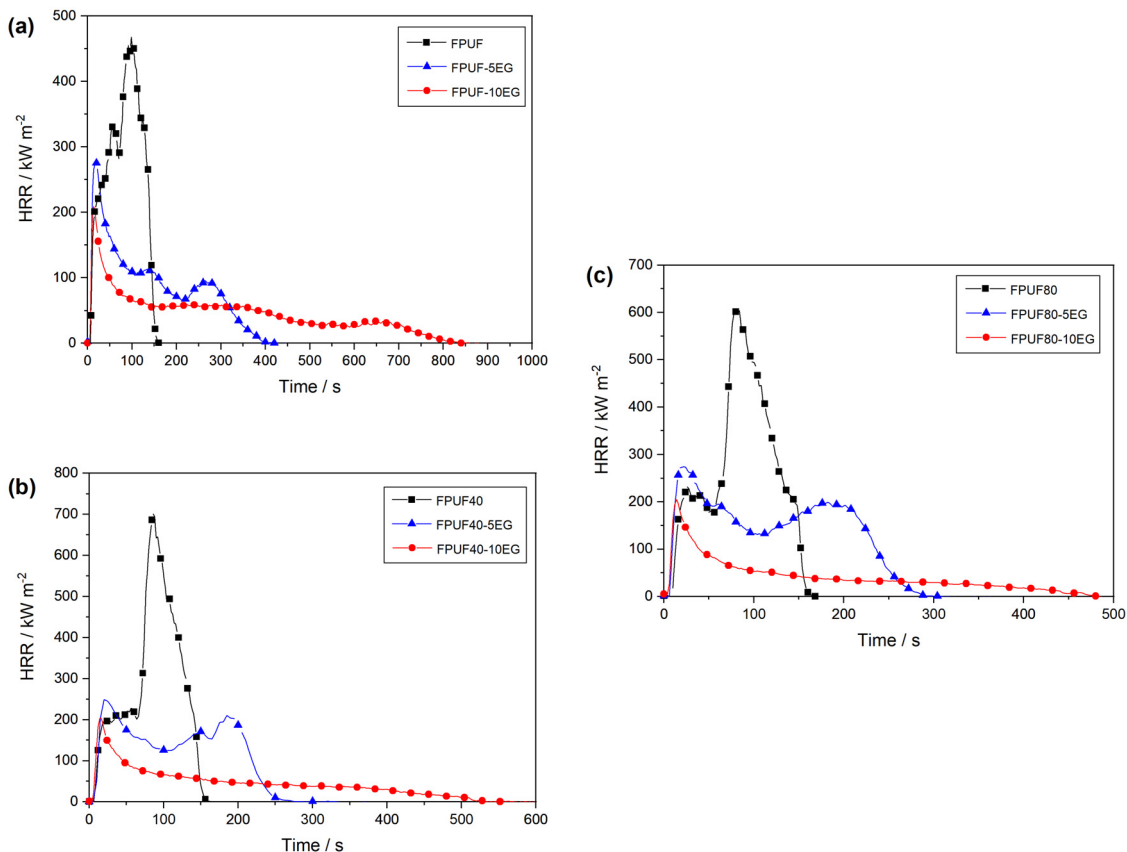
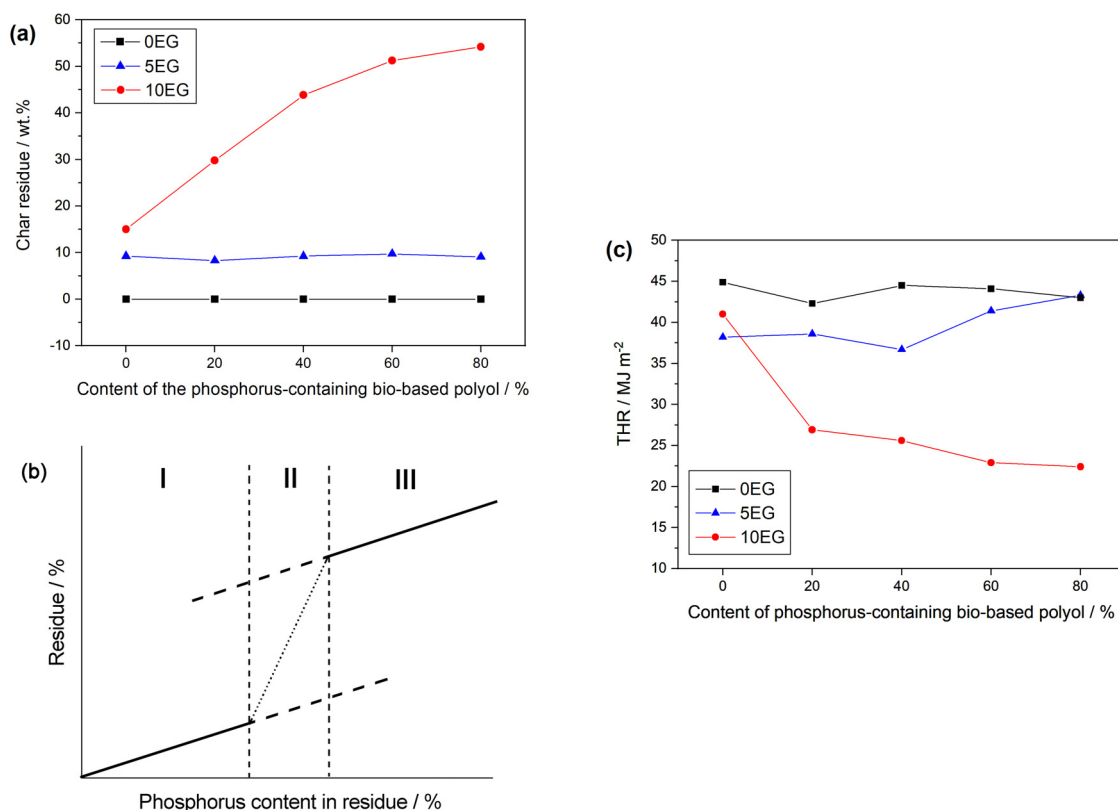


Fig. 8. Heat release rates of FPUFs with different weight percentages of additional expandable graphite; (a) FPUF, (b) FPUF40 and (c) FPUF80.

Table 5
UL 94 HBF results.

Material	Burning time (s)	Distance burned (mm)	Burning drops	Burning rate (mm/min)
FPUF	55	100	Yes	109
FPUF20	61	100	Yes	98
FPUF40	63.8	100	Yes	94
FPUF60	54.7	100	Yes	110
FPUF80	51.4	100	Yes	117
FPUF-5EG	53	100	No	113
FPUF20-5EG	123.4	100	No	48
FPUF40-5EG	73.1	100	No	82
FPUF60-5EG	105.6	100	No	57
FPUF80-5EG	118.6	100	No	51
FPUF-10EG	61	40	No	39
FPUF20-10EG	37.4	5	No	8
FPUF40-10EG	41.4	10	No	14.4
FPUF60-10EG	38	10	No	15.8
FPUF80-10EG	32	10	No	19

**Fig. 9.** (a) Char residue of FPUFs, (b) relationship between percentage of residue and the phosphorus content in residue, and (c) total heat release of FPUFs.

slight decrease in HRR during the first stage of burning. This may be due to the presence of phosphorus in the synthesized polyol. In the second stage, the pHRR of the FPUFs without EG (FPUF20, FPUF40, FPUF60 and FPUF80) increased compared to the pHRR of FPUF due to the incorporation of the P-containing polyol. This phenomenon may be explained by the low content of phosphorus in the FPUFs being consumed during the first stage of burning, and by the dangling carbon chains in the soybean-oil-based polyol acting as an effective fuel.

The effective heat of combustion (EHC) is measured in the cone calorimeter as a product of the effective heat of combustion of the volatiles and the combustion efficiency of the flame [41]. EHC is a tool to assess the efficiency of a flame retardant in terms of flame inhibition action and gas phase activity [37,39]. The average EHC of FPUF-5EGs did not evidence any significant flame retardancy in the gas phase as compared to that of FPUFs without

EG. We hypothesize that flame retardancy occurs mainly in the condensed phase. However, the average EHC of volatiles of FPUF-10EGs decreased compared to that of FPUFs and FPUF-5EGs. This phenomenon was attributed to the flame retardant mechanism of the phosphorus component in the gas phase [42,43]. For the FPUF, the EHC at the first stage was 20.7 MJ kg⁻¹, whereas that at the second stage was 26.2 MJ kg⁻¹. Although the EHC at the first stage of FPUF is somewhat lower than what was reported for comparable systems [37,44], overall EHC and the difference in EHC for the two stages is well comparable with literature. We believe that the separation in burning stages mainly controlled by different decomposition steps, the difference in composition of the FPUF, and different degrees of overlapping of the decomposition stages explain the results. Hereby some systems showed three separate stages, some only one, the EHC vary between 20 and 32 MJ kg⁻¹. The EHC of FPUFs always showed the lowest value at the first stage. At the

Table 6
Cone calorimeter data.

Sample	t_{ig} (s)	t_p (s)	PHRR (kW m ⁻²)	THR (MJ m ⁻²)	Average EHC# (MJ kg ⁻¹)	EHC ₁ (MJ kg ⁻¹)	EHC ₂ (MJ kg ⁻¹)	EHC ₃ (MJ kg ⁻¹)	Char residue (wt.%)	TSR (m ² m ⁻²)	MARHE (kW m ⁻²)
FPUF	5.5 ± 0.5	99 ± 1	492 ± 24	44.9 ± 2.4	25.7 ± 0.1	20.7 ± 1.7	26.2 ± 2.9	N.A.	-1.0 ± 1.3	383 ± 11.7	311 ± 10.4
FPUF20	5.5 ± 0.5	85 ± 3	600 ± 17	42.3 ± 3	28.3 ± 1.6	23.1 ± 0.4	31.5 ± 0.9	N.A.	-0.3 ± 0.3	418 ± 23	326 ± 10.1
FPUF40	6.5 ± 0.5	84 ± 2	682 ± 19	44.5 ± 1.1	26.8 ± 0.3	20.4 ± 1.0	28.7 ± 0.8	N.A.	0.3 ± 0.2	528 ± 13.2	328 ± 2.8
FPUF60	7.5 ± 0.5	85 ± 3	581 ± 32	44.1 ± 0.9	26.6 ± 0.1	20.4 ± 0.4	28.7 ± 0.1	N.A.	0.0 ± 0.1	603 ± 51.8	314 ± 2.9
FPUF80	6.5 ± 0.5	81 ± 3	597 ± 7	43.0 ± 1.1	26.9 ± 0.1	20.3 ± 0.5	29.3 ± 0.1	N.A.	-0.2 ± 0.4	660 ± 28.8	311 ± 4.2
FPUF-5EG	4.5 ± 0.5	20 ± 1	287 ± 12	38.2 ± 1.7	25.8 ± 0.1	24.3 ± 0.4	26.0 ± 0.5	28.7 ± 0.4	9.2 ± 0.5	222 ± 31.2	189 ± 2.8
FPUF20-5EG	5.5 ± 1.5	24 ± 4	297 ± 25	38.6 ± 0.9	26.4 ± 0.2	24.5 ± 0.3	26.3 ± 0.1	30.7 ± 0.1	8.3 ± 0.1	369 ± 8.6	203 ± 15
FPUF40-5EG	5 ± 0	21 ± 1	257 ± 8	36.7 ± 0.4	26.7 ± 0.1	24.2 ± 0.1	26.1 ± 0.1	31.7 ± 0.7	9.3 ± 0.5	373 ± 64.7	176 ± 8.7
FPUF60-5EG	6 ± 1	22 ± 1	262 ± 10	41.4 ± 1.3	26.9 ± 0.3	24.4 ± 0.7	26.4 ± 0.1	31.5 ± 0.8	9.7 ± 0.2	573 ± 0.7	183 ± 9.5
FPUF80-5EG	6 ± 2	25 ± 3	279 ± 5	43.3 ± 0.12	26.9 ± 0.1	24.9 ± 0.1	28.9 ± 0.1	N.A.	9.1 ± 0.1	710 ± 4.74	194 ± 0.4
FPUF-10EG	5.5 ± 0.5	15 ± 1	222 ± 13	41 ± 3.26	23.8 ± 0.5	23.8 ± 0.5	N.A.	N.A.	15.0 ± 0.2	55.1 ± 6.8	127 ± 2.1
FPUF20-10EG	5 ± 1	15 ± 1	194 ± 3	26.9 ± 0.7	24.5 ± 0.3	24.5 ± 0.3	N.A.	N.A.	29.8 ± 2	62.7 ± 2.1	121 ± 7
FPUF40-10EG	4.5 ± 0.5	16 ± 1	193 ± 11	25.6 ± 0.5	23.4 ± 0.1	23.4 ± 0.1	N.A.	N.A.	43.8 ± 1.4	65.4 ± 1.6	117 ± 7.5
FPUF60-10EG	4 ± 2	15 ± 1	204 ± 17	22.9 ± 0.39	23.7 ± 0.5	23.7 ± 0.5	N.A.	N.A.	51.2 ± 0.3	72.2 ± 2.7	119 ± 7.8
FPUF80-10EG	3.5 ± 2.5	15 ± 1	211 ± 6	22.4 ± 2.6	23.8 ± 0.8	23.8 ± 0.8	N.A.	N.A.	54.2 ± 4.5	91.2 ± 3.4	124 ± 0.6

+ t_p corresponds to the time to peak of heat release rate (PHRR).# EHC corresponds to the effective heat of combustion of the defined peak (Total heat release/ Total mass loss), (i.e. EHC₁, EHC₂ and EHC₃ correspond to the EHC of peak 1, peak 2 and peak 3, respectively).

second stage, higher values of EHC were recorded. The EHC value at the third stage was the worst.

The addition of EG caused a significant reduction in pHRR and MARHE values. As the EG provided great charring ability to form a thermally insulating barrier, it prevented further decomposition in the condensed phase and prolonged the time of burning. In Fig. 7b, all FPUFs containing 5-wt.% EG exhibit a similar first pHRR. Referring to the first pHRR, the addition of 5-wt.% EG resulted in a reduction of approximately 44% as compared to the reference FPUF. After the first sharp peak, the HRR dropped rapidly from around 280 kW m⁻² to 125 kW m⁻², due to the EG acting as an excellent protective layer against heat transfer and thermally protecting the underlying polymer. All FPUF-5EGs have second or third peaks that are lower than the first pHRR. A sharp peak appeared at the beginning because the material facing the heating source was not sufficiently protected by the EG. After consuming the very top layer, the expanded graphite accumulated to the next layers of material. Over time, more and more expanded graphite remained. The thicker layer of expanded graphite contributed to better flame retardancy. However, there were still second and third pyrolysis zones in FPUF-5EGs, due perhaps to the char from EG cracking, leaving the underlying materials exposed to the flame. This happens because the char layers are usually fragile and do not have enough adhesion to each other. Compared to FPUF-5EG, the second or third pHRR of FPUF-5EGs with synthesized polyol is more significant and earlier. This is probably because the dangling carbon chain in the synthesized polyol acted as a fuel source, enhancing flammability. MARHE is used as an index for the hazard of developing fires. The lower the value of MARHE, the better the fire performance. From Table 6, the value of MARHE is reduced when the amount of EG is increased. For FPUFs without EG, the value of MARHE is around 315 kW m⁻². When 5-wt.% and 10-wt.% of EG were added, the MARHE values decreased to around 190 kW m⁻² and 120 kW m⁻², respectively.

In Fig. 7c, the EG further reduced the first pHRRs in FPUF-10EGs (pHRRs at around 200 kW m⁻²) compared to that in FPUF-5EGs (pHRRs at around 280 kW m⁻²). The HRR surged to a sharp peak first and then spread over a wide area. The FPUF-10EG exhibited second and third peaks, but as these are significantly smaller and flatten, they are not considered to be a fire concern. Thus, the time to flameout was much longer. The FPUF-10EGs with the synthesized polyol exhibited only one obvious pHRR. The amount of EG in the FPUF-10EGs with the synthesized polyol was sufficient to build a better char layer with phosphorus, and protected against heat transfer and stopped further pyrolysis better than the FPUF-5EGs did. What is more this flame retardancy becomes strongly synergistic for FPUF-10EGs when increasing the P-containing polyol. The increase in char yield, the decrease in THR, and the decrease in burning time outperformed what can be expected for a superposition of the effects of EG and P-containing polyol. The FPUF-10EGs with the synthesized polyol left a great amount of char residue. Hardly any char residue was left after burning FPUF without EG, indicating that most of the materials were converted into volatiles. For FPUF-5EGs, voluminous worm-like char was formed and around 9% of char residue remained. As depicted in Fig. 9a, with the higher amount of phosphorus in FPUF-10EG, char yield at flameout increased significantly, up to 54-wt.%. This indicated that the phosphorus in the synthesized polyol induced the formation of a stronger char layer with the presence of EG to protect the material underneath during burning in the condensed phase. Compared to the schematic curve in Fig. 9b [39], char yield versus phosphorus content in the residue, it can be assumed that the curve of FPUF-10EG exhibits the key part, strong increase and leveling off, of the S-shaped curve concluded for the transition of a charring material with limited protective layer effect to a charring

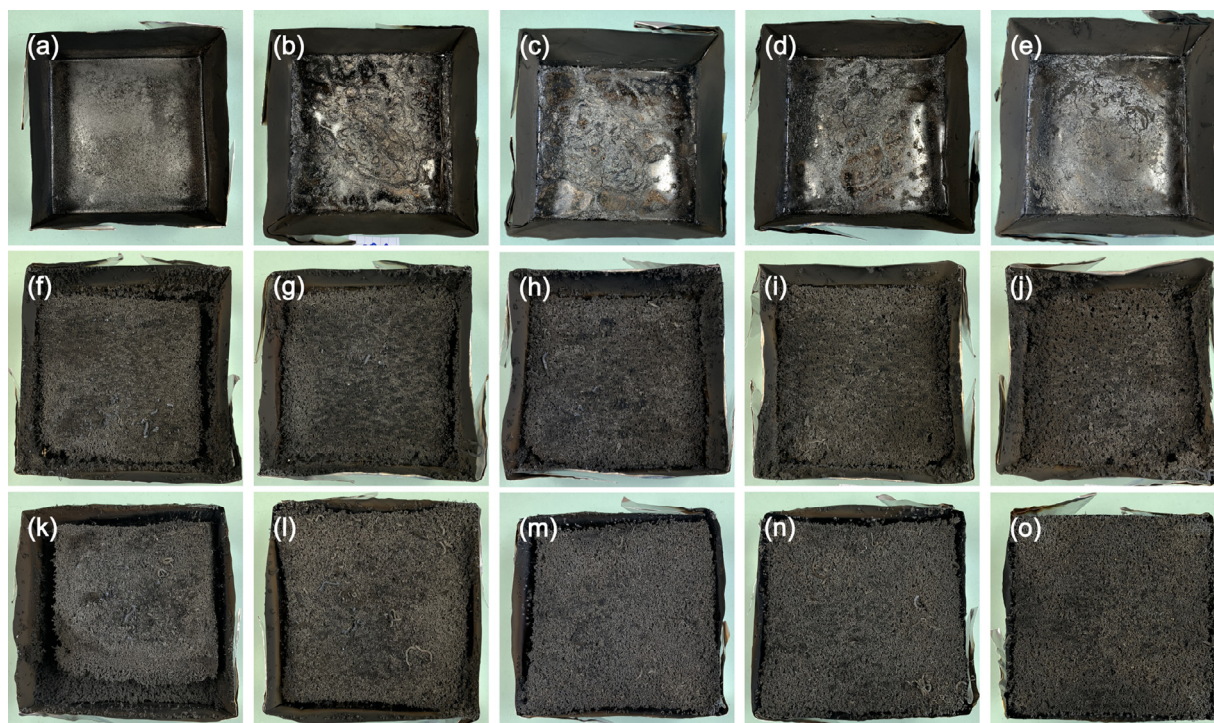


Fig. 10. Images of the fire residue (a) FPUF, (b) FPUF20, (c) FPUF40, (d) FPUF60, (e) FPUF80, (f) FPUF-5EG, (g) FPUF20-5EG, (h) FPUF40-5EG, (i) FPUF60-5EG, (j) FPUF80-5EG, (k) FPUF-10EG, (l) FPUF20-10EG, (m) FPUF40-10EG, (n) FPUF60-10EG, (o) FPUF80-10EG.

material with a protective layer effect efficient enough to result in incomplete pyrolysis.

Fig. 9a and c show that the results of the char yield and THR are comparable. The THR of FPUFs and FPUF-5EGs remained around 40 MJ m^{-2} . The char residue of FPUF-OEGs and FPUF-5EGs was also kept to 0-wt.% and 9-wt.%, respectively, although the content of the synthesized polyol was increased. However, the THR of FPUF-10EGs was reduced by almost 50% with higher content of synthesized polyol, decreasing from 41.3 MJ m^{-2} to 22.4 MJ m^{-2} . This behavior is related to the char yield of FPUF-10EGs. With the increasing content of the synthesized polyol, the char yield of FPUF-10EGs increased noticeably and the THR was reduced accordingly. This phenomenon indicated that the thermal stability and insulation of the char residue was adequate to prevent the materials from burning completely.

Considering Fig. 8a–c, the peak in the second stage for FPUF with increasing amount of EG became flatter, and the time to flameout became longer. The time to the highest peak of heat release rate (PHRR) decreased with increasing EG content.

3.5.4. Fire residue

The photographs of the fire residue from the samples after cone calorimetry measurements are shown in Fig. 10. Fig. 11 shows the SEM images of the fire residue. The FPUF collapsed into a pool and was completely consumed during the cone calorimetry measurement. Therefore, there was nearly no residue after burning. Thin layers of glassy inorganic residue were obtained from FPUF20, FPUF40, FPUF60 and FPUF80. This glassy layer was defined as polyphosphate ash. The phosphorus group from the synthesized polyol decomposed into polyphosphoric acid, and finally degraded to glassy polyphosphate [45,46]. For FPUFs with EG, the formed char layer provided a thermal barrier protecting the materials underneath, reducing the rate of further decomposition. The higher the content of EG, the more compact the expanded graphite, and thus the more superior the intumescent effect. As concluded from the char yield, a synergistic effect took place be-

tween phosphorus and EG. The char yield increased notably with the increased amount of phosphorus in FPUF-10EG. The integrity of the expanded graphite residue was retained because of the adhesive effect of the phosphorous compound [23]. It was reported that there is strong interfacial bonding between different char residues, which strengthened the integrity and continuity of the intumescent carbonization layers, leading to a stronger barrier effect in the condensed phase [47,48].

3.6. Smoke and toxic gas measurements

The smoke produced in fire poses a major threat to victims of accidental fire. Smoke particles hinder the visibility of escape routes and may retard rescue operations because of their light absorbing and scattering properties. Also, most fire casualties are caused by smoke inhalation, not by burns from the flames. The toxic gases and soot generated by burning polyurethane cause poisoning and suffocation to human beings. Carbon monoxide (CO) and hydrogen cyanide (HCN) are the two major asphyxiants released during the burning of polyurethane. Hence, assessments of smoke and toxic gases are critical for evaluating the fire safety of materials. The cone calorimeter and smoke density chamber are small scale fire tests; these were used to determine the smoke density and smoke hazard of the materials.

3.6.1. Cone calorimeter

Rate of smoke release (RSR), total smoke release (TSR) and carbon monoxide production rate (COP) curves, illustrated in Fig. 12a–c, respectively, provide the data measured by cone calorimeter for evaluating the emissions of smoke and toxic gases. Phosphorus usually inhibits flames efficiently by increasing CO production. This is because phosphorus free radicals presented in the gas phase lead to incomplete combustion, which inhibits the conversion from CO to CO_2 [49]. Although, relevant flame inhibition was not unambiguously proven in the cone calorimeter, the release of P-containing volatiles was shown by the evolved gas analysis and is proposed

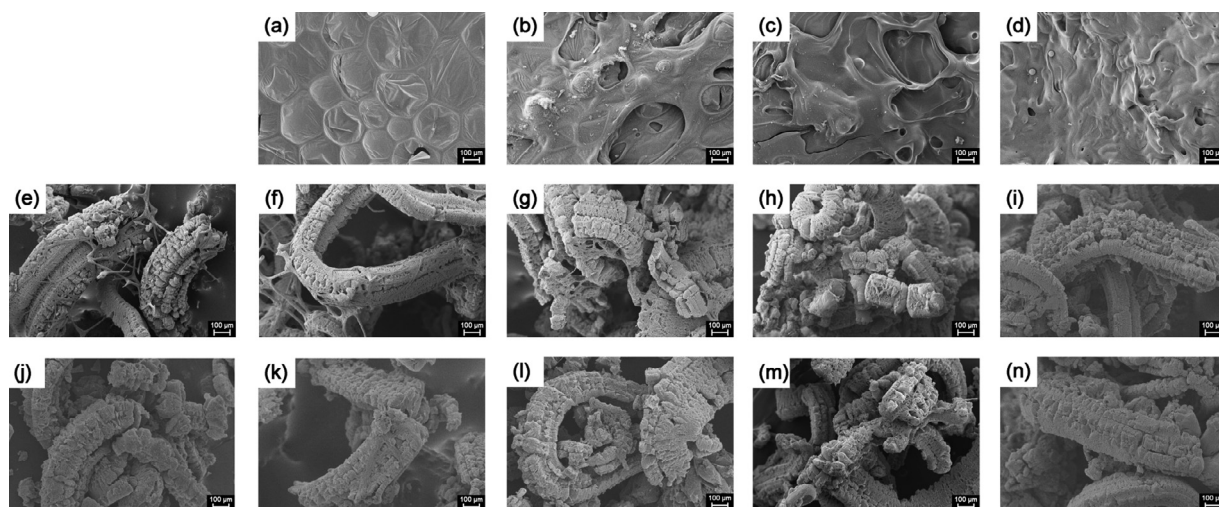


Fig. 11. SEM images of fire residue of (a) FPUF20, (b) FPUF40, (c) FPUF60, (d) FPUF80, (e) FPUF-5EG, (f) FPUF20-5EG, (g) FPUF40-5EG, (h) FPUF60-5EG, (i) FPUF80-5EG, (j) FPUF-10EG, (k) FPUF20-10EG, (l) FPUF40-10EG, (m) FPUF60-10EG, (n) FPUF80-10EG.

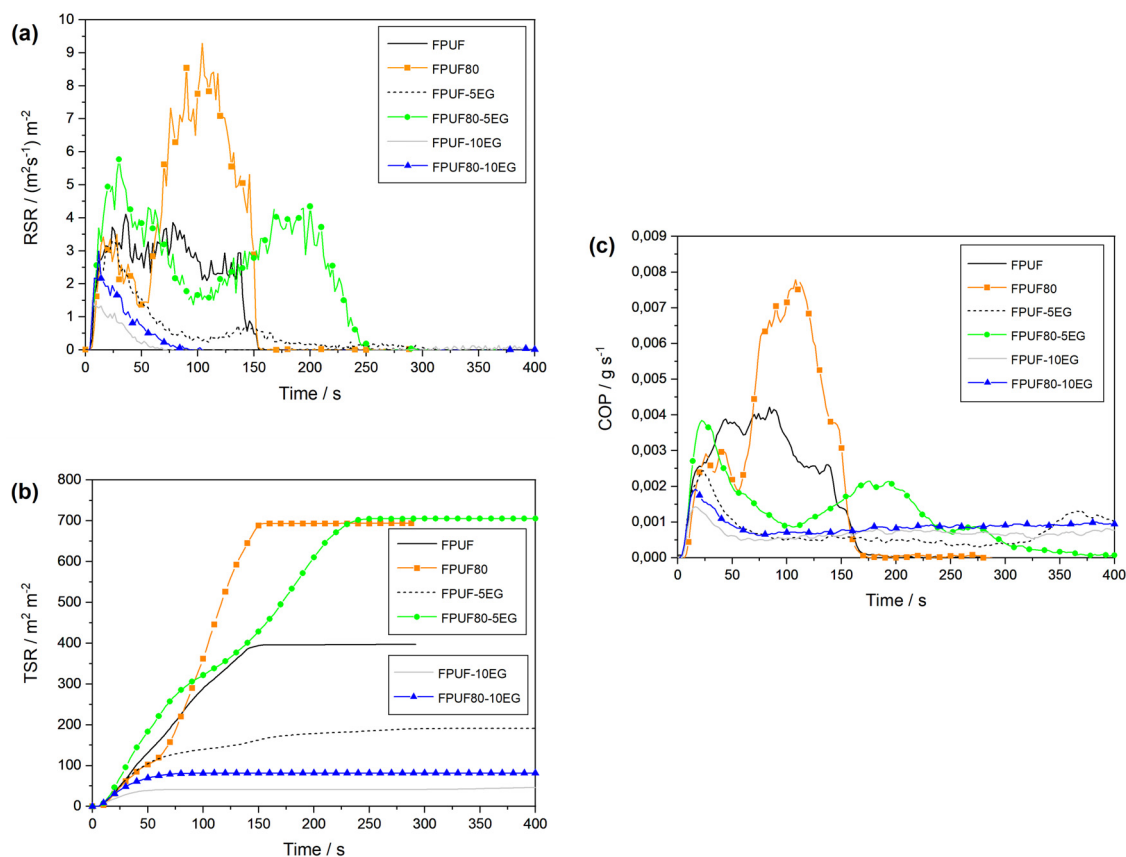


Fig. 12. (a) Rate of smoke release (RSR), (b) total smoke release (TSR) and (c) carbon monoxide production rate (COP) curves for selected samples.

to enhance the CO-production. Compared to FPUF, FPUF80 obviously produces more smoke, because of the phosphorous soybean-oil-based polyol is a char promotor and larger decomposition fragments are produced due to the incomplete pyrolysis. 10-wt.% of EG in the foams predominantly contributed the effectiveness of smoke suppression and since the RSR and TSR were reduced remarkably. The 10-wt.% of EG generally reduced more than 80% of the total smoke production. This amount of accumulated expanded graphite was sufficient to produce a compact carbonaceous char structure that increases the residence time of the smoke particles

in the pyrolysis zone. It provides a higher retardancy by enhancing the charring of aromatics instead of releasing smoke particles. Furthermore, Fig. 12c shows that the CO production of FPUF-10EG was reduced by more than 60% as compared to that of FPUF. The adequate amount of EG reduced the production of CO efficiently. Therefore, the EG in the polymer matrix played the main role in reducing total smoke production and the production of CO.

3.6.2. Smoke density chamber

The smoke density chamber is an elementary tool for investigating the fire safety of materials. In the smoke density test, spe-

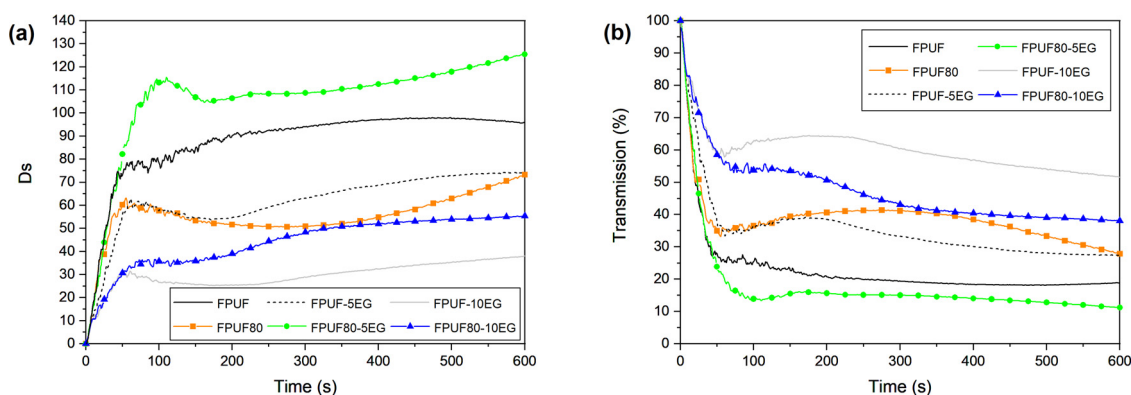


Fig. 13. (a) Specific optical density and (b) transmission of the selected FPUFs burned with a pilot flame.

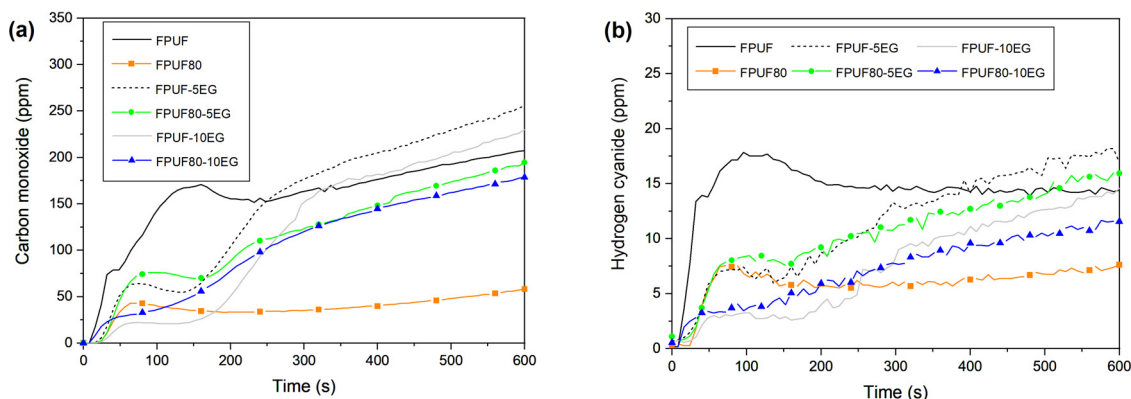


Fig. 14. (a) Carbon monoxide and (b) hydrogen cyanide released from the selected samples burned with a pilot flame.

cific optical density (D_s) and light transmission (T) are the important parameters measured by a photometric element to determine the amount of smoke released from the materials during burning. Specific optical density is a dimensionless parameter of the amount of smoke generated per unit area by a material during burning. Light transmission (T) is detected by a photomultiplier which integrates the light intensity over the visible spectrum [50]. The photometric scale is comparable to the optical scale of human vision. Accordingly, a higher transmission of light beams means that people have higher chance of escaping a fire [51]. Specimens 75 mm $\times$ 75 mm $\times$ 25 mm in size were exposed to a radiant heat source of 25 kW m⁻² in the chamber with the use of a pilot flame.

FPUF shows an obvious decrease in D_s when only the weight percent of EG is increased in Fig. 13a. EG worked as an effective smoke suppressant in FPUF. To compare between FPUF and FPUF80, D_s decreased with increasing phosphorus content. However, for the samples with the same content of EG (FPUF-5EG/FPUF80-5EG and FPUF-10EG/FPUF80-10EG), higher phosphorus content increased the D_s . The data of transmission are displayed in Fig. 13b. The percentage of transmission corresponds to the visibility for fire evacuation. FPUF-10EG showed the greatest percentage of light transmission among the selected samples.

Fig. 14a and b show the amount of CO and HCN, respectively, released during the burning of selected FPUFs. In all of the selected samples, the results show that phosphorus reduces CO and HCN emission. Interestingly, the HCN emission of FPUF-5EG, FPUF80-5EG, FPUF-10EG and FPUF80-10EG increased steadily, while for FPUF and FPUF80 it increased drastically at the beginning then leveled off. This suggests that the presence of EG in FPUFs may change the mechanism of HCN emission.

Data on smoke production from the cone calorimeter are obtained using the dynamic air flow method, while those from a sealed smoke density chamber are accessed under conditions of static accumulation [52,53]. The quality and quantity of smoke are readily influenced by different combustion conditions [54]. As the two tests are performed under different ventilation conditions, flow and accumulation, the results do not coincide with each other. Therefore, two sets of the data are discussed separately.

4. Conclusion

Phosphorus-grafted soybean-oil-based polyol for FPUFs was successfully synthesized. The use of reactive bio-based flame retardants is an attractive approach to achieve two aims at once in polymer matrix, improving fire performance and providing an alternative to reduce the use of petroleum byproducts. The flame retardant FPUFs were synthesized by replacing petrochemical polyol with synthesized soybean-oil-based polyol and adding EG. FPUFs were prepared with different amounts of synthesized soybean-oil-based polyol and EG in order to study their flame retardancy. The rigidity of the foam was increased to some extent and the foamability were somewhat affected when using high amounts of synthesized polyol. These limitations might be balanced out adjusting the formulation in future works. With higher loadings of EG, the results from LOI, UL 94 HBF and the cone calorimeter consistently showed greater enhancement of flame retardancy. The THR and char yield from cone calorimeter testing revealed that EG and phosphorus work exceptionally well together in the condensed phase. A nearly 50% reduction in the THR for FPUF-10EGs was realized with substitution of 80-wt.% of phosphorus synthesized polyol. The char yield of FPUFs with 10-wt.% EG surged when phosphorus content was increased. Thus, the ratio of EG to phos-

phorous soybean-oil-based polyol is crucial for good flame retardancy performance. Apart from the improvement in flame retardancy, EG reduced the amount of smoke and toxic gases released during burning with pilot flame in a smoke density chamber. TGA results indicated that the FPUF with phosphorus-grafted soybean-oil-based polyol was more thermally stable than the reference FPUF.

To summarize, the cooperation of phosphorus-grafted soybean oil with EG provided flame retardancy to FPUF by facilitating the formation of char residues with outstanding barrier effect. Increasing the P-content of the phosphorus-grafted soybean oil may be proposed as promising strategy for future development.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yin Yam Chan: Conceptualization, Methodology, Validation, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration. **Chao Ma:** Conceptualization, Investigation, Resources. **Feng Zhou:** Conceptualization, Investigation. **Yuan Hu:** Conceptualization, Resources, Supervision, Project administration, Funding acquisition. **Bernhard Scharrel:** Conceptualization, Methodology, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Acknowledgements

The authors thank D. Schulze for his contribution to the mechanical tests of the materials. Also, the help from T. Raspe and Dr. S. Krüger with the smoke density chamber coupled with FTIR was highly appreciated. This project was financed by the DFG (*Deutsche Forschungsgemeinschaft*) (SCHA 730/19-1) and the NSFC (*National Natural Science Foundation of China*) (51761135113).

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4.5 Flame retardant combination with expandable graphite/phosphorus/CuO/castor oil in flexible polyurethane foams

Yin Yam Chan, Andreas Korwitz, Doris Pospiech and Bernhard Schartel. *ACS Appl. Polym. Mater.* **2023**. Doi: 10.1021/acsapm.2c01969.

Status: This article was accepted and published. <https://doi.org/10.1021/acsapm.2c01969>

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First author contribution:

- Conceptualization
- Methodology
- Validation
- Investigation
- Writing – Original draft, review and editing
- Visualization
- Project administration

Contributions from other authors:

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 - Methodology
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 - Methodology
 - Resources
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 - Supervision
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 - Funding acquisition

Abstract

A series of flexible polyurethane foams (FPUFs) was prepared with single and different combinations of flame retardants and additives. Expandable graphite (EG), phosphorous polyol (OP), copper (II) oxide (CuO) and/or castor oil (CAS) was/were added to FPUF during the foam preparation in a one-step process. The purpose of the study is to evaluate the synergistic effects of the flame retardants, additives, and the presence of bio-based content on the mechanical properties, flame retardancy, and smoke behavior of FPUFs. The combination of 10 wt.% EG and 5 wt.% OP in FPUF significantly improves the char yield. In the cone calorimeter experiment, the char yield is nearly three times higher than that with 10 wt.% EG alone. The smoke behavior is additionally evaluated in a smoke density chamber (SDC). Comparing the samples with a single flame retardant, 10 wt.% of EG in FPUF greatly reduces the amount of smoke released and the emission of toxic gases. Replacing the amount of 10 wt.% polyether polyol in FPUF with CAS maintains the physical and mechanical properties and fire behavior and enhances the bio-based content. The presence of 0.1 wt.% CuO in FPUF effectively reduces the emission of hydrogen cyanide. As result, this study proposes a multi-component flame retardant strategy for FPUF to enhance the biomass content and address the weaknesses in flame retardancy, smoke and toxic gas emissions.

Flame retardant combinations with expandable graphite/phosphorus/CuO/castor oil in flexible polyurethane foams

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Keywords: flexible polyurethane foam, flame retardancy, synergistic effect, smoke behavior, expandable graphite, bio-based

Abstract

A series of flexible polyurethane foams (FPUFs) was prepared with single and different combinations of flame retardants and additives. Expandable graphite (EG), phosphorous polyol (OP), copper (II) oxide (CuO) and/or castor oil (CAS) were added to FPUF during the foam preparation in a one-step process. The purpose of the study is to evaluate the synergistic effects of the flame retardants, additives, and the presence of bio-based content on the mechanical properties, flame retardancy, and smoke behavior of FPUFs. The combination of 10 wt.% EG and 5 wt.% OP in FPUF significantly improves the char yield. In the cone calorimeter experiment, the char yield is nearly three times higher than that with 10 wt.% EG alone. The

smoke behavior is additionally evaluated in a smoke density chamber (SDC). Comparing the samples with a single flame retardant, 10 wt.% of EG in FPUF considerably reduces the amount of smoke released and the emission of toxic gases. Replacing the amount of 10 wt.% polyether polyol in FPUF with CAS maintains the physical and mechanical properties and fire behavior and enhances the bio-based content. The presence of 0.1 wt.% CuO in FPUF effectively reduces the emission of hydrogen cyanide. As result, this study proposes a multi-component flame retardant strategy for FPUF to enhance the biomass content and address the weaknesses in flame retardancy, smoke and toxic gas emissions. A starting point is disclosed for future product development.

1. Introduction

Flexible polyurethane foam (FPUF) is prone to fire. It burns rapidly due to its porous open-cell structure (i.e., high surface-to-mass ratio), making it difficult to be effectively flame retarded. Improving the flame retardancy of FPUF is critical to prevent serious fire hazards that jeopardize human lives, because FPUF is ubiquitous in our daily surroundings, used not only in upholstered furniture, mattresses, and seats in transportation, [1] but also as quasi universal lightweight and insulation material all over the world. To improve the flame retardancy of FPUF, flame retardants are added as additives to the polymer matrix by mechanical mixing during the preparation process. However, not all flame retardants are suitable for incorporation in FPUF formulations, as they may disrupt the balance between the gelling and blowing reactions due to increased viscosity, leading to a collapse of the foam structure. [2]

In this work, expandable graphite (EG) and the commercially available phosphorous polyol Exolit® OP 560 (OP) are used as flame retardants for FPUF. Many studies have demonstrated that EG is an effective intumescent flame retardant for FPUF. [2-7] EG is a kind of graphite intercalated with acid (usually sulfuric acid) in the presence of an oxidizing agent. After being heated up to 200 °C, the EG expands hundreds of times to generate a “worm-like” structure,

acting as a protective layer for the unburned material underneath. [8-10] Unlike EG, OP is a reactive flame retardant with terminal hydroxyl groups, forming chemical bonds directly with the polymer network. Phosphorous compounds in polyurethane can generally function both in the gas phase and the condensed phase. [11-13] However, according to the related research studies on FPUFs with OP, excess OP destroys the cellular structure of FPUF because the excess is not chemically linked to the network. [14,15] Hence, in this work, only 5 wt.% of polyether polyol was replaced by OP to avoid foam collapse during the foaming process. Different studies have reported that there is a synergistic effect between EG and phosphorus in FPUF during burning. [4, 16-19] The system of EG and phosphorus not only improves flame retardancy, but also reduces the smoke emission of FPUF during combustion, which is critical since toxic fumes have always been regarded as the major killer in fires. Copper (I) oxide (Cu_2O) has been commonly chosen as an inhibitor for smoke and toxicants due to its adsorption and catalytic conversion capabilities in polyurethane foams. [20-22] Copper (II) oxide (CuO) has seldom been reported in the literature as an additive to suppress the release of smoke and toxicants. In this work, CuO was used in FPUF to investigate its effectiveness in reducing smoke as well as toxic gases.

Environmental issues associated with synthetic polymers have always been a major concern, since most of them are made from petrochemical derivatives. Using natural resources such as plant oils is an alternative to produce polyurethane in a sustainable manner. [23-28] In this study, castor oil (CAS) is used to replace part of the petrochemical polyol and thereby increase the renewable bio-based content in FPUF in order to improve biodegradability and eco-friendliness. CAS is a non-edible renewable resource extracted from *Ricinus communis*. It is a natural polyol as it consists of terminal hydroxyl groups on its alkyl chains. Due to the high hydroxyl value of CAS, it can replace only some of the petrochemical polyols in this formulation of FPUF to avoid collapse of the cellular foam structure. [29-31] The purpose of this work was to

investigate the mechanical properties, flame retardancy and smoke behavior among different combinations of the selected additives (EG, OP, CuO and CAS) in FPUF through a series of fire testing methods and observe how the bio-based ingredient influences the properties of the resulting FPUFs. Using commercially available materials, this feasibility study addresses multicomponent flame retardant systems that are close to application and may be used as starting point for evidence-based future product development.

2. Experimental

2.1 Materials

Polyether polyol (VORANOLTM 3322 Polyol; average OH number: 48 mg KOH/g; molecular weight: 3506 g/mol; nominal functionality: 3) was provided by Dow Europe GmbH (Horgen, Switzerland). Dimethylethanolamine (Dabco[®] DMEA), tin-II-isoctotatate (100%, Kosmos[®] T9) and polyether polysiloxane (Tegostab[®] BF 2370) were supplied by Evonik Operations GmbH (Essen, Germany). Toluylene diisocyanate (mixture of isomers) for synthesis (TDI) was purchased from Merck Chemical GmbH (Darmstadt, Germany). Deionized water was used as a chemical blowing agent in the foaming procedure. Expandable graphite (EG) with an expansion ratio of 270 to 325 and a particle size of +50 mesh (>300 µm, ≥75% minimum) was purchased from Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany). Exolit[®] OP 560 polyol (OP) (hydroxyl number: 400–500 mg KOH/g; phosphorus content: 10–13% wt/wt; Acid number: max. 2 mg KOH/g) was provided by Clariant AG (Muttensz, Switzerland). Nano copper oxide powder (CuO) (99+%) and castor oil (CAS) (100%) were purchased from abcr GmbH (Karlsruhe, Germany) and Thermo Fisher (Kandel) GmbH (Kandel, Germany), respectively. The metal oxide was used as a nanoparticle to achieve high activity. The selection of materials was oriented toward the feasible production of a systematically varied set of FPUFs acting as representative case example. The complex multicomponent approach is based on commercially available raw materials and may be used as direct starting point for evidence-based future

product development There is plenty of room for optimization, such as by varying the flame retardant polyol, for instance using a polyol with a higher phosphorus content such as Exolit® OP 550 (16–18% wt/wt), using an alternative expandable graphite (different size, or coated), [32] or optimizing the metal oxide with regard to cost efficiency.

2.2 Sample preparation

The foams were prepared by one-pot method and formed in an open paper mold 125 mm x 125 mm x 160 mm (height x width x height) in size to allow free foaming. The type and amount of flame retardant/additives used in each FPUF sample are listed in Table 1. Part A (polyether polyol, dimethylethanolamine, tin-II-isooctotate, polyether polysiloxane, water and the additives (EG/ OP/ CuO/ CAS)) was stirred for 5 min in a 500 mL disposable plastic cup using a mechanical stirrer at 2000 rpm. Then the weighted part B (TDI) was added to the blended part A and the mixture was stirred at 2000 rpm for 7 s. The mixture was then poured into the mold, where the foam started to rise freely. Afterward, the foam was cured at 80 °C in an oven for 24 h. The specimens used in the following tests were cut from the core of the freely risen foams. The surface and interface parts of the foams were segregated, so that only specimens with homogenous morphologies were investigated.

Table 1. Formulation of the samples

Sample	Polyether polyol (g)	Surfactant and catalysts* (g)	Water (g)	EG (g)	OP (g)	CuO (g)	CAS (g)	TDI (g)
FPUF	90.9	0.54	3.66	-	-	-	-	46.8
FPUF-10EG	90.9	0.54	3.66	13.38	-	-	-	46.8
FPUF-0.1CuO	90.9	0.54	3.66	-	-	0.13	-	46.8

FPUF-5OP	86.36	0.54	3.66	-	4.54	-	-	46.8
FPUF-5OP-10EG	86.36	0.54	3.66	13.38	4.54	-	-	46.8
FPUF-5OP-0.1CuO	86.36	0.54	3.66	-	4.54	0.13	-	46.8
FPUF-5OP-10EG- 0.1CuO	86.36	0.54	3.66	13.38	4.54	0.13	-	46.8
FPUF-10CAS	81.81	0.54	3.66	-	-	-	9.09	46.8
FPUF-5OP-10CAS	77.27	0.54	3.66	-	4.54	-	9.09	46.8
FPUF-5OP- 10CAS-10EG	77.27	0.54	3.66	13.38	4.54	-	9.09	46.8
FPUF-5OP- 10CAS-0.1CuO	77.27	0.54	3.66	-	4.54	0.13	9.09	46.8
FPUF-5OP- 10CAS-10EG- 0.1CuO	77.27	0.54	3.66	13.38	4.54	0.13	9.09	46.8

*Surfactant and catalysts represent the mixture of 0.18 g of dimethylethanolamine, 0.18 g of tin-II-isooctotatate and 0.18 g of polyether polysiloxane

2.3 Measurements and characterization

2.3.1 Morphology

A scanning electron microscope (SEM) Zeiss EVO 10 (Oberkochen, Germany) was used to observe the core structure of the foams at a position perpendicular to the foam rising direction, and the char residues after the cone calorimeter measurement. SEM was performed with a constant electron high tension (EHT) voltage of 10 kV in a chamber under high vacuum. The specimens were sputter-coated with a 15 nm layer of gold on the surface to improve conductivity and prevent charging prior to investigation.

2.3.2 Physical and mechanical properties

The apparent density of the samples was measured according to ISO 845. The mechanical properties were determined by measuring the tensile strength and compression strength with a Zwick Z010 (Ulm, Germany) universal testing machine in accordance with ISO 1798 and ISO 3386-1, respectively. In the compression test, three cycles were performed per specimen. In tensile and compression tests, four and three specimens were measured for each sample, respectively.

2.3.3 Thermal decomposition

Thermogravimetric analysis (TGA) was used to measure the change in the sample's mass over time as a function of temperature under a continuous constant flow of nitrogen gas. The thermal decomposition behavior of the samples was measured by a TG 209 F1 Iris from Netzsch Instruments (Selb, Germany). The samples were first milled into fine powder using a CryoMill from Retsch (Haan, Germany). 10 mg of powdered sample was placed in the aluminum oxide crucible. After placing the crucible in the furnace, a heating program at a heating rate of 10 K/min from 40 °C to 650 °C was started under 30 mL/min nitrogen. TGA, in combination with Fourier Transform Infrared Spectroscopy (FTIR) Tensor 27 FT-IR produced by Bruker (Ettlingen, Germany), allowed the gaseous products evolved from the samples to be examined during thermal decomposition.

2.3.4 Fire behavior

All specimens were placed in an environment of 23 °C and 50% relative humidity for at least 48 h before measurement. The limiting oxygen index (LOI) was measured at room temperature according to ISO 4589-2 with a test specimen of foam II 150 mm x 10 mm x 10 mm in size (length x width x thickness), using equipment from Fire Testing Technology Limited (West Sussex, United Kingdom). The horizontal UL 94 burning test (UL 94 HBF) was carried out in accordance with ISO 9772. A specimen 150 mm x 50 mm x 10 mm in size was used in this test. The foam was placed horizontally. The measurement determines the spread speed of flame and

the dripping condition of the samples. Cone calorimeter tests were performed according to ISO 5660. The device was manufactured by Fire Testing Technology Limited (West Sussex, United Kingdom). The specimen 100 mm x 100 mm x 50 mm in size (length x width x thickness) was fitted in an aluminum foil tray and exposed horizontally to an external heat flux of 25 kW m^{-2} with a distance of 25 mm between the cone heater and the surface of the specimen. All samples were measured twice. If any key result deviated by more than 10%, a third measurement was performed.

2.3.5 Smoke and toxic gas measurements

A smoke density chamber (SDC) produced by Fire Testing Technology Limited (West Sussex, United Kingdom) was used to determine the smoke production of flammable specimens in a static airflow chamber. The measurement was performed following the ISO 5959 standard on a specimen 75 mm x 75 mm x 25 mm in size (length x width x thickness) fitted in a sample holder and exposed to an external heat flux of 25 kW m^{-2} under forced flaming conditions. SDC was used in combination with an FTIR spectrometer, which can collect qualitative and quantitative data on the gas composition of the smoke during the burning process.

3. Results and discussion

3.1 Morphological characterization and measurement of mechanical properties

The analysis of morphology is critical because the mechanical properties of the FPUFs are substantially affected by cell wall thickness and cell size. FPUFs typically contain closed, open, and partially open cells. [33] The foam structure of the specimen is homogeneous and without any different surface morphologies, because they are all cut from the inner part of the produced foam. The images of a cross section of the sample were taken at 100 times magnification. All samples show very similar, complete, and intact open-cell structures of foam as shown in Figure 1. Table 2 shows that the density and the morphology of all samples is highly comparable. Even

samples with different kinds of additive added exhibit no significant differences in terms of morphology. This means the foam preparation process did not affect these properties of the foams.

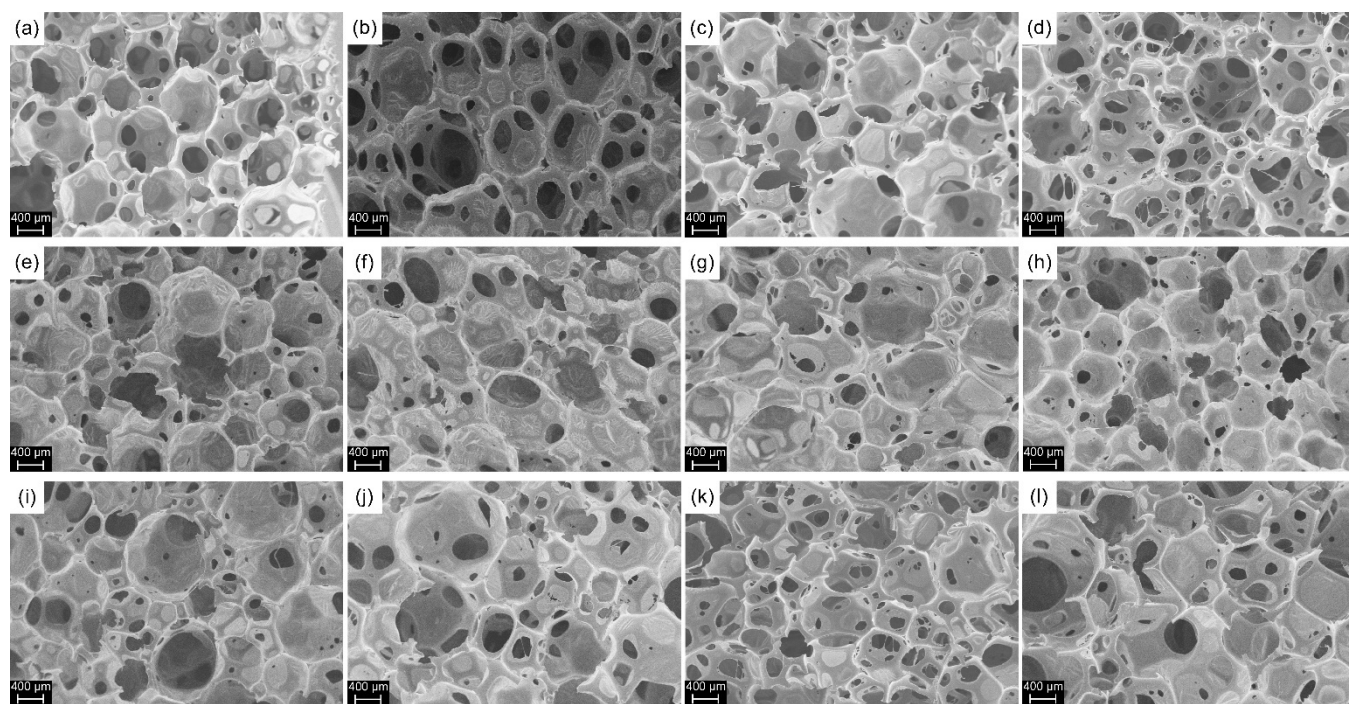


Figure 1. SEM images of (a) FPUF, (b) FPUF-10EG, (c) FPUF-0.1CuO, (d) FPUF-5OP, (e) FPUF-5OP-10EG, (f) FPUF-5OP-0.1CuO, (g) FPUF-5OP-10EG-0.1CuO, (h) FPUF-10CAS, (i) FPUF-5OP-10CAS, (j) FPUF-5OP-10CAS-10EG, (k) FPUF-5OP-10CAS-0.1CuO and (l) FPUF-5OP-10CAS-10EG-0.1CuO

Table 2. Density and mechanical properties of samples

Sample	Density (kg m ⁻³)	Tensile strength (kPa)	Elongation at break (%)	Compressio n stress at 40% compression (kPa)	Compressio n stress at 60% compression (kPa)
FPUF	33.9 ± 1.9	133.4 ± 6.6	119.5 ± 8.9	5.91 ± 0.64	11.53 ± 1.26
FPUF-10EG	33.7 ± 1.9	154.8 ± 3.2	146.1 ± 2.2	14.8 ± 0.6	35.97 ± 4.09
FPUF-0.1CuO	35.8 ± 3.4	142.8 ± 15.9	119.4 ± 21.9	7.55 ± 0.94	16.69 ± 3.74
FPUF-5OP	32.2 ± 2.8	100.3 ± 7.2	102.3 ± 16.9	6.77 ± 1.69	17.04 ± 5.97
FPUF-5OP-10EG	34.5 ± 1.1	131.7 ± 11.2	123.2 ± 17	4.9 ± 0.34	10.19 ± 0.89
FPUF-5OP-0.1CuO	38.9 ± 1.3	114.4 ± 5.2	119.8 ± 8	4.88 ± 0.73	12.07 ± 3.29
FPUF-5OP-10EG-0.1CuO	34.5 ± 0.5	145.9 ± 6.8	128.8 ± 7.9	5.37 ± 0.22	11.69 ± 0.44
FPUF-10CAS	38.3 ± 2	163.2 ± 40.8	130.3 ± 30.1	10.82 ± 3.24	28.93 ± 11.52
FPUF-5OP-10CAS	37.6 ± 2.3	120.6 ± 6.04	128.4 ± 7.9	4.47 ± 1.24	9.6 ± 3.29
FPUF-5OP-10CAS-10EG	33.2 ± 2.7	125.5 ± 9.8	106.1 ± 4	4.67 ± 0.37	10.3 ± 1.4
FPUF-5OP-10CAS-0.1CuO	36.1 ± 2.6	138.3 ± 7.5	136.1 ± 6.1	5.55 ± 1.04	12.95 ± 2.95
FPUF-5OP-10CAS-10EG-0.1CuO	37.3 ± 2.4	133.5 ± 4.4	125.6 ± 6.4	4.26 ± 0.19	8.92 ± 0.53

According to the results of mechanical tests in Table 2, in general all samples show similar tensile strength and elongation at break. Moreover, most of the samples show comparable compression stress at 40% and 60% compression. The replacement of petrochemical polyol with 5 wt.% OP in FPUF reduced the tensile strength and elongation at break. This is because FPUF-5OP has a higher crosslinking density than FPUF, since OP has a higher OH number. The results show that FPUF-10EG and FPUF-10CAS improved all the parameters of mechanical properties: tensile strength, elongation at break, and compression stress at 40% and 60% compression.

3.2 Pyrolysis: Thermogravimetric analysis (TGA)

The thermal decomposition behavior of FPUFs was studied. Mass loss during pyrolysis under a nitrogen atmosphere was measured using TGA. Table S1 summarizes the results obtained from the TGA measurement. Figure 2 shows the mass and DTG (the first derivative of mass (T) curve) curves of the samples. The mass curve of all samples consists of two decomposition stages. The first decomposition stage is attributed to the breaking of the polyurethane bonds (namely hard segments), while the second decomposition stage is related to the decomposition of soft segments, mainly the polyols. [34,35] All samples had a similar decomposition temperature in the first decomposition stage. The mass curve of the FPUFs containing EG shifted to higher temperatures in the second decomposition stage, implying that the samples containing EG decomposed at higher temperatures. The FPUF containing EG had the highest amount of residue at 600 °C because the graphite could not evaporate during thermal decomposition and remained in the crucible. The amount of residue of FPUF-5OP at 600 °C was double that of FPUF due to phosphorus acting as a charring agent in the condensed phase. [36,37]

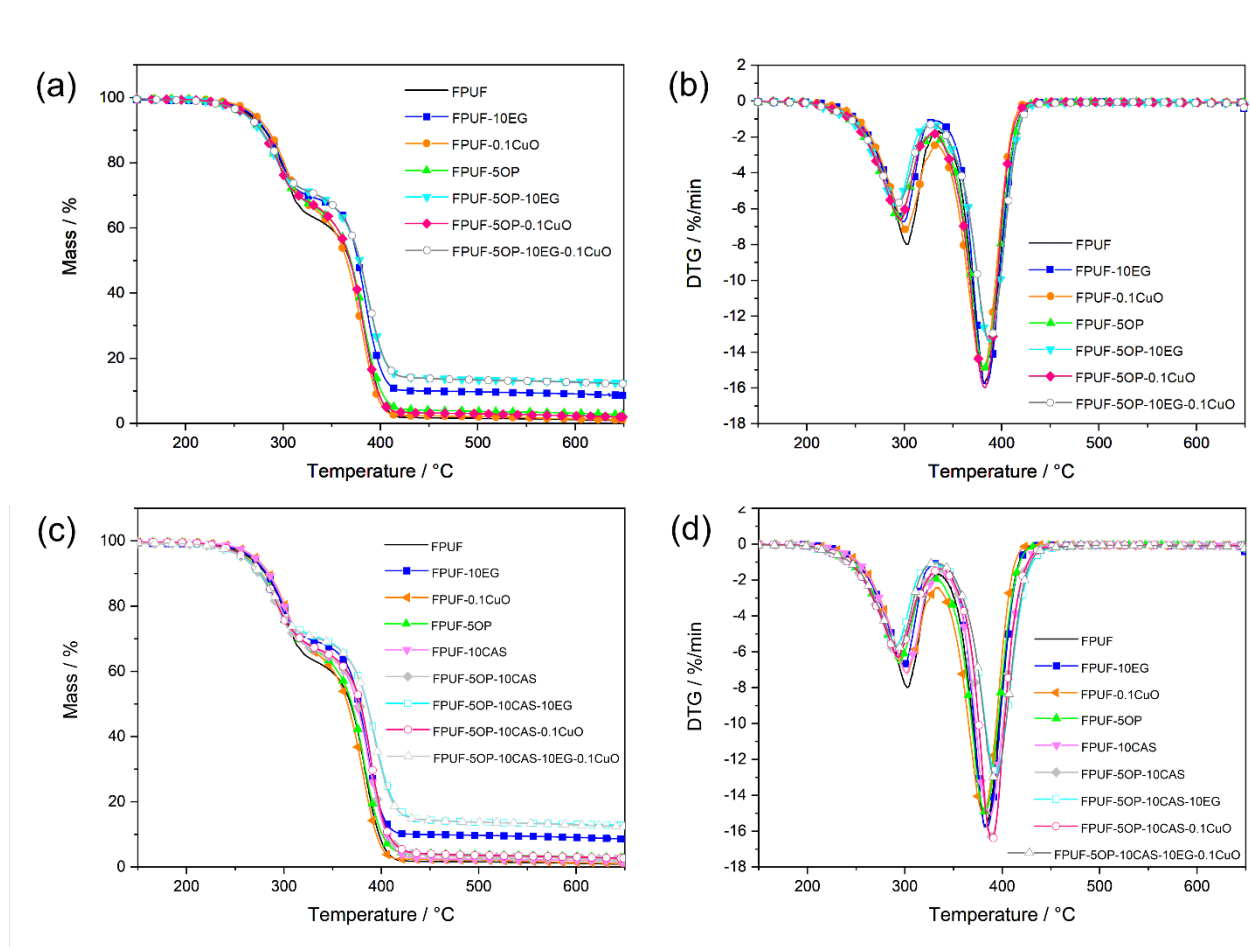


Figure 2. (a) Mass curves and (b) DTG curves of FPUF-OP-EG-CuOs; (c) Mass curves and (d) DTG curves of FPUF-OP-CAS-EG-CuOs

3.3 Fire behavior: Reaction to the small flame

Table S2 exhibits the LOI and UL 94 horizontal test results, addressing the flammability at the beginning of a fire. Aside from the used flame retardants, the flammability of PU foams depends on their morphology; fire properties such as the LOI can usually be described as function of the density. [38, 39] It should be noted that the foam production and specimen preparation yield such a similar foam morphology that any significant impact of morphology or density on the LOI and UL 94 results was ruled out. FPUF and FPUF-0.1CuO showed the lowest value, 18 vol.%. This means that 0.1 wt.% CuO alone did not influence flammability. FPUF-5OP-10CAS-10EG-0.1CuO reached the highest value among the samples: 24.4 vol.%. FPUF-10EG and FPUF-5OP had 21 vol.% and 21.2 vol.%, respectively. Generally, the presence of CAS

slightly increased the LOI value of the FPUFs. There was a slight synergistic effect between 5 wt.% OP and 0.1 wt.% CuO in FPUF. There was a clear synergistic effect between 5 wt.% OP and 10 wt.% of CAS in FPUF. The fire behavior of the samples in reaction to small flames was also tested by UL 94 HBF. Fire phenomena such as self-extinction and dripping were observed and recorded. Except for FPUF, none of the samples dripped burning drops that ignited the underlying cotton. This proved that all additives had an anti-dripping effect on the foams. FPUF and FPUF-0.1CuO burned at a burning rate of 113 mm/min. The burning rate of FPUF-CAS was slightly reduced to 100 mm/min. Apart from FPUF, FPUF-0.1CuO and FPUF-10CAS, the rest of the samples exhibited self-extinguishing behavior before the 25 mm mark of the specimens was reached. The UL 94 HBF results were consistent with the LOI results.

3.4 Fire behavior: Cone calorimeter

Various parameters such as peak heat release rate (PHRR), total heat release (THR), average effective heat of combustion (Av-EHC), residue (wt.%), total smoke release (TSR) and maximum average rate of heat emission (MARHE) were collected in the test and tabulated in Table 3. The fire behavior of foams is strongly influenced by the foam morphology, for instance higher density yields increasing fire loads (THR) and longer burning times. [39] Comparing foams with the same morphology and density ensures that the impact of the flame retardant components on the fire behavior is investigated, as the additives' impact on morphology and foaming is excluded. The HRR and THR curves of the samples are displayed in Figure 3. FPUF consists of two peaks of HRR. The first peak is associated with the rupture of the urethane bond in the hard segment and is accompanied by the collapse of the foam structure. The second peak corresponds to the decomposition of the soft segment. [34, 40-42] The second peak (470 kW m^{-2}) is much higher than the first peak (273 kW m^{-2}) because a pool fire was created during the second stage of burning, which dominates the burning process. [41, 43] 10 wt.% of EG reduced the PHRR substantially, making it even lower than the first peak of FPUF. All samples with

EG have a reduced PHRR, higher char yield, lower total smoke release and a lower MARHE. Nano-CuO did not reduce the smoke release in FPUF. EG reduced the MAHRE and EHC considerably. EHC is expressed as the total heat release per total mass loss. The sample with 5 wt.% of OP had a lower EHC due to flame inhibition, the gas phase activity of the phosphorus compounds released. Notably, the samples with both 5 wt.% of OP and 10 wt.% of EG further reduced the EHC value to less than 20 MJ kg^{-1} . The reduction in the EHC of FPUF with the combination of OP and EG was supported by an interplay of flame inhibition, charring, and a protective layer. It is also notable that the char yield of FPUF with EG and OP was much higher than that with only EG, increasing from 17.7 wt.% (FPUF-10EG) up to 51.6 wt.% (FPUF-5OP-10EG), an increase of nearly three times. This was due to a synergistic effect of the phosphorus compound and EG on the char yield. [4, 44, 45] In addition to the enhanced charring of the PU, pyrolysis was largely incomplete under the protective residue functioning as heat shield. During burning, OP increased charring efficiency and became glassy polyphosphate, lending a gluing effect to EG which strengthened the expanded graphite to form an excellent protective barrier against heat flux. Phosphorus was pyrolyzed into phosphoric acid derivatives to catalyze the carbonization of polymers at elevated temperatures. Bourbigot et al. [36] showed that polyaromatic species are crosslinked with phosphohydrocarbonaceous bridges to form a voluminous thermal insulation layer. As a result, the underlying material undergoes incomplete pyrolysis. [16, 17, 46] This behavior led to reductions in PHRR, burning time and THR. Thus, it is confirmed that the flame retardancy modes of action work in both the gas phase and the condensed phase. Small, insignificant HRR peaks can be observed in FPUF-10EG throughout the burning process. This is because cracks appeared between the EG layers, causing side burning by exposing the inner unburned material to the heating source. The FPUF sample was extinguished by complete consumption of the fuel. FPUF-5OP-10EG and FPUF-5OP-10EG-0.1CuO exhibit fire behavior different from FPUF, and were extinguished by the excellent thermal barrier that formed before everything was consumed. The difference in char yield

between them (51.6 wt.% and 20.9 wt.%) due to CuO deteriorated the thermal protective layer, thus prolonging the burning time. Therefore, FPUF-5OP-10EG-0.1CuO had a longer burning time and less char yield than FPUF-5OP-10EG. FPUF-5OP-10CAS-10EG-0.1CuO had the lowest value of THR (15 MJ m⁻²). FPUF-5OP-10EG reduced the total burning time compared to the sample with only 10 wt.% EG. The THR of FPUF-5OP was slightly reduced, but the PHRR was not reduced by the phosphorous polyol (OP).

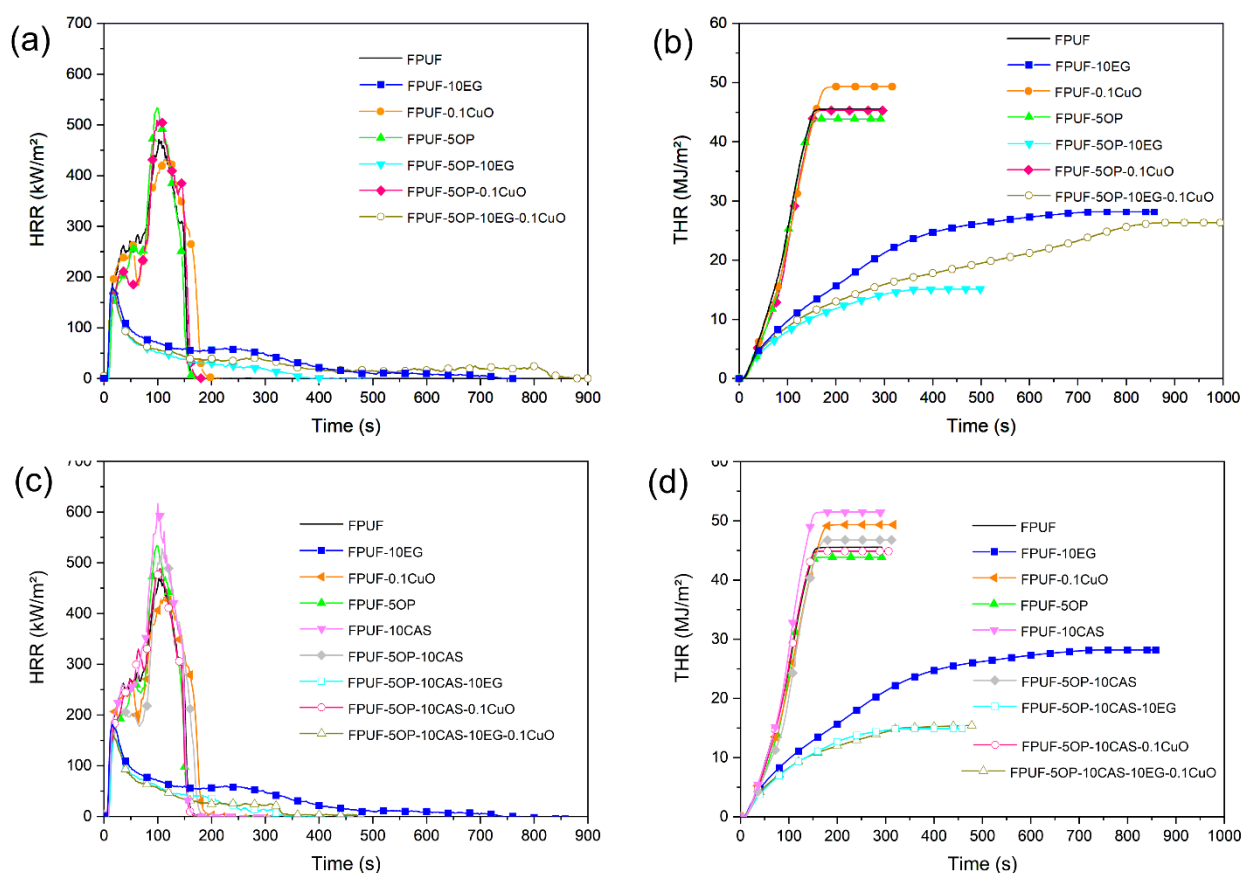


Figure 3. (a) Heat release rate and (b) total heat release rate of FPUF-OP-EG-CuOs; (c) heat release rate and (d) total heat release rate of FPUF-OP-CAS-EG-CuOs

Table 3. Table of cone calorimeter results

Sample	PHRR (kW m ⁻²)	THR (MJ m ⁻²)	Av-EHC (MJ kg ⁻¹)	Residue (wt.%)	TSR (m ² m ⁻²)	MARHE (kW m ⁻²)
FPUF	452 ± 19	42.2 ± 2.3	27.5 ± 2.6	0.1 ± 0.1	278 ± 19	296 ± 1
FPUF-10EG	191 ± 9	30.7 ± 2.6	22.1 ± 0.5	17.7 ± 0.8	42 ± 10	122 ± 4
FPUF-0.1CuO	456 ± 24	44.5 ± 4.3	24.9 ± 0.1	0.1 ± 0.1	303 ± 20	304 ± 19
FPUF-5OP	525 ± 9	41.5 ± 2.1	22.9 ± 0.2	2.7 ± 0.2	494 ± 20	284 ± 10
FPUF-5OP-10EG	166 ± 1	16.3 ± 1.3	18.9 ± 1.5	51.6 ± 0.2	67 ± 2	105 ± 5
FPUF-5OP-0.1CuO	477 ± 32	43.5 ± 1.4	23 ± 0.1	2.9 ± 0.4	550 ± 5	294 ± 5
FPUF-5OP-10EG-0.1CuO	180 ± 3	26.7 ± 0.4	19.6 ± 0.3	20.9 ± 1.2	68.7 ± 10	114
FPUF-10CAS	603 ± 14	48.1 ± 2.1	25.1 ± 0.1	0.2 ± 0.2	352 ± 18	330 ± 11
FPUF-5OP-10CAS	503 ± 24	43.7 ± 2.9	23.4 ± 0.2	1.7 ± 0.4	570 ± 28	295 ± 13
FPUF-5OP-10CAS-10EG	159 ± 6	16.9 ± 2.1	19.9 ± 0.2	49.3 ± 1.7	80 ± 1	100 ± 5

FPUF-5OP- 10CAS-0.1CuO	510 ± 21	41.6 ± 2.5	23.3 ± 0.2	1.6 ± 0.2	518 ± 33	292 ± 7
FPUF-5OP- 10CAS-10EG- 0.1CuO	165 ± 1	15 ± 0.1	19.8 ± 1	59.3 ± 0.7	68 ± 3	103 ± 2

3.5 Fire residues

The representative photographs and SEM images of the fire residue from the samples after cone calorimeter measurements are shown in Figure S1 and Figure 4, respectively. Studying the morphology of fire residue is important to understand the burning behavior. FPUF collapsed into a pool fire which consumed nearly all the material during burning. [43, 47] The residue of FPUF was minimal, as seen in Figure S1(a). Figure 4(a) shows the small fragments of the polyurethane residue of FPUF. Figure 4(c) (FPUF-0.1CuO) also shows the fragments of residue, but with many tiny holes. Figure 4(h) (FPUF-10CAS) shows that a part of continuous residue was split apart. The conclusion is that these kinds of residue are fragile and not suitable to work as a protective layer for underlying materials. Figure 4(d) (FPUF-5OP) shows a continuous flat surface of residue without large holes. As shown in Figure 4(e), Figure 4 (g), Figure 4 (j), and Figure 4 (l) (FPUF-5OP-10EG, FPUF-5OP-10EG-0.1CuO, FPUF-5OP-10CAS-10EG, and FPUF-5OP-10CAS-10EG-0.1CuO), EG was agglomerated by the glassy polyphosphate mixed with FPUF residue. Figure 5 shows a higher magnification SEM micrograph of FPUF-5OP-10EG to explain the synergistic effect between phosphorus and EG on char yield. [46] EG expanded several times, becoming voluminous and “worm-like” char during burning. There are many fibrous residues containing polyphosphate, which formed a continuous network with additional expanded graphite. They enhanced the adhesion between the expanded graphite, thereby improving the integrity and continuity of the protective char layer and preventing

further pyrolysis of the underlying material. Less heat flux is transferred to the pyrolysis front, eventually leading to incomplete pyrolysis, which maintains the high apparent char yield of the specimens in cone calorimeter measurements. Without the presence of phosphorous flame retardant, Figure 4(b) (FPUF-10EG) shows that the fibrous residue was brittle, so that most of the fibers did not connect to other areas of expanded graphite. In Figure 4(f) (FPUF-5OP-0.1CuO), cracks and holes appear on the surface, which indicate that the residue was fragile. The surface of FPUF-5OP-10CAS (Figure 4(i)) is uneven, with many holes. The residue of FPUF-5OP-10CAS-0.1CuO (Figure 4(k)) had irregular holes on the surface. The high weight percentage of residue for FPUF-5OP-10EG, FPUF-5OP-10CAS-10EG and FPUF-5OP-10CAS-10EG-0.1CuO is visible in the photographs of residue in Figure S1(e), Figure S1(j) and Figure S1(l), respectively. These pictures show the structural integrity of the carbonaceous char without any curving. The more complete structural integrity of the carbonaceous char, the greater amount of material underneath and therefore the higher weight percentage of residue was recorded. The curving of the carbonaceous char in FPUF-10EG and FPUF-5OP-10EG-0.1CuO resulted in the exposure of the bottom to the flame. Therefore, a lower weight percentage of residue remained. Hence, OP and CAS improved the structural integrity of carbonaceous char, but CuO deteriorated it.

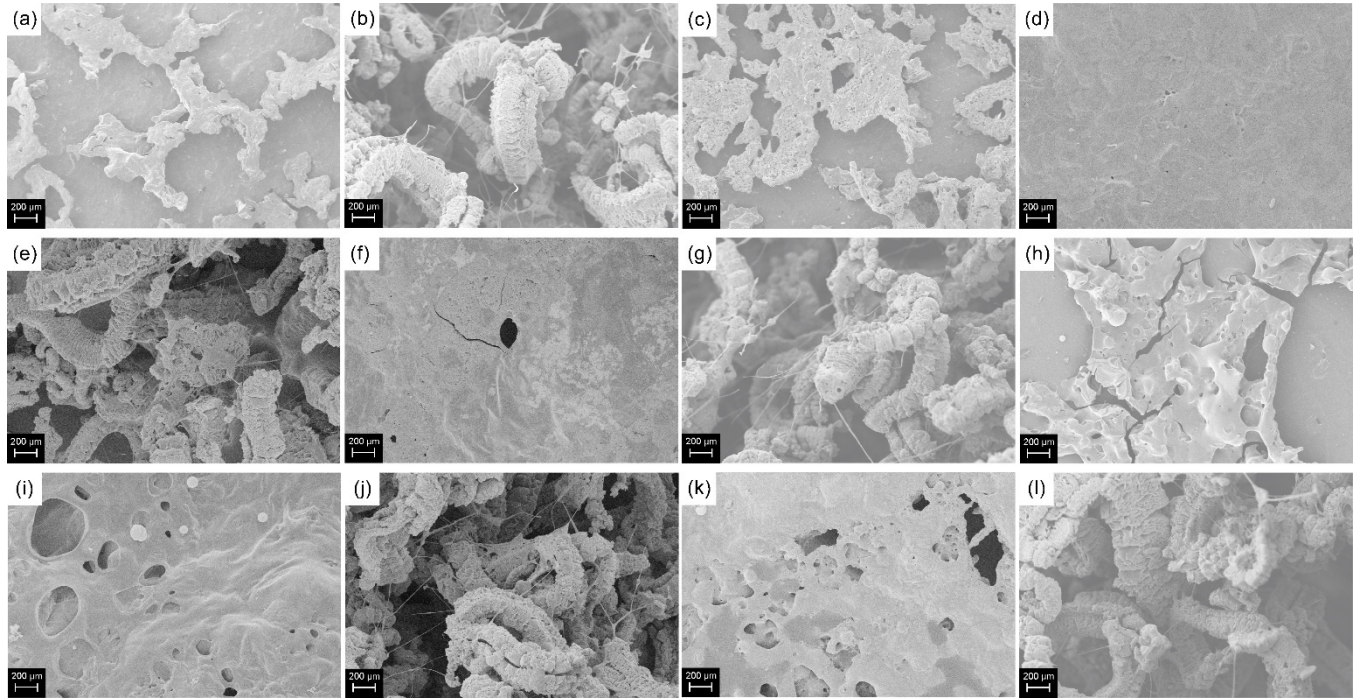


Figure 4. SEM images of fire residue of (a) FPUF, (b) FPUF-10EG, (c) FPUF-0.1CuO, (d) FPUF-5OP, (e) FPUF-5OP-10EG, (f) FPUF-5OP-0.1CuO, (g) FPUF-5OP-10EG-0.1CuO, (h) FPUF-10CAS, (i) FPUF-5OP-10CAS, (j) FPUF-5OP-10CAS-10EG, (k) FPUF-5OP-10CAS-0.1CuO and (l) FPUF-5OP-10CAS-10EG-0.1CuO after cone calorimeter measurement

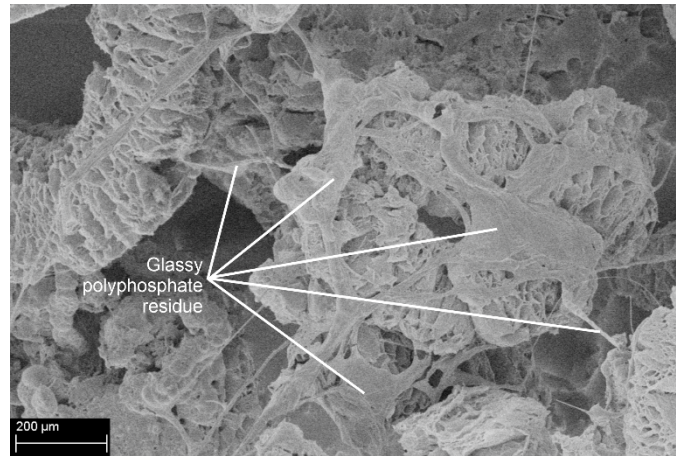


Figure 5. SEM picture of fire residue of FPUF-5OP-10EG after cone calorimeter measurement

3.6 Smoke and toxic gas measurements

It is crucial to assess the quantity and quality of smoke emitted by materials, as smoke is always the cause of suffocation in fires. However, the yield of smoke released depends on various

factors such as ambient temperature, the availability of oxygen, type of ignition, and air flow. Therefore, detailed smoke measurements were performed under two different conditions, good ventilation and controlled ventilation. In addition to smoke, toxic gases cannot be ignored during fires. Carbon monoxide is the most common asphyxiant in fires due to incomplete combustion. Hydrogen cyanide is one of the gaseous products released by nitrogenous materials during burning. [48] Moreover, hydrogen cyanide is about 25 times more toxic than carbon monoxide because it forms cyanide ions in the blood, preventing cellular respiration. [49] Therefore, these two toxic gases were analyzed in the smoke measurements of the FPUF samples.

3.6.1 Smoke measurement: Cone calorimeter

The smoke release was measured with a cone calorimeter under well ventilated conditions. According to Figure 6(a), 10 wt.% EG in FPUF released a remarkably small amount of smoke because the expanded graphite prolonged the residence time of smoke particles in the pyrolysis zone. [17,19] More aromatics were charred, and fewer light smoke particles were eventually released. 0.1 wt.% CuO released slightly more smoke. Compared with FPUF, FPUF-5OP and FPUF-10CAS released more smoke. It is worth noting that 5 wt.% OP substantially increased the smoke release of FPUF (66% higher than FPUF), because the phosphorus worked in the gas phase to cause incomplete combustion and released more and larger particles, such as smoke and soot. Figure 6(b) shows the graph of the carbon monoxide production rate (COP) of selected samples. FPUF-10EG exhibited the lowest COP. The COP of FPUF-5OP was twice that of FPUF. This is due to incomplete combustion caused by phosphorous radicals, resulting in inhibited conversion of carbon monoxide into carbon dioxide, even in the presence of sufficient ambient oxygen. [37] The COP of FPUF-0.1CuO and FPUF-10CAS was similar to that of FPUF. EG suppressed the smoke and the amount of carbon monoxide released significantly.

Figure 6(c) and Figure 6(d) show that the TSR and COP in mixed systems were reduced by EG to very low levels even in the presence of OP.

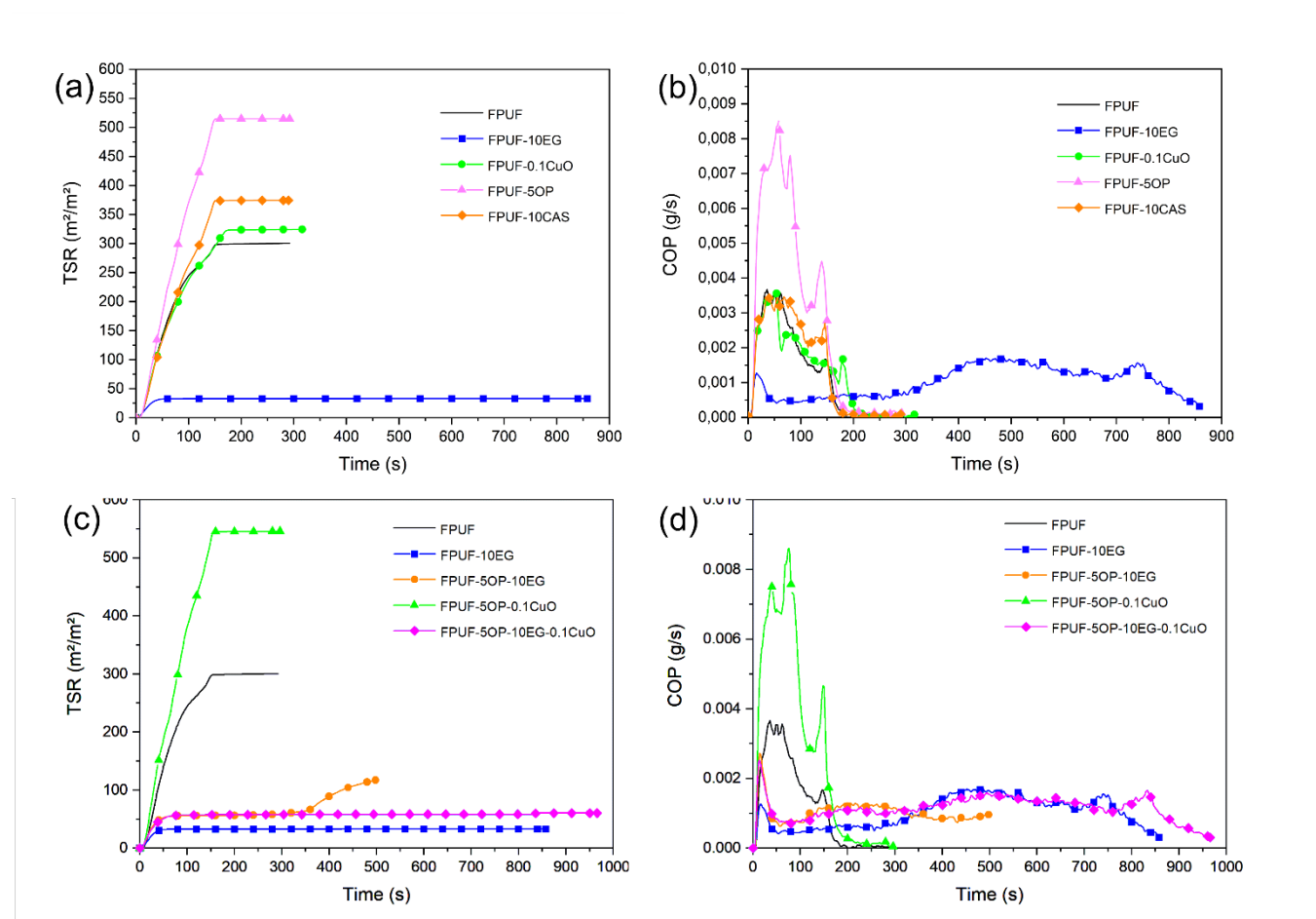


Figure 6. (a) Total smoke release, (b) carbon monoxide production rate curves of selected FPUFs with single additives, (c) total smoke release and (d) carbon monoxide production rate curves of selected FPUFs with mixed additives

3.6.2 Smoke measurement: Smoke density chamber

The specimens were burned under ventilation-controlled conditions in the smoke density chamber (SDC). According to the results of the specific optical density (D_s) measurements in Figure 7(a), 10 wt.% of EG in FPUF suppressed 65% of the smoke released by FPUF during the burning process. 0.1 wt.% of CuO in FPUF inhibited more than 30% of smoke release. However, in this case, 5 wt.% OP and 10 wt.% CAS did not play a role in suppressing smoke due to incomplete combustion. Figure 7(b) shows the light transmission of the smoke, which represents visibility during fire evacuation. The D_s value and transmission percentage of PFUF-

5OP and FPUF-10CAS are similar to those of FPUF. From the above analysis, 10 wt.% of EG is sufficient to reduce the smoke emission for FPUF under controlled ventilation conditions.

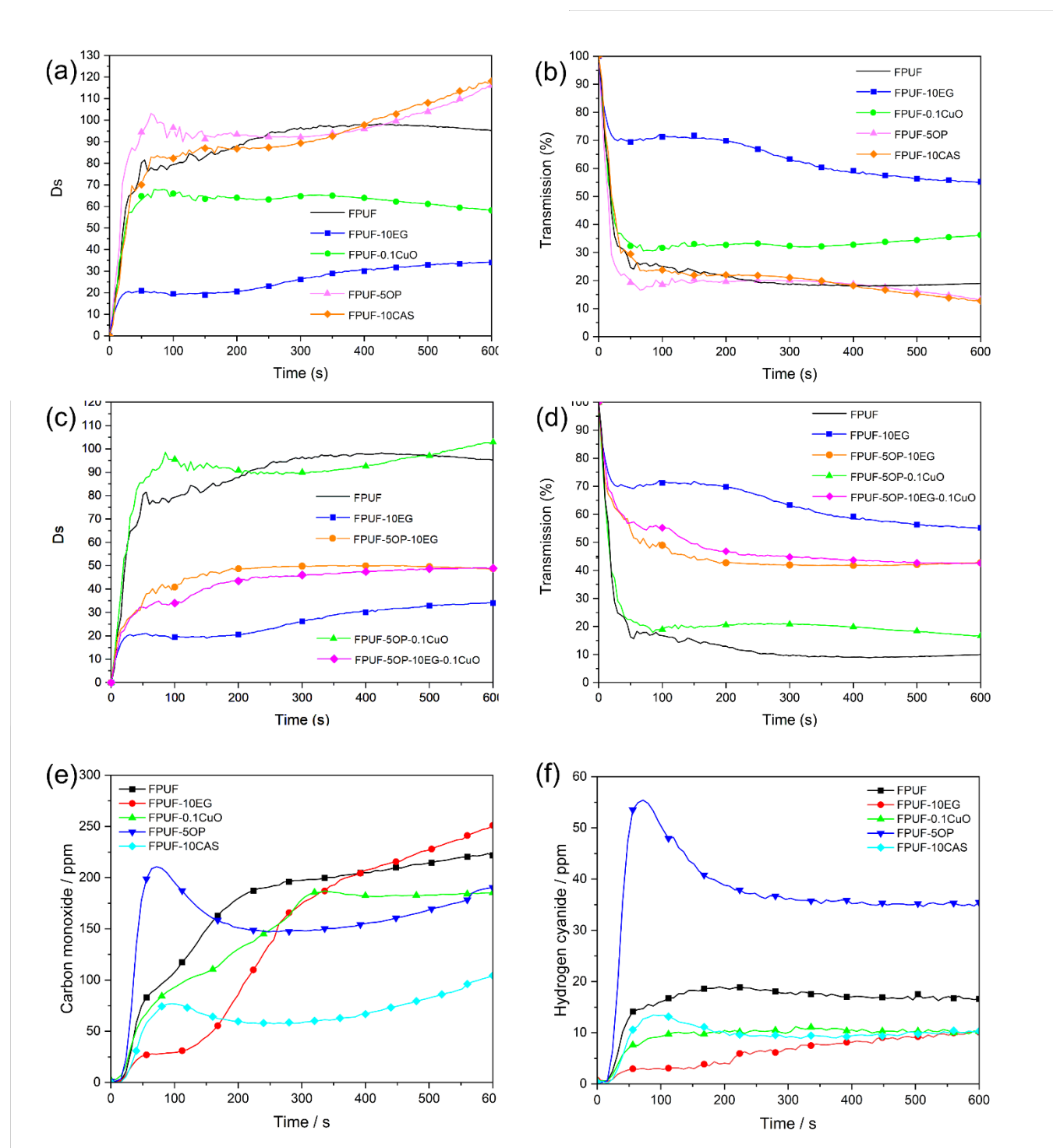


Figure 7. Smoke density chamber coupled with FTIR gas analysis: (a) Specific optical density, (b) transmission of the selected samples with single additives, (c) specific optical density, (d) transmission of the selected FPUFs with mixed additives, (e) carbon monoxide, and (f) hydrogen cyanide released from the selected samples burned with a pilot flame

To study the smoke release from FPUF combined with EG, OP and/or CuO, some samples were selected for comparison in Figure 7(c) and Figure 7(d). The D_s of FPUF-5OP-10EG-0.1CuO was slightly lower than that of FPUF-5OP-10EG at the beginning of burning, but they were the same at the end of the measurement. This means CuO initially suppressed the smoke release. Comparing the D_s of FPUF-5OP-10EG-0.1CuO and FPUF-5OP-0.1CuO, the addition of 10 wt.% effectively suppressed the smoke overall, especially apparent in the large reduction in the initial stage.

3.6.3 Toxic gas measurement

Besides smoke, toxic gases, especially carbon monoxide (CO) and hydrogen cyanide (HCN), are considered to be major hazards for people escaping fires. CO and HCN can cause asphyxiation because they block the uptake of oxygen by cells. [48] Therefore, CO and HCN were selected for toxic gas analysis. Figure 7(e) and Figure 7(f) show the emission of CO and HCN, respectively, from the selected samples burned with a pilot flame. The data were obtained from the FTIR coupled with SDC. Figure 7(e) shows that 5 wt.% of OP increased the emission of CO significantly at the beginning of the test. The CAS significantly reduced the emission of CO, which is more than half of the emissions from FPUF. EG significantly reduced the release of CO at the beginning of the test. In Figure 7(f), FPUF-5OP doubled the emissions of HCN. At the beginning of the test, the concentration of HCN surged to the highest peak, which means the 5 wt.% OP significantly increased the emission of HCN at the beginning of pyrolysis. The average EHC of FPUF-5OP from the cone calorimeter measurement decreased, while the amounts of CO and HCN increased. This means flame inhibition took place in the gas phase. EG decreased the emission of HCN effectively at the beginning of burning. Both CuO and CAS reduced the concentration of HCN during burning. The CuO particles in FPUF were exposed to HCN; the surface of CuO nanoparticles were reported to absorb and destruct HCN efficiently. [50, 51]

4. Conclusions

The results on flexible polyurethane foams flame retarded with different flame retardants obtained in this study revealed that EG is an outstanding flame retardant and smoke suppressant for FPUF according to the results from the cone calorimeter, smoke density chamber and toxic gases analysis. EG works mainly in the condensed phase to act as a protective char. EG significantly reduced the emission of CO and HCN at the beginning of burning under ventilation-controlled conditions. Furthermore, EG considerably reduced the concentration of HCN throughout the smoke density chamber test. The synergistic effect between phosphorus and EG resulted in a significant increase in char yield in cone calorimeter measurements. The combination of phosphorus and EG serves as an excellent option for dual flame retardant systems in FPUF. Although OP created a great deal of smoke during burning, the presence of EG suppressed the smoke effectively. The replacement of 10 wt.% by polyol with CAS not only increased the bio-based content in FPUF, but also maintained the physical and mechanical properties, and the fire behavior was similar to that without CAS. It is concluded that the presence of 0.1 wt.% of CuO additive effectively reduced the release of HCN from FPUF. An appropriate multi-component additive approach in FPUF combined with flame retardants, smoke suppressant and biomass substantially improved flame retardancy, smoke suppression, and bio-based content while reducing toxic gas emissions. This study provided insight into comprehensively improving the required properties of FPUF for the future.

Associated Content

Supporting Information Available:

Table S1 TGA results, Table S2: LOI & UL 94 results, and Figure S1: Photographs of the fire residues.

Acknowledgements

This project was funded by the DFG (Deutsche Forschungsgemeinschaft) (SCHA 730/19-1). The authors thank Dietmar Schulze for conducting the mechanical tests on the materials. The assistance of Tina Raspe and Dr. Simone Krüger with the smoke density chamber coupled with FTIR is highly appreciated.

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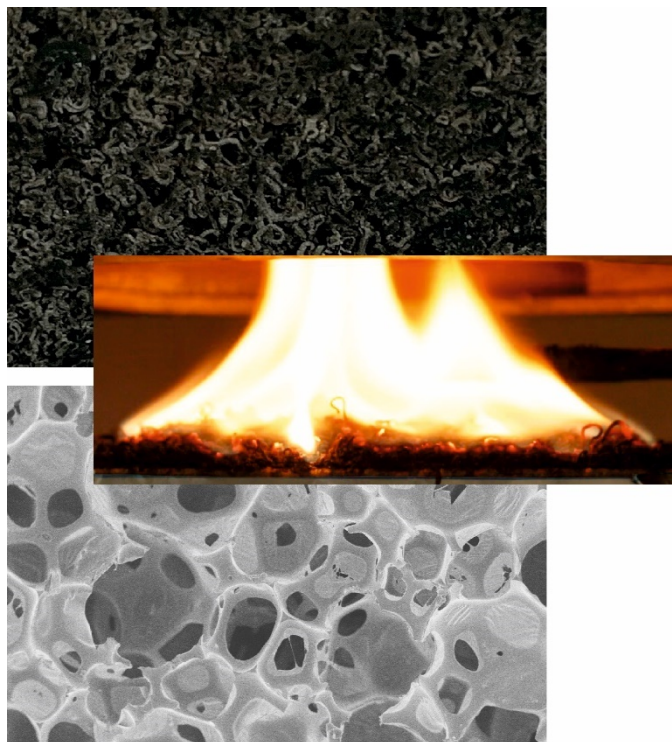
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TOC graphic



Supporting Information

Flame retardant combinations with expandable graphite/phosphorus/CuO/castor oil in flexible polyurethane foams

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Table S1. Selected data obtained from TGA (mass and DTG curves) of the FPUF samples

Sample	T _{5%} (°C)	* T _{max1} [#] (°C)	T _{max2} [#] (°C)	Δ T _{max1} and T _{max2} (°C)	Residue at 600 °C (%)	Δ Mass 1 [^] (%)	Δ Mass 2 [^] (%)
FPUF	265.0 ±0.6	302.6 ±0.3	383.2 ±0.5	80.6	1.6 ± 0.4	36.9 ± 0.1	60.6 ± 0.1
FPUF- 10EG	267.9 ±1.0	299.3 ±0.4	384.5 ±0.2	85.2	9.4 ± 0.4	30.3 ± 0.1	59.3 ± 0.2
FPUF- 0.1CuO	269.0 ±1.4	301.6 ±0.6	382.1 ±1.6	80.5	1.3 ± 0.1	33.9 ± 0.3	63.8 ± 0.3
FPUF- 5OP	260.5 ±0.5	295.2 ±0.1	382.4 ±0.3	87.2	3.32 ± 0.2	32.9 ± 0.1	63.0 ± 0.1
FPUF- 5OP- 10EG	260.3 ±0.7	292.2 ±1.0	387.7 ±0.5	95.5	12.7 ± 0.1	28.6 ± 0.3	57.9 ± 0.4
FPUF- 5OP- 0.1CuO	262.9 ±1.0	297.2 ±1.0	382.7 ±0.2	85.5	2.4 ± 0.1	32.4 ± 0.4	64.3 ± 0.5
FPUF- 5OP- 10EG- 0.1CuO	260.7 ±0.2	293.4 ±0.3	387.4 ±0.4	94	12.9 ± 0.2	28.6 ± 0.2	57.5 ± 0.1
FPUF- 10CAS	270.0 ±0.2	302.0 ±0.6	387.7 ±0.8	85.7	1.9 ± 0.1	33.6 ± 0.1	63.9 ± 0.1
FPUF- 5OP- 10CAS	256.9 ±0.1	293.4 ±0.4	389.1 ±0.1	95.7	2.6 ± 0.1	33.3 ± 0.1	63.1 ± 0.1

FPUF-	259.3	291.9	393.4	101.5	13.2 ± 0.6	28.8 ± 0.1	57.4 ± 0.2
5OP-	± 1.3	± 0.8	± 0.1				
10CAS-							
10EG							
FPUF-	260.7	293.9	389.6	95.7	3.0 ± 0.1	33.1 ± 0.1	63.5 ± 0.2
5OP-	± 0.9	± 0.7	± 0.5				
10CAS-							
0.1CuO							
FPUF-	259.4	292.6	392.1	99.5	12.8 ± 0.2	29.1 ± 0.1	57 ± 0.2
5OP-	± 0.6	± 0.5	± 0.8				
10CAS-							
10EG-							
0.1CuO							

* T_{5%}: Temperature at 5% mass loss

T_{max1}: First maximum of thermal decomposition rate; T_{max2}: Second maximum.

^ Δ Mass 1: Mass loss of the 1st decomposition stage; Δ Mass 2: Mass loss of the 2nd decomposition stage.

Table S2. LOI and UL 94 horizontal test results

Sample	LOI (vol.%)	Self-extinguished before the 25 mm mark	Burning drops	Burning rate (mm/min)
FPUF	18.0 ± 0.4	No	Yes	113
FPUF-10EG	21.0 ± 0.2	Yes	No	0
FPUF-0.1CuO	18.0 ± 0.2	No	No	113
FPUF-5OP	21.2 ± 0.1	Yes	No	0
FPUF-5OP-10EG	23.6 ± 0.2	Yes	No	0
FPUF-5OP-0.1CuO	22.0 ± 0.1	Yes	No	0
FPUF-5OP-10EG- 0.1CuO	22.8 ± 0.1	Yes	No	0
FPUF-10CAS	18.4 ± 0.2	No	No	100
FPUF-5OP-10CAS	22.2 ± 0.2	Yes	No	0
FPUF-5OP-10CAS- 10EG	24.0 ± 0.2	Yes	No	0
FPUF-5OP-10CAS- 0.1CuO	21.4 ± 0.2	Yes	No	0
FPUF-5OP-10CAS- 10EG-0.1CuO	24.4 ± 0.2	Yes	No	0

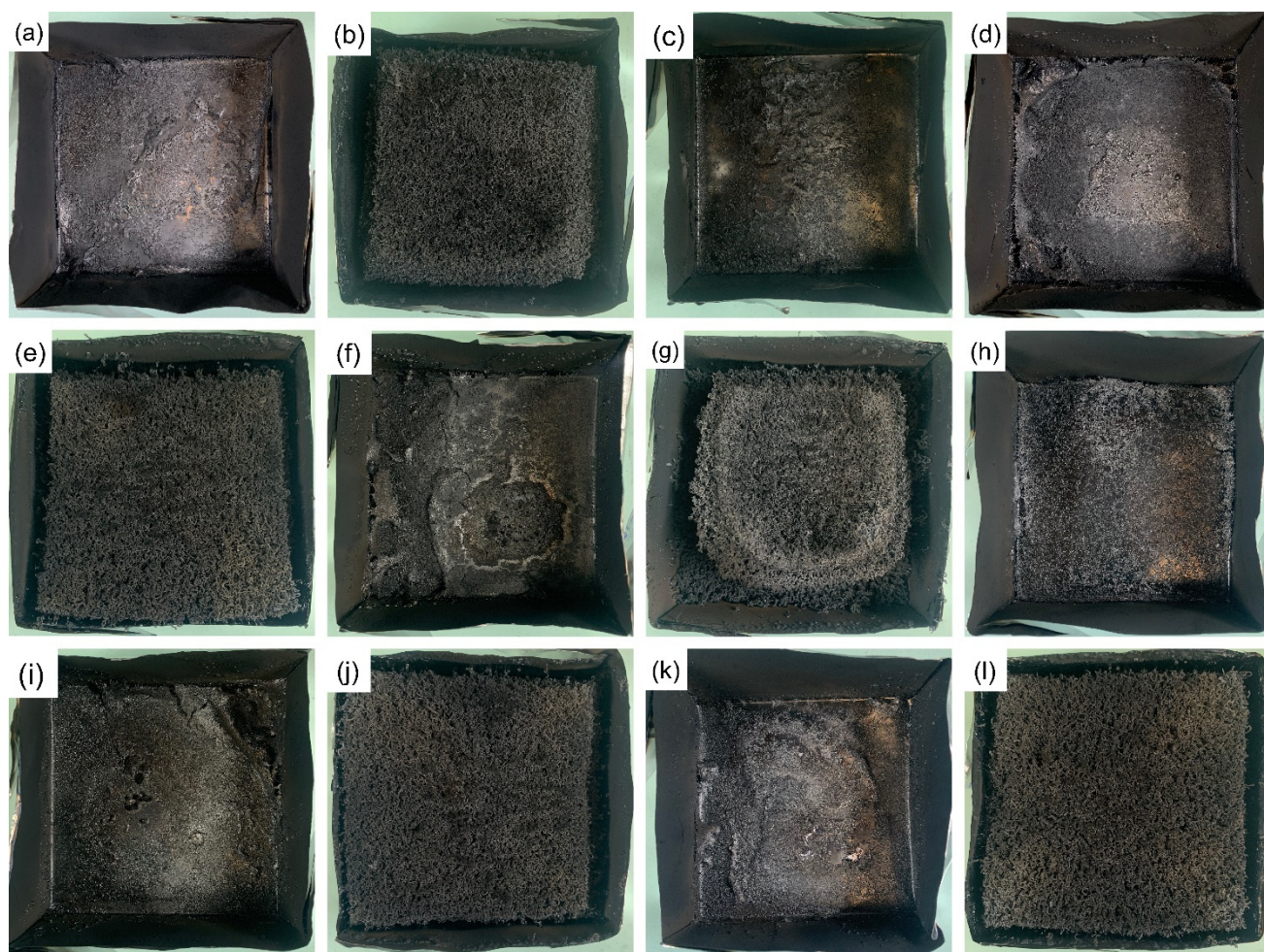


Figure S1. Photographs of the fire residue of (a) FPUF, (b) FPUF-10EG, (c) FPUF-0.1CuO, (d) FPUF-5OP, (e) FPUF-5OP-10EG, (f) FPUF-5OP-0.1CuO, (g) FPUF-5OP-10EG-0.1CuO, (h) FPUF-10CAS, (i) FPUF-5OP-10CAS, (j) FPUF-5OP-10CAS-10EG, (k) FPUF-5OP-10CAS-0.1CuO and (l) FPUF-5OP-10CAS-10EG-0.1CuO after cone calorimeter measurement

4.6 It takes two to tango: Industrial benchmark PU-foams with expandable graphite/P-flame retardant combinations

Yin Yam Chan and Bernhard Schartel. *KGK*. **2022**, 75(6), 39-46.

Status: This article was accepted and published.

First author contribution:

- Conceptualization
- Methodology
- Validation
- Investigation
- Writing – Original draft, review and editing
- Visualization
- Project administration

Contributions from other authors:

- Bernhard Schartel
 - Conceptualization
 - Methodology
 - Resources
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 - Supervision
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 - Funding acquisition

Abstract

Polyurethane foams (PUF) are generally flammable, so they are limited in some applications due to strict fire safety requirements. In this study, three distinct industrial benchmark polyurethane foams containing synergistic combinations of expandable graphite (EG) and phosphorous flame retardants (P-FR) were investigated one by one for their fire performance and smoke behavior. This paper aims to substantiate the hypothesis that the combination of EG and P-FR used in polyurethane foams yields a top-notch composite in terms of flame retardancy and smoke behavior by meeting the demanding requirement of low maximum average heat emission (MARHE) and smoke emission in a variety of applications, like advanced materials in construction, lightweight materials for railways, and more.

It takes two to tango: Industrial benchmark PU-foams with expandable graphite/P-flame retardant combinations

Keywords: polyurethane foam, expandable graphite, phosphorus flame retardant

Short summary:

Polyurethane foams (PUF) are generally flammable, so they are limited in some applications due to strict fire safety requirements. In this study, three distinct industrial benchmark polyurethane foams containing synergistic combinations of expandable graphite (EG) and phosphorous flame retardants (P-FR) were investigated one by one for their fire performance and smoke behavior. This paper aims to substantiate the hypothesis that the combination of EG and P-FR used in polyurethane foams yields a top-notch composite in terms of flame retardancy and smoke behavior by meeting the demanding requirement of low maximum average heat emission (MARHE) and smoke emission in a variety of applications, like advanced materials in construction, lightweight materials for railways, and more.

Es gehören immer zwei dazu: Industrie-Benchmark PU-Schäume mit expandierbarem Graphit / P-Flammschutz-Kombinationen

Schlagworte: Polyurethanschaum, Blähgraphit, Phosphor, Flammschutzmittel

Kurze Zusammenfassung:

Polyurethanschaumstoffe (PUF) sind im Allgemeinen entflammbar, so dass sie in einigen Anwendungen aufgrund strenger Brandschutzanforderungen eingeschränkt sind. In dieser Studie wurden drei verschiedene industrielle Benchmark-Polyurethanschaumstoffe, die synergistische Kombinationen von expandierbarem Graphit (EG) und phosphorhaltigen Flammschutzmitteln (P-FR) enthalten, auf ihr Brandverhalten und Rauchverhalten untersucht. Ziel dieser Arbeit ist es, die Hypothese zu untermauern, dass die Kombination von EG und P-FR in Polyurethanschaumstoffen einen erstklassigen Lösungsansatz in Bezug auf Flammschutz und Rauchverhalten ergibt, der die anspruchsvollen Anforderungen an eine niedrige maximale durchschnittliche Wärmeemission (MARHE) und Rauchemission in einer Vielzahl von Anwendungen erfüllt, wie z. B. fortschrittliche Materialien im Bauwesen, Leichtbaumaterialien für den Schienenverkehr und vieles mehr.

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1. Introduction

Flame retardancy mechanisms and thus flame-retardant modes of action and efficiency are usually quite specific, due to the distinct reactions between flame retardant, additives, fillers, adjuvants, and polymeric material. [1-4] Considering the application of the product, like furniture, building material, materials used in transportation, or electrical engineering, flame retardancy is also specific with respect to the desired protection goal, fire scenario, and characteristic test specimen. [5-7] Preventing the ignition of housings in electrical engineering demands for different approaches than reducing the flame spread of a flooring. Further, different flame retardants are favored for the same polymer depending on whether bulk, composite, fibers or foam is addressed. As an alternative to replace highly efficient halogenated flame retardants, current flame retardancy in commercially successful systems is done with specifically tailored, often multicomponent solutions. [8,9] For this task, a multitude of different non-halogenated flame retardants usually applied in multicomponent approaches are used to cover the large number of different products and applications. Rather general approaches such as using flame retardants containing Br together with Sb_2O_3 or ammonium polyphosphate with pentaerythritol are rare. [10] One of these rare and extraordinary champions in currently commercial flame retardant materials is the synergistic combination of expandable graphite (EG) and phosphorous flame retardant (P-FR) in polyurethane foams (PUF). [11-13] The combination of EG and P-FR effectively addresses the challenges of obtaining a low heat release rate, and low smoke and toxic products emission during burning for PUF. This combination of EG and P-FR is reported by several studies to show a pronounced synergistic effect of EG and P-FR. [14-16] This article tries to turn the spotlight on the concept by

highlighting three very different industrial benchmarks for flame retarded PUFs. Because the examples were chosen to cover the breadth of the field, they complement each other to form a comprehensive picture. They act together strongly, underlining the superior combination of EG and P-FR.

2. Experimental

2.1 Materials

Sylomer® SR and Sylomer® FR products were purchased from Getzner Werkstoffe GmbH (Bürs, Austria). Sylomer® is a flexible polyurethane elastomeric foam used in construction, mechanical engineering, shipbuilding, and rail vehicles. [17] The damping characteristics of Sylomer® SR and Sylomer® FR are optimized mainly for ships and railway applications and cover a large range. Sylomer® FR series is a flame retardant product family which can be used to tackle specific fire safety requirements. Halogen-free flame retardant rigid foam (PB-165) was purchased from Polymerics GmbH (Berlin, Germany). PB-165 contains flame retardants in a combination with EG and recycled ABC extinguishing powder (composed of monoammonium phosphate and ammonium sulfate). [18] PB-165 is used as a filling material for cable and pipe penetrations in walls, floors, and ceilings. In the case of fire, the foam ensured fire resistance against fully developed fires. PU high-performance foam (EP4311) was obtained from Rühl PUROMER GmbH (Friedrichsdorf, Germany). EP4311 is used in lightweight construction applications like rail vehicles, with EG and P-FR as flame retardants. The samples of PB-165 were prepared by pressing the 2K cartridge into a metal box and allowing it to rise freely in the mold. Other samples were already structured as foam when received from the companies.

2.2 Physical and mechanical properties measurements of foam

The apparent density of the samples was measured following ISO 845. The compression stress of Sylomer® SR and Sylomer® FR products was determined in accordance with ISO 3386-1. The tensile strength and elongation at break of EP4311 were measured according to ISO 1798. The compression stress, tensile strength and elongation at break were measured by a Zwick Z010 universal testing machine (Ulm, Germany). Four cycles per specimen were performed for the compression test. For both the tensile and the compression tests, four test specimens were measured for each material.

2.3 Fire behavior measurements

All the specimens used were conditioned at a temperature of 23 ± 2 °C and a relative humidity of 50 ± 5 % for at least 48 h in accordance with ISO 554. The limiting oxygen index (LOI) was determined at ambient temperature according to ISO 4589-2, using a specimen size of 150 mm x 10 mm x 10 mm (length x width x thickness). Cone calorimeter tests were performed in accordance with ISO 5660. The specimen size used in the cone calorimeter was 100 mm x 100 mm x 13 mm (length x width x thickness) for all of the materials. Each specimen was placed in an aluminum foil tray and exposed horizontally to an external heat flux of 50 kW m^{-2} with a distance of 35 mm between the cone heater and the surface of the specimen. This slightly greater distance was used to give the materials some freedom to show intumescence without disturbing the heat flux over the test specimen area. [19,20] Both the oxygen index apparatus and cone calorimeter were manufactured by Fire Testing Technology Limited (West Sussex, United Kingdom).

2.4 Smoke and toxic gas measurements

A smoke density chamber (SDC), manufactured by Fire Testing Technology Limited (West Sussex, United Kingdom), was used to determine the smoke generation from the samples in a static airflow chamber. The measurement was performed in accordance with ISO 5959 on samples 75 mm x 75 mm x 13 mm (length x width x thickness) in size, mounted in a sample holder and exposed to an external heat flux of 25 kW m⁻², with a distance of 35 mm between the heat source and the specimen surface under forced flaming conditions.

3. Results and discussion

3.1 Example 1: Sylomer® SR and Sylomer® FR products

Sylomer® SR and Sylomer® FR products show a semi-open cellular structure under scanning electron microscopy (SEM) in Figure 1. The cells vary in size, corresponding to the density of the foams. The smaller the cell size, the higher the density.

Sylomer® SR and Sylomer® FR samples are available in distinct densities, and they are used in different damping applications. The compression stress of the products depends on their apparent density. As shown in Table 1, the higher the apparent density, the higher the compression stress at both 40% and 65% compression.

In Table 2, the LOI value of the Sylomer® FR series is much higher than that of the Sylomer® SR series. The Sylomer® SR series has an LOI value of around 23 vol.-%, while the Sylomer® FR series has remarkably high LOI values ranging around 38 to 40 vol.-%. Sylomer® FR is more difficult to ignite and the foams are self-extinguishing.

The cone calorimeter was used to determine the fire behavior of the samples. Important parameters such as time of ignition (t_{ig}), peak heat release rate (PHRR), total heat release (THR), average of apparent effective heat of combustion (av. EHC), weight percentage of residue at flameout, and the maximum average rate of heat emission (MARHE) are shown in Table 2.

Figure 2 shows the HRR curves of the Sylomer® SR and Sylomer® FR for better display of the flame retardant efficiency on the HRR. The Sylomer® SR series displayed a plateau at the beginning of burning due to the collapse of the foam structure. The temperature was high enough to turn the solid material into a molten melt and became a pool fire. [21] As a result, the HRR surged to its extremely high PHRR. Once the molten melt was burned off, the flame extinguished. The density of the Sylomer® SR series and thus the mass of the test specimens generally affect the PHRR and the THR. The higher the density, the higher the PHRR and THR. Comparing the Sylomer® SR series and the Sylomer® FR series, the PHRR of Sylomer® FR is only one tenth as high as that of Sylomer® SR. The burning time of Sylomer® FR series is much longer than that of the SR series due to the thermal protective layer formed in the Sylomer® FR series. Sylomer® FR has much higher percentage of residue due to incomplete pyrolysis of the underlying material shielded by protective layer of the expanded graphite. The THR of the Sylomer® FR series is significantly reduced. To explain the burning behavior of the Sylomer® FR series in detail, Figure 3 is used to show the heat release rate curve along with real-time photos of one of the Sylomer® FR samples, FR418, as an example. ① Once the specimen was exposed horizontally to the cone heater, the material began to smolder and the EG expanded even without a flame due to the high temperature. ② When the specimen was ignited, the HRR immediately increased to only around 100 kW m^{-2} until a sufficient protective layer was formed. ③ Due to the presence of the underlying expanded graphite, the thickness of the residue kept increasing. ④ Therefore, the HRR kept decreasing due to the good thermal protection and the flame was even extinguished after 213 s. The protective layer resulted in incomplete pyrolysis, thus reducing the THR and PHRR. ⑤ Since we used no frame for the samples in the cone calorimeter test, artificial edge burning occurred afterwards. The HRR rose again from 213 s to 250 s due to the edge burning. ⑥ Afterward, the HRR climbed to 250 kW m^{-2} and the burning was more intense due to the cracks at the edges and volatile flammable material escaping from the bottom of the specimen through the cracks. ⑦ When volatile fuel

from the material was burned out, the flame extinguished at around 600 s. The occurrence of the second burning and thus second PHRR is due to the edge burning we provoked through measuring without the frame. This second burning proved that the main flame retardant mode of action is the efficient protective layer preventing complete pyrolysis in the first burning. Expanded graphite is apparent as the dominant component of the protective fire residue. Nevertheless, the interaction with P-FR, matrix, and adjuvants is the key to stabilizing the fire residue and optimizing its performance. [12,15,22] As seen in Figure 2b, edge burning did not occur in FR428, and the PHRR was only around 100 kW m^{-2} . The PHRR value is consequently much lower when compared to other FR series samples. In Table 2, two values were given for PHRR, THE, and MARHE when the artificial second burning was observed. All Sylomer® FR samples have a MARHE value below 90 kW m^{-2} , which means they meet the demanding fire requirement of EN 45545.

Sylomer® SR did not form a protective layer, and almost all the material burned off, taking SR18 as an example as shown in Figure 4a. In Figure 4b, taking FR418 as an example, the protective layer expanded to more than four times its original height for Sylomer® FR samples.

The smoke behavior under a static environment was measured by the SDC. The specific optical density of the samples (D_s) and VOF4 is displayed in Figure 5. The D_s of a Sylomer® SR and a Sylomer® FR are plotted on the same graph because their apparent densities are comparable. The D_s of the Sylomer® FR series is very low compared to that of the Sylomer® SR series, amounting to just 1/10. The combination of EG and P-FR in Sylomer® provides the material with excellent smoke suppression. The thermal protective layer created by expanded graphite yielded crucially incomplete pyrolysis as the basis for smoke reduction. Sylomer® FR emitted an extremely low amount of smoke in the first 4 minutes, giving people more time to evacuate from fires.

The investigated products are applied as damping materials; hence they are a kind of flexible PUF. Reducing both their high PHRR and pronounced smoke emission by a factor of 10 at the same time to fulfill the demanding EN 45545 requirements is an extraordinary achievement. Usually, such a challenge in flexible PUF development turns out to be a mission impossible; it cannot be realized by the common approaches of flame inhibition, charring, and protective layer. The combination of EG and P-FR is optimized, extinction occurs when 90% of the material remains not pyrolyzed, which is impressive.

3.2 Example 2: PB-165

Figure 6 shows the morphology of PB-165. The cell structure looks somewhat destroyed, like ragged spheres with tattered cell walls. Nevertheless, the structure is rather homogeneous and indicates a rather low density.

Table 3 lists the fire performance and smoke emission behavior data for PB-105. The LOI value of PB-165 is very high (>50 vol.-%), which means that it is not only self-extinguishing, but also difficult to burn in an existing fire. In Figure 7a, the HRR spiked to the first peak within 10 s after ignition, as the material burned without efficient protection at the beginning. The protective layer was gradually built up by the expanded graphite, forming an excellent thermal protective layer, and the HRR decreased to around 58 kW m^{-2} . The HRR increased towards the end of burning due to some cracks in the protective layer. The HRR then reached its second peak. The HRR curve pattern shows a pronounced two-peak shape, one sharp peak at the beginning and one broad peak at the end, separated by a clear minimum in HRR in between. The HRR curve pattern is similar to wood [23], also a porous charring material. For wood, a second burning stage at the end is proposed, as the destruction of intermediate char may be accompanied by a second pyrolysis front at high temperatures. The MARHE value of PB-165 is around 80 kW m^{-2} , which is low enough to reach the requirement of European EN 45545

standard. Figure 7b shows the Ds and transmission curves from the SDC measurement. The amount of smoke released was extremely low. At the end of the test, the light transmission remained high, which means that visibility for escape is high. As shown in Figure 8, after the cone calorimeter measurement the height of the specimen expanded to 3 times its original height, from 13 mm to 40 mm. This thick protective layer significantly reduced the heat transfer to the underlying material and thereby reduced the HRR.

PB-165 was developed for fire resistant applications in building construction. It is a PUF foam used, for instance, to close openings in fire protection walls. Indeed, it is developed to resist a fully developed fire, a fire protection goal that transcends the usual domain of flame retardants. Reduction in HRR and smoke emission is not what the material is designed for. The excellent flame retardancy of PUF achieved is a byproduct, nevertheless this example underlines the outstanding and superior effect of combining EG with P-FR and adjuvants.

3.3 Example 3: EP4311

The SEM image of EP4311 is displayed in Figure 9. Most of the cells are closed. Some cell walls and structures are quite large. The multicellular structure appears to approximate separated bubbles dissolved in the polymer matrix, as is typical for a foam with higher density. Table 4 lists the physical and mechanical properties of EP4311.

The very high LOI value shown in Table 5 proved that EP4311 is not flammable. The LOI value of over 50 vol.-% means it is self-extinguishing and difficult to burn.

Figure 10a shows the HRR curve of EP4311. Since the specimen without protection was initially exposed to the cone heater, the HRR quickly reached its PHRR (85 kW m^{-2}). After that, the HRR decreased rapidly because of the formation of thermal protective layers dominated by the expanded graphite in the system. The HRR remains at around 50 kW m^{-2} for some time.

The HRR of the EP4311 was further decreased because of the accumulation of expanded graphite after 188 s, which can be interpreted as flameout, and reached a plateau of very low HRR, marking a kind of afterglow. There is no obvious second PHRR found in the graph. As shown in Figure 10b, the D_s was still low at the end of the test, which means the concentration of smoke was low to provide people more time to escape from fires. Figure 11 shows the residue after the cone calorimeter measurement of EP4311. The residue increased to 4 times its original height, forming a thermal protective layer to reduce heat transfer from the top to the material underneath.

EP4311 is a typical material used in lightweight construction. This PUF is used to replace bulk material, as it weighs only half as much as a technical polymer. Railroad vehicles are a typical application for this type of product, as they must meet the rigorous demands of the EN 45545 standard. The combination of EG with P-FR is used to achieve the demanding fire safety level.

4 Conclusion

All the examples with flame retardants (EG and P-FR) exhibit a very high LOI value, low HRR and low D_s , reducing fire and smoke hazards. The combination of EG and P-FR serves as an excellent way to improve the flame retardancy of PUF products. The synergistic effect of EG and P-FR creates more char residue during burning, forming an efficient thermal protection barrier to prevent further pyrolysis and burning of the underlying materials. Expanded graphite dominates the fire residue. The height of the protective residue is around 3 to 5 times the original height of the test specimens. The very efficient thermal insulation causes extinction far before pyrolysis is completed. The results indicate that as little as just 10 wt.-% of the PUF may be pyrolyzed. The massive reduction in consumption of the PUF reduces the fuel release rate and fire load. Furthermore, it is a direct and efficient way to reduce the release of smoke and toxic products.

To conclude, the combination of EG and P-FR is used successfully in commercial PUF systems and achieves the highest standards like MARHE and the smoke requirements of EN 45545. The combination of EG and P-FR is one of the rare general highly efficient approaches in flame retardancy.

Acknowledgements

The authors are grateful to Dietmar Schulze for his contribution to the mechanical tests of the materials and Tina Raspe and Dr. Simone Krüger for their support with the SDC. Dr. Ulrich Fehrenbacher from RÜHL PUROMER GmbH is acknowledged for providing the material EP4311.

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Table 1 Apparent density and compression stress results of Sylomer® SR and Sylomer® FR products

Sample	Apparent density/ kg m⁻³	Compression stress at 40% compression / kPa	Compression stress at 65% compression/ kPa
SR18	191.0 ± 9.4	36.4 ± 0.1	124.5 ± 13.9
SR28	218.2 ± 1.5	48.4 ± 0.5	149.7 ± 2.7
SR42	251.1 ± 0.4	72.8 ± 0.3	226.4 ± 1.9
SR55	267.4 ± 0.1	98.7 ± 0.3	332.2 ± 3.4
SR110	407.3 ± 0.4	232.5 ± 1.9	1064 ± 7.4
FR418	262 ± 0.6	38.1 ± 0.5	132.2 ± 1.5
FR428	293.6 ± 1.6	65.4 ± 0.8	267.7 ± 5.7
FR442	332.7 ± 10	87.4 ± 1.2	345.8 ± 15
FR455	383.1 ± 0.1	108.2 ± 1.4	463.2 ± 1.7
FR4110	484.8 ± 29	238.7 ± 1.8	1383.7 ± 55.9

Table 2 Fire performance and smoke behavior results of Sylomer® SR and Sylomer® FR products, with the data in brackets are the overall burning result

* VOF4 is a cumulative value of specific optical densities in the first 4 min. of the test

Sample	LOI / vol.-%	t _{ig} / s	PHRR/ kW m ⁻²	THR/ MJ m ⁻²	Average EHC/ MJ kg ⁻¹	Residue at flameout / wt.-%	MARH E/ kW m ⁻²	Max. specific optical density (D _s max)	VOF4*
SR18	26.0±0.2	9±1	1441±21	63.2±3.2	27.0±0.1	1.9±0.1	589±1	386±36	879±37
SR28	22.2±0.1	9±1	1718±4	73.2±0.4	27.4±0.1	2.1±0.1	645±8.1	396±20	775± 3
SR42	22.2±0.2	8±1	1610±104	83.2±0.8	27.2±0.3	2.6±0.2	640±8	468±12	838±34
SR55	23.6±0.2	9±1	1980±80	89.6±1.0	27.6±0.4	2.8±0.2	686±10	467±15	838±2
SR110	22.5±0.1	10±1	2691±190	129±17.9	27±2.7	6.5±3.3	785±74	494±7	789±14
FR418	40.2±0.1	5±1	106±4 (270±17)	15±0.5 (46.2±1.5)	19.6±0.5	28.1±0.5	71±2 (87±9)	42±1	41±1
FR428	38.0±0.1	7±1	104±7	7.5±1.7	18.9±0.8	89.3±2.1	68.3±3.5	49.0±0.3	30.2±1.9
FR442	40.1±0.1	8±1	110±9 (298±23)	22±2 (65±5)	20.8±1.6	27.4±2.1	63.8±4.9 (84±25)	44.8±0.9	22.4±2.1
FR455	39.6±0.2	8±1	103±4 (293±12)	25±1 (71±3)	20.6±0.8	28.2±1.1	62±2 (86±15)	50.2±0.5	18.3±0.9
FR4110	34.4±0.2	12±1	105±5 (248±16)	14±1 (100±6)	20.4±1.5	18.0±5.7	68±4 (113±12)	58±3	11.± 0.6

Table 3 Fire performance and smoke behavior data of PB-165

	Apparent density/ kg m⁻³	LOI/ vol.-%	Maximum specific optical density (D_s max)	VOF4
PB-165	134.7±1.3	51.3±0.1	38.9±6.5	66.4±13.2
<i>t_{ig}/s</i>	PHRR/ kW m⁻²	THR/ MJ m⁻²	Average EHC/ MJ kg⁻¹	Residue at flameout/ wt.-%
2.5±0.5	112±10	19.7±0.5	18±0.1	37.3±2.6

Table 4 Apparent density and mechanical test results of EP4311

	Apparent density / kg m⁻³	Tensile strength / kPa	Elongation at break / %
EP4311	505.4 ± 3.4	986.5 ± 25.7	36.5 ± 1.8

Table 5 Fire performance and smoke behavior data of EP4311

	LOI/ vol.-%	Maximum specific optical density (Ds max)	VOF4		
EP4311	54.4 ± 0.2	65.0 ± 11.8	20.4 ± 0.5		
<i>t_{ig}/s</i>	PHRR/ kW m ⁻²	THR/ MJ m ⁻²	Average EHC/ MJ kg ⁻¹	Residue at flameout/ wt.-%	MARHE/ kW m ⁻²
11± 0.1	86.7 ± 1.8	7.8 ± 1.7	16.1 ± 0.7	92.3 ± 1.9	51.1 ± 0.7

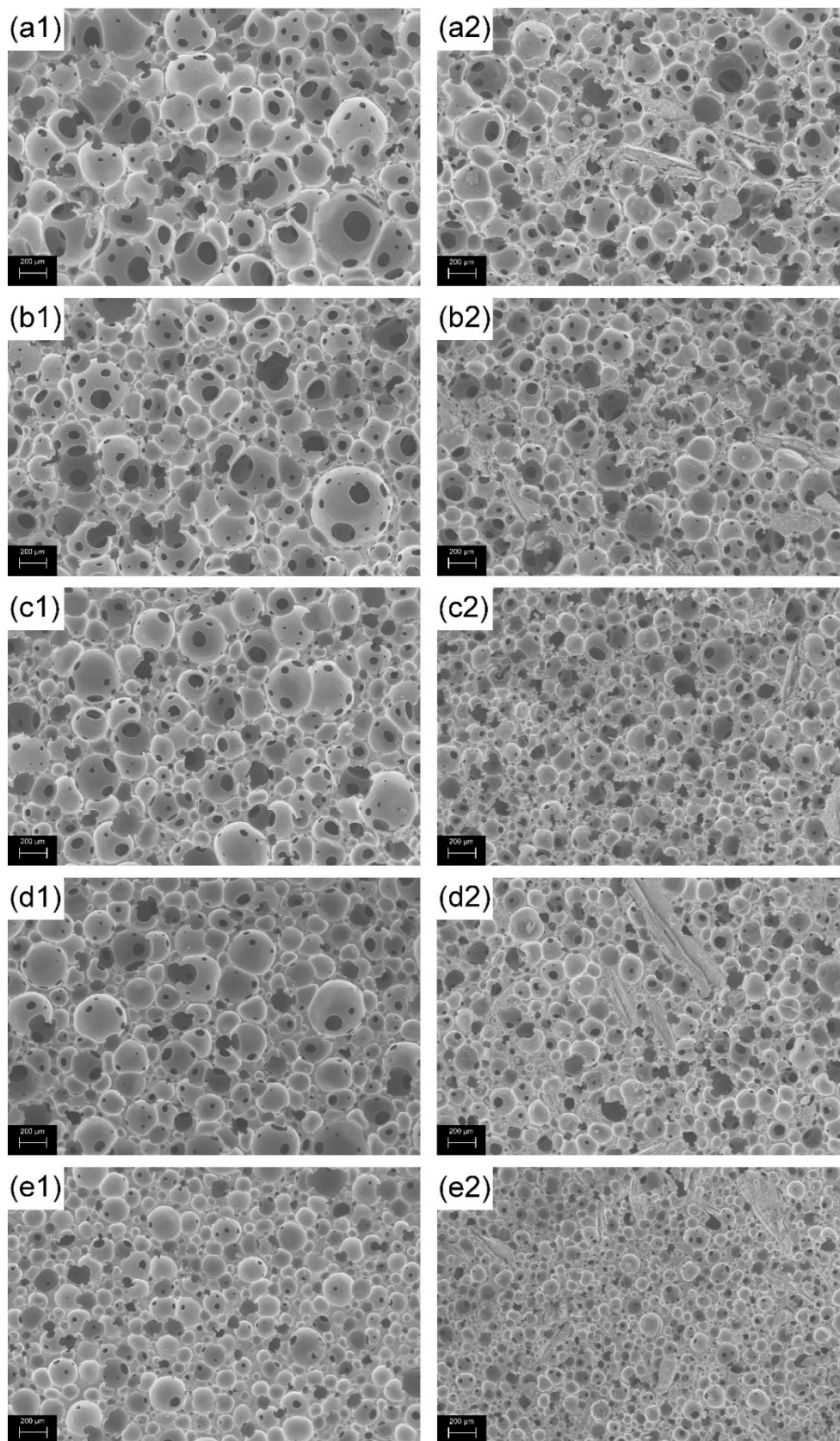


Figure 1 SEM images of Sylomer® (a1) SR18, (a2) FR418, (b1) SR28, (b2) FR428, (c1) SR42, (c2) FR442, (d1) SR55, (d2) FR455, (e1) SR110, and (e2) FR4110

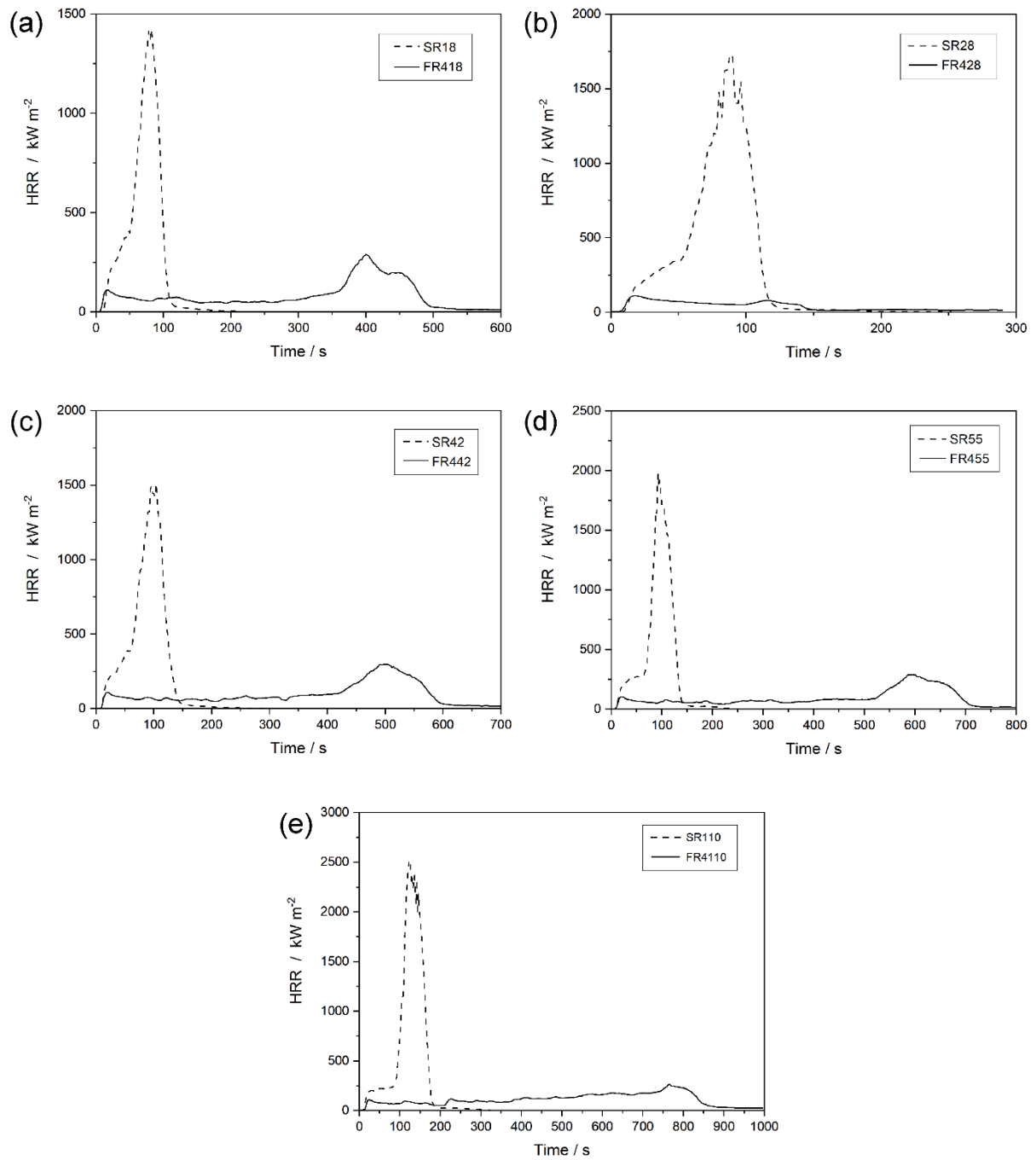


Figure 2 Heat release rate curves of (a) SR18 & FR418, (b) SR28 & FR428, (c) SR42 & FR442, (d) SR55 & FR455, and (e) SR110 & FR4110

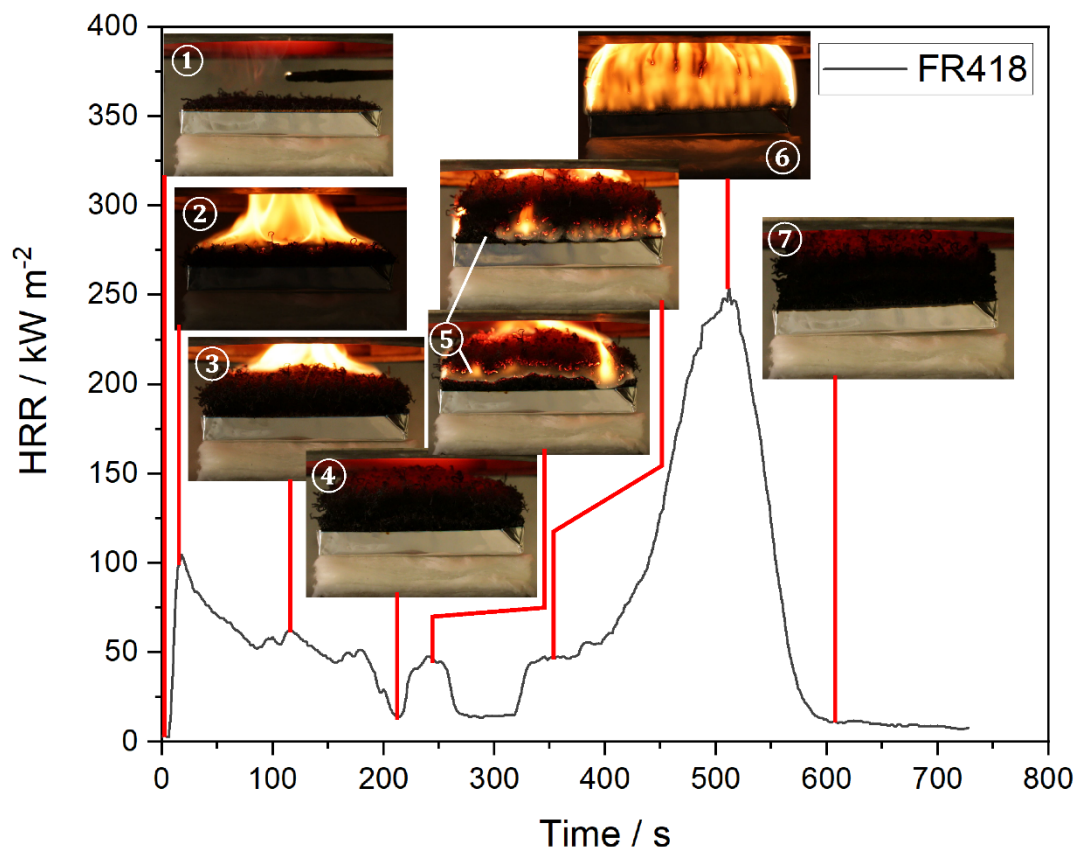


Figure 3 Heat release rate curve with real-time photos of FR418

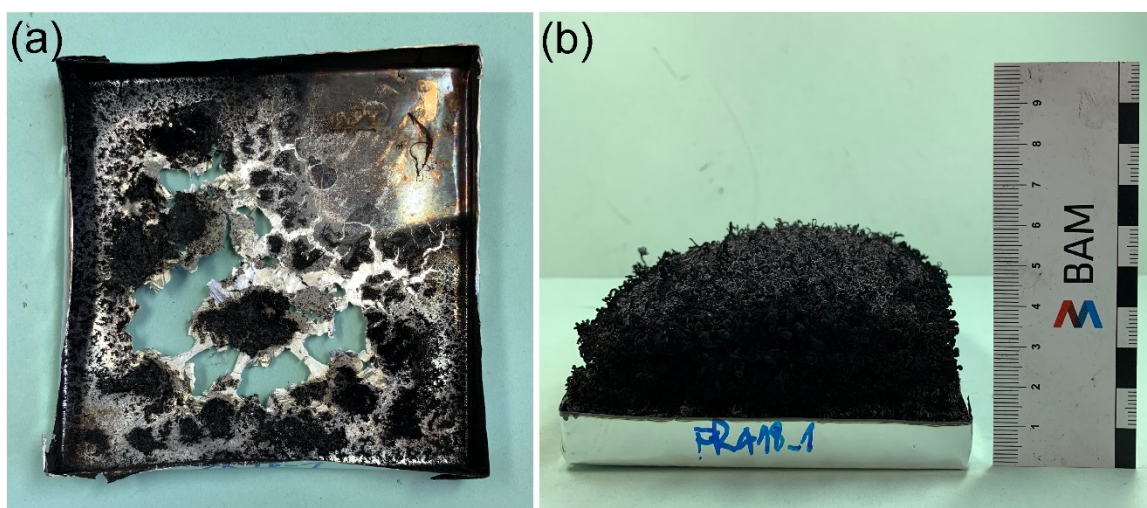


Figure 4 Residue after cone calorimeter measurement of (a) SR18 and (b) FR418

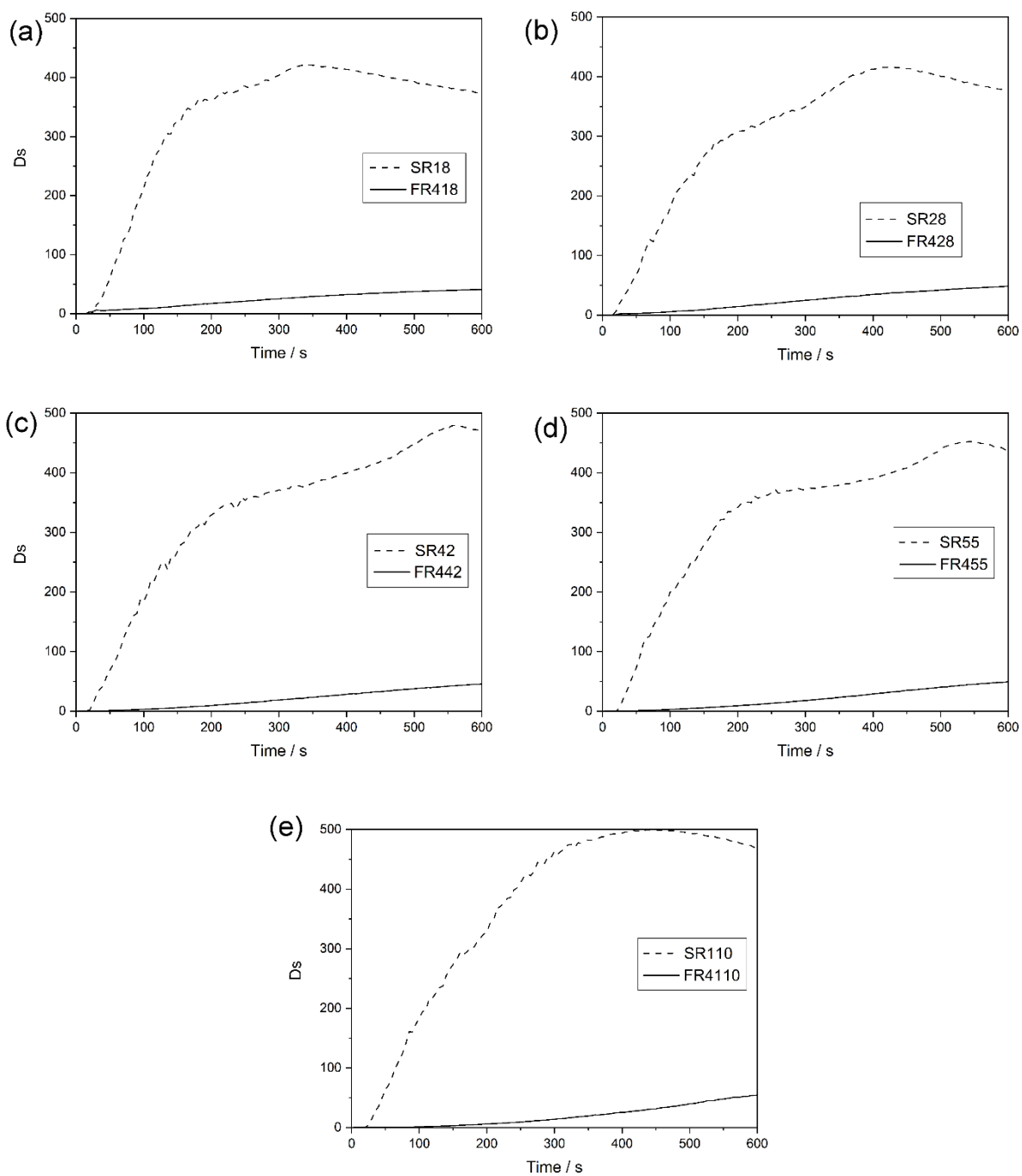


Figure 5 Specific optical density curves of (a) SR18 & FR418, (b) SR28 & FR428, (c) SR42 & FR442, (d) SR55 & FR 455, and (e) SR110 & FR4110

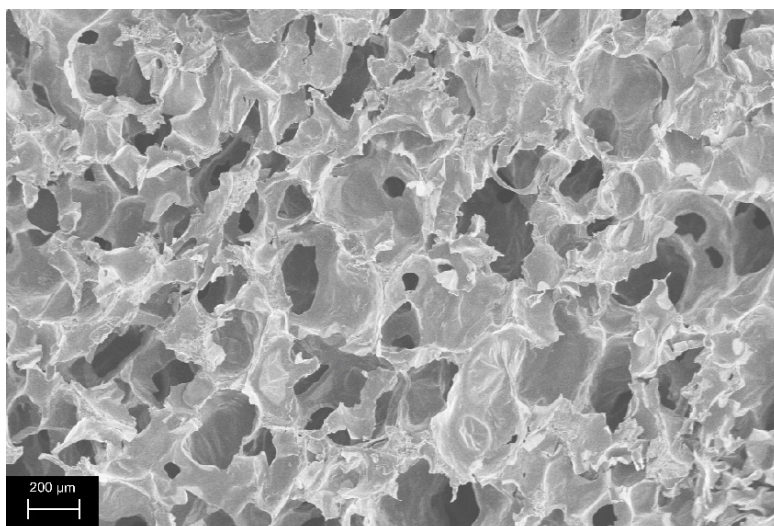


Figure 6 SEM image of PB-165

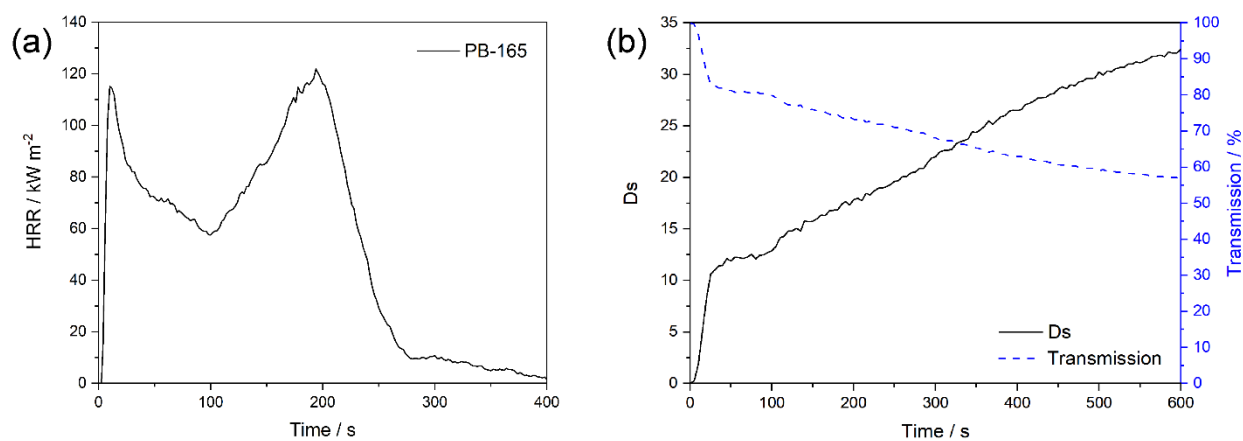


Figure 7 (a) Heat release rate curve and (b) specific optical density and transmission curves of PB-165



Figure 8 Residue after the cone calorimeter measurement of PB-165

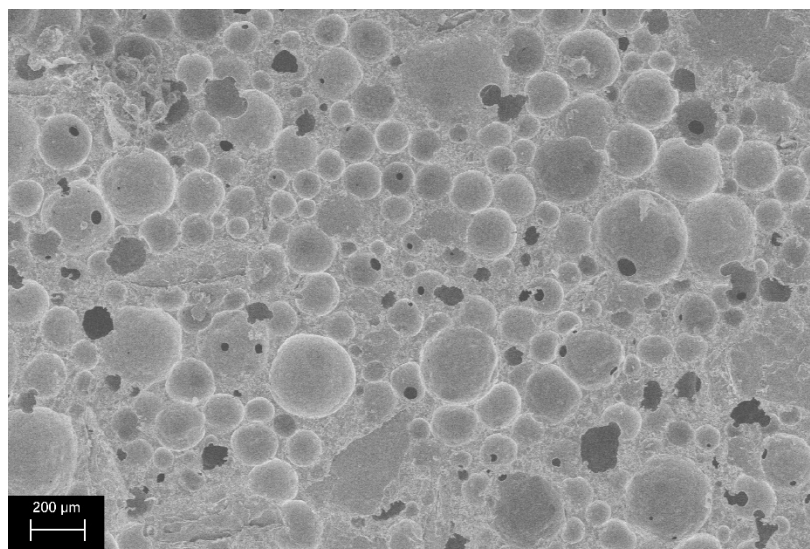


Figure 9 SEM image of EP4311

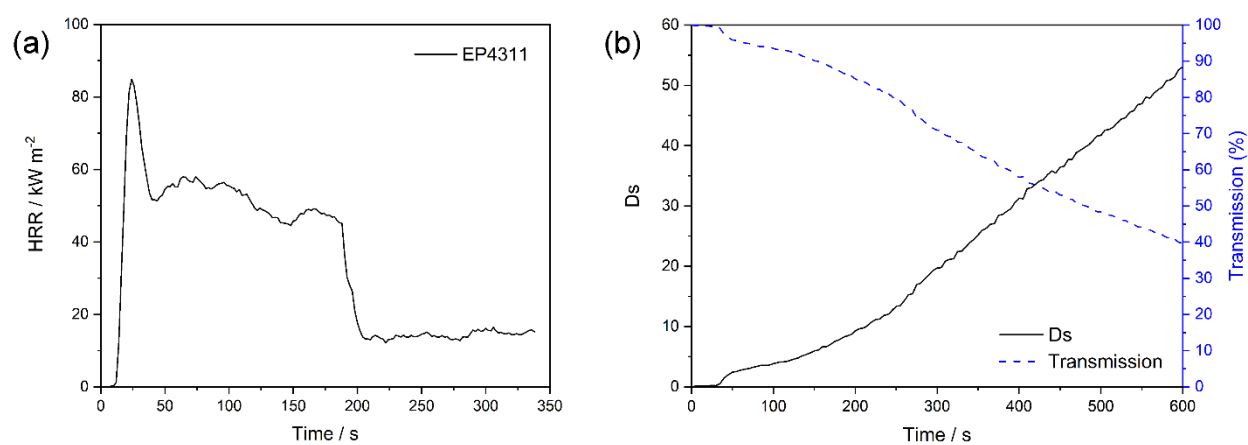


Figure 10 (a) Heat release rate curve and (b) specific optical density and transmission curves of EP4311



Figure 11 Residue after the cone calorimeter measurement of EP4311

4.7 It takes two to tango: Synergistic expandable graphite – phosphorus flame retardant combinations in polyurethane foams

Yin Yam Chan and Bernhard Schartel. *Polymers*. **2022**, *14*, 2562. Doi: 10.3390/polym14132562.

Status: This article was accepted and published. <https://doi.org/10.3390/polym14132562>

First author contribution:

- Conceptualization
- Methodology
- Validation
- Investigation
- Writing – Original draft, review and editing
- Visualization
- Project administration

Contributions from other authors:

- Bernhard Schartel
 - Conceptualization
 - Methodology
 - Resources
 - Writing – Original draft, review and editing
 - Supervision
 - Project administration
 - Funding acquisition

Abstract

Due to the high flammability and smoke toxicity of polyurethane foams (PUFs) during burning, distinct efficient combinations of flame retardants are demanded to improve the fire safety of PUFs in practical applications. This feature article focuses on the one of the most impressive halogen-free combinations in PUFs: expandable graphite (EG) and phosphorus-based flame retardants (P-FRs). The synergistic effect of EG and P-FRs mainly superimposes the two modes of action, charring and maintaining a thermally insulating residue morphology, to bring effective flame retardancy to PUFs. Specific interactions between EG and P-FRs, including the agglutination of the fire residue consisting of expanded-graphite worms, yields an outstanding synergistic effect, making this approach the latest champion to fulfill the demanding requirements for flame-retarded PUFs. Current and future topics such as the increasing use of renewable feedstock are also discussed in this article.

Article

It Takes Two to Tango: Synergistic Expandable Graphite–Phosphorus Flame Retardant Combinations in Polyurethane Foams

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Abstract: Due to the high flammability and smoke toxicity of polyurethane foams (PUFs) during burning, distinct efficient combinations of flame retardants are demanded to improve the fire safety of PUFs in practical applications. This feature article focuses on one of the most impressive halogen-free combinations in PUFs: expandable graphite (EG) and phosphorus-based flame retardants (P-FRs). The synergistic effect of EG and P-FRs mainly superimposes the two modes of action, charring and maintaining a thermally insulating residue morphology, to bring effective flame retardancy to PUFs. Specific interactions between EG and P-FRs, including the agglutination of the fire residue consisting of expanded-graphite worms, yields an outstanding synergistic effect, making this approach the latest champion to fulfill the demanding requirements for flame-retarded PUFs. Current and future topics such as the increasing use of renewable feedstock are also discussed in this article.

Keywords: synergy; phosphorus-containing flame retardant; expandable graphite; polyurethane foams



Citation: Chan, Y.Y.; Schartel, B. It Takes Two to Tango: Synergistic Expandable Graphite–Phosphorus Flame Retardant Combinations in Polyurethane Foams. *Polymers* **2022**, *14*, 2562. <https://doi.org/10.3390/polym14132562>

Academic Editors: Jelena Vasiljević and Ivan Jerman

Received: 27 May 2022

Accepted: 21 June 2022

Published: 23 June 2022

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1. Introduction

As fire safety has always been a major concern, fire protection is in high demand. One of the key approaches to improving fire protection entails adding flame retardants to polymeric materials, because most synthetic polymers are easily ignited due to their high content of hydrocarbons, an excellent fuel for fires. Currently, efficient flame retardancy is achieved through specific solutions tailored to different kinds of polymeric materials, as they have different properties [1–3]. Flame retardancy is specific with respect to the flame-retardant mechanisms and to the flame retardant's reactions with polymeric materials [4–7] and with other ingredients, such as additional flame retardants, fillers/fibers, additives, adjuvants, and synergists [8].

Flame retardancy is specific with respect to the protection goal and fire scenario; ignition scenarios require different approaches from developing fires or fully developed fires [9]. Different flame retardants are even favored for the same polymer depending on whether it is applied in bulk, as a composite, or in the form of fibers or foam. Thus, a multitude of different flame retardants in various combinations are used to protect the entire spectrum of foam-containing consumer goods [10]. Generalized approaches of efficient combinations working in different matrices, such as flame retardants containing Br combined with Sb₂O₃ or ammonium polyphosphate (APP) with pentaerythritol (PER), are rare; furthermore, environmental concerns mean that halogen-free systems are preferred. One of the champions among the currently proposed flame retardants that has found application in today's products is the synergistic combination of expandable graphite (EG) with a phosphorous flame retardant (P-FR). This approach has become legendary for the excellent flame retardancy it provides to polyurethane foams (PUFs) [11–14]. In this feature article, we turn the scientific spotlight on the concept, mechanisms, and role of

the synergistic combinations of EG and P-FRs in PUFs in order to evoke the applause this approach deserves [15–18].

1.1. Polyurethane Foams (Flexible and Rigid)

Polyurethane foams (PUFs) have been used in a wide range of applications because their physical and mechanical properties can be customized by changing the chemical composition. PUFs are divided into two main categories: flexible polyurethane foams (FPUFs) and rigid polyurethane foams (RPUFs) [19–21]. The main chemicals used in the formulation for PUFs are polyols, isocyanates, catalysts, surfactants, and blowing agents. The differences in the physical and mechanical properties of FPUFs and RPUFs depend mainly on the chemical characteristics of the reactants—the polyols and the isocyanates. Urethane linkages form in PUFs through a polyaddition reaction between the hydroxyl group of polyols and the NCO groups of isocyanates [22–24]. Nevertheless, the functionality of polyols and the type of isocyanate used are different in RPUFs and FPUFs. The relationship among the average molecular weight, functionality, and OH value of polyols is shown in Equation (1). These parameters are key characteristics that define the properties of polyols and ultimately affect the property profile of polyurethanes when polyols react with diisocyanates. For example, increasing the OH value leads to a higher crosslink density in polyurethane.

$$M_n = \frac{z \times 56106}{\text{OH value}} \quad (1)$$

where M_n and z are the average molecular weight and the functionality, respectively.

For RPUFs, polyols with shorter chains exhibiting higher functionality ($z = 2.5\text{--}5$) are combined with polymeric diphenylmethane diisocyanate (pMDI) in order to generate more crosslinks, providing more strength, thereby increasing rigidity. As a result, the apparent density of RPUFs is higher than that of FPUFs due to the former's higher crosslink density [25,26]. Accordingly, RPUFs are more commonly used in construction, transportation, and refrigeration because of their extremely low thermal conductivity due to their closed-cell structure, which is superior to that of other commercially available insulation materials [27,28]. Because FPUFs are so flexible, long-chained polyols with lower functionality ($z = 2\text{--}3$) and toluene diisocyanate (TDI) are typically the main components added [29]. The open-cell structure of FPUFs contains cell window, strut, and strut join. Such morphology offers different degrees of cushioning, making it a frequent material choice in furnishings, automotive seating, mattresses, and packaging.

1.2. Polyisocyanurate Foams and Polyurethane Foams

Although polyisocyanurate foams (PIRFs) and polyurethane foams (PUFs) have similar chemical compositions, PIRFs exhibit considerably better flame retardancy than PUFs. As PUFs have a more balanced equivalent weight ratio of the isocyanate group and the hydroxyl group of polyols (NCO/OH ratio $\approx 1.05\text{--}1.1$), they mainly form urethane linkages, while the much higher excess amount of isocyanates in PIRFs usually yields isocyanurates via trimerization reaction. Due to the higher content of ring structures, PIRFs produce more char during burning, which ensures superior fire behavior. Günther et al. [27] compared the morphology of PIRF and RPUF residues with cone calorimeter measurements; the better fire behavior of PIRFs was attributed to the dense, thick cellular structure residue retained to some degree as thermal insulation, while RPUFs showed a thin, brittle residue layer. Therefore, the residue from PIRFs protects the underlying material better than the residue from PUFs during burning.

1.3. Flammability and Smoke Toxicity during Burning of Polyurethane Foams

Despite all the advantages enjoyed by PUFs, one of their major problems is high flammability. Regardless of whether RPUFs or FPUFs are used, both forms of PUFs present highly porous and cellular-structured material that easily catches fire. Because the cell walls and struts are thermally thin, they can be heated to the ignition temperature swiftly,

causing early ignition [30]. Meanwhile, the low thermal conductivity makes the entire specimen thermally thick, which concentrates the heat at the surface, resulting in rapid flame spread. Therefore, the flame retardancy of polyurethane foams needs to be improved to meet high fire protection standards. Due to the open-cell structure and higher surface-to-mass ratio, FPUFs have higher flammability than RPUFs [31]. FPUFs show a lower tendency to char and a higher tendency to yield liquid products and thus collapse and yield pool fires. Figure 1, which illustrates the chemical structure, shows that PUFs are predominantly composed of combustible elements such as carbon and hydrogen, which increase the growth rate of fire. Apart from their flammability, PUFs evolve poisonous gases during burning, including carbon monoxide, nitrogen oxides, and hydrogen cyanide, as well as a large amount of smoke particles, all of which threaten human lives. The quality and quantity of poisonous gas evolved from the same material vary with different oxygen concentrations and burning temperatures [32,33].

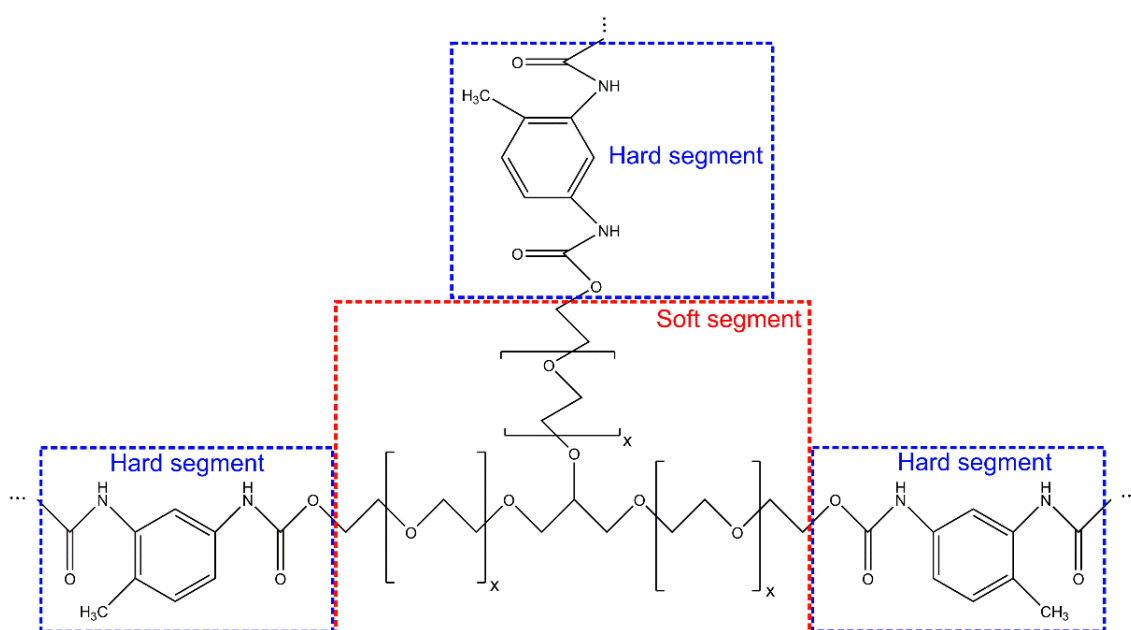


Figure 1. Chemical structure of flexible polyurethane foams.

1.4. Commercial Flame Retardants for PUFs

To cope with the flammability of PUFs, additive and reactive flame retardants are often introduced into the matrix to delay ignition and reduce heat release in the event of a fire, thereby slowing flame spread. Compared with RPUFs, it is more difficult to enhance structural frame retardancy of FPUFs. This is because flame retardants added physically often increase the viscosity of the polymer system and limit foam growth. The flame retardant is mainly embedded in the thin cell struts, causing the structure to collapse under the weight of the additive during the foaming process.

In the past, dispersing halogenated flame retardants such as organochlorine and organobromine compounds in polyurethane foams were very attractive for the industry, because they work effectively in the gas phase and greatly reduce heat release during burning [10]. However, the hydrogen halides released from halogenated flame retardants during burning are highly corrosive, are toxic to human beings, and may pollute the environment. Due to environmental and biological health concerns, some countries have already considered legislation restricting the use of flame retardants containing halogen. As a result, more and more halogen-free and environmentally friendly flame retardants have been developed and used in recent decades [34]. Today, dimethyl methylphosphonate (DMMP) [35], triaryl phosphates [36], melamine [31,37], aluminum hydroxide (ATH), expandable graphite (EG) [38–40], and ammonium polyphosphate (APP) [41,42] are common

halogen-free additive flame retardants for polyurethane foams. Many studies have found that mixing two flame retardants or combining two or more flame-retardant elements in a single compound can increase the flame-retardant efficiency. This phenomenon is called synergism [43]. Li et al. [44] investigated the flame retardancy of RPUFs combined with DMMP and modified APP. They found that DMMP and modified APP enhanced flame retardancy through good coordination in the gas phase and the condensed phase. Wang et al. [45] synthesized a flame retardant containing phosphorus and nitrogen in RPUFs. The foam with the flame retardant formed a protective char layer, which enhanced flame retardancy. Tris(1-chloro-2-propyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCP), both with two flame-retardant chemical elements (i.e., halogen and phosphorus), are still common additive flame retardants for polyurethane foams [10]. Most additive flame retardants deteriorate the morphology and mechanical properties of polymers. Hence, reactive flame retardants are an alternative to improve flame retardancy by chemically bonding to the polyurethane structure without excessively damaging the PUF structure. Phosphorous polyols are used as reactive flame retardants to replace petrochemical polyols in the formulation. Commercial non-halogenated phosphorous polyols such as Exolit® OP 550 and Exolit® OP 560 from Clariant AG (Muttenz, Switzerland) are successfully used in the industry. However, it is worth noting that FPUFs are sensitive to the hydroxyl number of polyols [46,47]. Higher hydroxyl values of polyols may cause the structure of FPUFs to collapse. Therefore, determining the appropriate amounts and types of polyols is the key to successful foaming.

2. Task

2.1. Burning Behavior of Rigid and Flexible Polyurethane Foams

In terms of burning behavior, FPUFs can be ignited more easily than RPUFs, and fire propagates more quickly because of their lower density and open-cell structure [48,49], while RPUFs have a higher density and a closed-cell structure [26]. The curves of the heat release rate (HRR) of FPUFs from cone calorimeter measurements are displayed in Figure 2. For FPUFs, the curve exhibits three stages. In the first step (i), the surface of the foam is heated up; then, decomposition is initiated, and the foam ignites. According to the two-step decomposition of polyurethane, mainly, urethane bonds decompose, and the volatile pyrolysis products of the hard segments feed the flame. After this ignition stage (i), in stage (ii), the foam is covered by a molten layer of pyrolyzing polyurethane, such that the foam burns, collapses, and forms a pool of intermediate liquid pyrolysis products. After the first peak or plateau-like burning in stage (ii), the heat release rate surges to another, higher peak in stage (iii), because the remaining material burns in a violent pool fire [48,50,51]. The differences between the different burning stages can be described by the temperature–thickness relationship. Figures 2 and 3 show the temperature–thickness relationship of FPUFs and RPUFs during different stages of burning, respectively. At the beginning of burning, individual cell walls or struts behave as thermally thin materials, such as a film or fiber. After ignition in stage (i), the very top layer of FPUFs at d_0 is consumed under the influence of thermal radiation, forming a thin pyrolysis zone at the first pyrolysis temperature (T_{p1}). The yielded liquid pyrolysis products mainly belong to the soft segments, and the volatiles released mainly belong to the hard segments. The excellent thermal insulation of the foam results in a rapid decrease in temperature across the intact foam, as the entire unmolten part is thermally thick. As heating continues, stage (ii) is reached, with the next few layers from the top of the FPUF also collapsing and melting, forming a thicker pyrolysis zone. Due to the good convection of the molten melt from d_1 to d_2 , the melt is considered to reach the same pyrolysis temperature at T_{p1} . As the remaining unburned material is still thermally thick, its temperature decreases inversely toward the bottom of the material. The cellular structure melts and collapses in stage (ii), resulting in a pool fire (iii), generally at the second pyrolysis temperature (T_{p2}) from d_3 to d . The high fluidity of the melt under high temperatures exhibits a constant temperature due to

convection. Almost no heat flux is attributed to further heating in stage (iii), but the heat flux is completely transferred to pronounced pyrolysis.

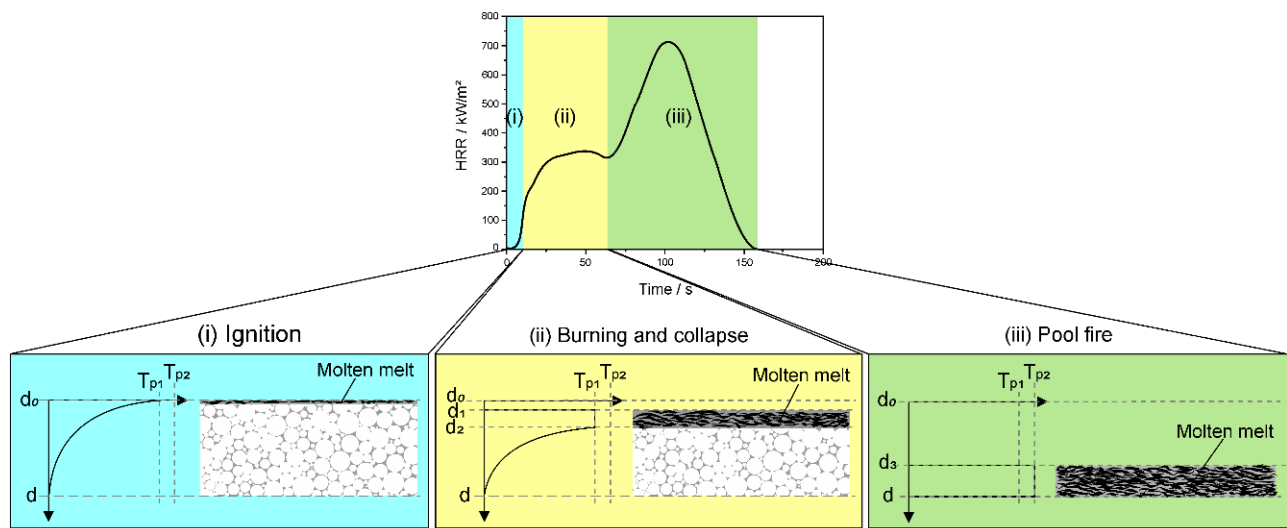


Figure 2. Temperature–thickness relationship of flexible polyurethane foams during different burning stages.

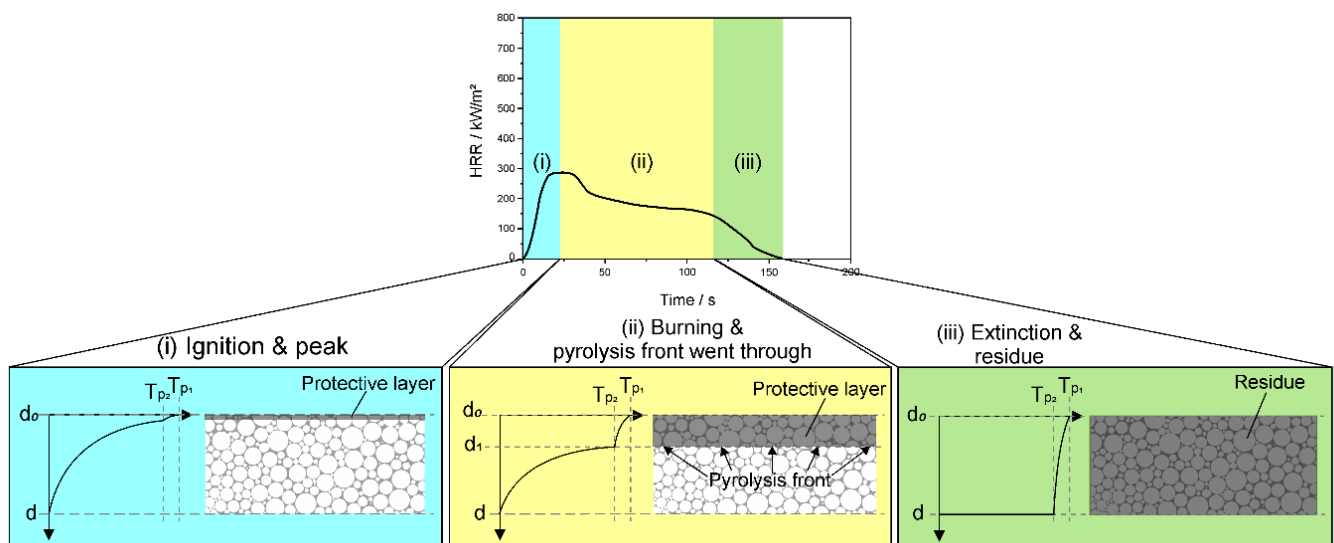


Figure 3. Temperature–thickness relationship of rigid polyurethane foams during different burning stages.

RPUFs behave quite differently from FPUFs during burning, showing the typical HRR curve for residue-forming materials in Figure 3 [9,26,27]. After ignition in stage (i), they reach the PHRR immediately, undergoing distinct charring at T_{p1} , with no structural collapse and no formation of a pool fire because of their higher crosslink density. The char on the top acts as a protective layer, shielding the material underneath. The PHRR is subsequently followed by steady burning in stage (ii) at a lower HRR. The pyrolysis front at T_{p2} continuously consumes the material downward from the top (d_0) to d_1 . Due to the effective protective layer formed, the temperature of the unburned material from d_1 to d decreases inversely toward the bottom of the material. The length of the steady-burning phase in the HRR curve depends on the amount of combustible material [26]. Therefore, less heat is released by RPUFs as the char yield increases [9,27]. In stage (iii), the pyrolysis front at T_{p2} moves to the bottom of the material, and the flame is finally extinguished.

2.2. Role of Selecting Contents of Isocyanate, Polyol, Foaming Agent, and Flame Retardants

Polyurethane chemistry is based on the high reactivity of isocyanates. Diisocyanates are organic compounds with two isocyanate groups, which are widely used to link polyols together through an exothermic reaction between isocyanates and hydroxyl groups in order to build crosslinked polyurethane. The content of diisocyanates in the formulation influences the thermal stability, rigidity, and fire behavior of PUFs. For instance, any excess isocyanates are converted into trimers by trimerization (see Figure 4), called isocyanurate rings [52]. Isocyanurates improve flame retardancy because the presence of a ring structure facilitates charring, forming a protective layer in the condensed phase. Apart from isocyanurates, side products such as polyurea with urea linkages are formed through the reaction of isocyanates with amine-terminated compounds. Polyurea provides the foam with rigidity and thermal stability.

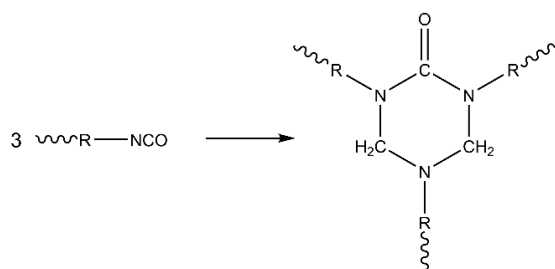


Figure 4. Trimerization of isocyanates.

Polyester polyols and polyether polyols are the two main types of polyols. The difference in chemical structure between ester and ether is shown in Figure 5. Polyether polyols have more resistance to hydrolysis but are less stable to oxidation; the inverse is true for polyester polyols. Polyurethane foams based on polyether polyols have a lower decomposition temperature in air than those based on polyester polyols. To improve the fire behavior of PUFs, flame-retardant polyols such as VORAGUARD™ Polyol from The Dow Chemical Company (Midland, MI, USA) and Exolit® OP 560 from Clariant AG (Muttenz, Switzerland) are used. Another way to enhance the flame retardancy of PUFs is to use aromatic polyols to promote char yield during burning [53].

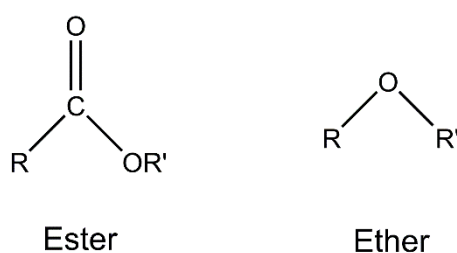


Figure 5. Ester and ether bonds.

The blowing agent is a factor that is believed to influence the burning behavior of RPUFs due to their closed-cell structure. Chemical and physical blowing agents can be used to encourage the foaming process. Water acts as a chemical blowing agent that reacts directly with isocyanates to release carbon dioxide, which is an inert gas. Pentane, cyclopentane, and hydrofluorocarbon are common physical blowing agents [54]. Physical blowing agents are flammable, so they bring a degree of flammability to the closed-cell structure of RPUFs. Physical blowing agents are trapped in the foam and act as additional fuel during burning. Therefore, the selection of suitable blowing agents may also be significant for the flame retardancy of RPUFs.

Effective flame retardants help to improve the fire behavior of materials by increasing the time to ignition and decreasing the HRR to diminish fire spread. The selection of flame retardants usually depends on the structure–property relationship, processing,

compatibility with the polymer matrix, costs, and the applications of polymeric materials [55]. However, there is no all-rounded flame retardant that can be applied to all materials. Adding char promoters such as phosphorous compounds is beneficial to the flame retardancy of RPUFs because the structure of rigid foams is favorable to char due to the high crosslink density during burning. In this case, a higher yield of char residue is generated, and the protective layer formed provides better thermal insulation to the material in the condensed phase, thus releasing less heat. A high loading of additive-type flame retardants is usually required for FPUFs to achieve the desired flame retardancy; however, it usually results in poor mechanical properties of the material. It is suggested that using reactive-type flame retardants is a good strategy to improve the fire behavior of FPUFs while limiting their influence on mechanical properties. Besides using a single flame retardant, combining two flame retardants or even more in one polymer system has made an excellent impression on researchers and the industry, as the right combination of flame retardants can create excellent flame retardancy.

2.3. Effective Flame-Retardant Approaches

The flame-retardant modes of action fall into two categories, namely, those that take place in the condensed phase and those that take place in the gas phase. The flame retardants that work in the condensed phase enhance carbonaceous char, reducing the release of combustible volatiles and acting as a protective layer to reduce the mass loss rate, and in some systems, to cause incomplete pyrolysis. Gas-phase flame retardants release non-combustible gases during decomposition to reduce the effective heat of combustion by fuel dilution or release radical scavengers to reduce the combustion efficiency (χ) of the flame (flame inhibition). Extremely active $\text{OH}\cdot$ and $\text{H}\cdot$ free radicals form during the burning of hydrocarbon fuels, and the system is subjected to an exothermic oxidative chain reaction [56]. To reduce the heat release from the reaction, reactive radicals are scavenged from the gas-phase flame retardants to replace $\text{OH}\cdot$ and $\text{H}\cdot$. It is an efficient way to inhibit the flame, but smoke and CO yield are increased. Many outstanding flame retardants exhibit several mechanisms in parallel, such as flame inhibition and a melt-flow retreat effect [57]. Zammarano et al. [58] studied the heat release rate (HRR) and melt dripping of FPUFs with carbon nanofibers, and the results showed that the system successfully built an entangled fiber network that eliminated melt dripping by increasing the viscosity of the melt and thus formed a protective layer on the surface of the polymer matrix to reduce the HRR. Kempel et al. [59] analyzed the competitive and collaborative relationship among melt dripping, gasification, charring, flame inhibition, and combustion through the particle finite element method in order to understand the complex behaviors of polymeric materials during UL 94 testing. In conclusion, there are two combinations of flame-retardant approaches that serve as effective strategies to enhance the flame retardancy of foams: (1) flame inhibition + enhancement of melt flow and dripping; (2) charring + maintaining structural integrity of the foam or fire residue.

(1) Flame inhibition + enhancement of melt flow and dripping

Flame retardancy can be improved by the combination of flame inhibition in the gas phase and a retreat effect due to increased melt flow in the condensed phase [56,59]. The most important factor affecting the dripping behavior of polymers in fire is melt viscosity. A polymer with low melt viscosity tends to drip during combustion. Although melt flow and dripping can be detrimental to the burning polymers, at the same time, they offer an opportunity to slow flame spread or even cause extinguishment, as they remove mass and heat from the pyrolysis zone [60]. For instance, the flame inhibition of PUFs can be achieved by releasing compounds containing phosphorus during burning, and melt flow and dripping can be enhanced by plasticizers or radical generators in the condensed phase.

(2) Charring + maintaining structural integrity

Flame retardants produce carbonaceous char in the condensed phase that forms a layer that protects the material underneath. However, these char layers are usually

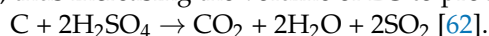
fragile and easily form cracks or even collapse, resulting in the exposure of the underlying unburned material to the flame and causing some side burning. Therefore, maintaining the structural integrity of the foam or intumescent fire residues and the mechanical and thermal stability of char is a way to reinforce the barrier to the underlying material against heat and mass transfer.

3. Burning Behavior of Polyurethane Foams with a Single Flame Retardant

EG and phosphorus compounds are quite commonly proposed as effective single flame retardants in PUFs [61–65]. EG and phosphorus have their own specific flame-retardant modes of action and behave differently during burning. In this section, the details of EG and phosphorus compounds as flame retardants in PUFs are individually discussed.

3.1. Expandable Graphite

Natural graphite inherently has a layered structure. Intercalation is an important process to turn natural graphite flakes into EG. Therefore, EG is usually prepared by inserting oxidants, such as sulfuric acid, nitric acid, phosphoric acid, and acetic acid, between the layers of graphite [66]. The acid decomposes into gases, causing the graphite layers to be forced apart, thereby expanding graphite during heating. It mainly acts in the condensed phase by enhancing the char yield [63,65]. The burning behavior of PUFs with EG is illustrated in Figure 6. EG expands in size by several hundred times, developing a loose, porous “worm-like” structure to form a low-density thermal insulation layer, thereby protecting the underlying material from the heat source and slowing down pyrolysis by decreasing the release of volatile compounds. A minor factor in reducing flammability is that EG releases incombustible gases, such as CO_2 , SO_2 , and H_2O , which helps to dilute the combustible gases surrounding the flame [38,66]. As the temperature rises, the sulfuric acid reacts with graphite, which leads to the oxidation of graphite to form CO_2 , water, and SO_2 , thus increasing the volume of EG to provide flame retardancy to the materials.



However, as shown in Figure 7, expanded graphite is usually fragile and loose. Due to the low adhesion of expanded-graphite char, cracks are easily formed, and more heat flux is exposed to the underlying polymer matrix. Improving the flame retardancy of PUFs by increasing the amount of EG is a challenge. Greater amounts of EG tend to deteriorate the mechanical properties, because EG acts as a nucleating agent to disrupt the structure of the foam [61,67]. In addition, the thermal insulating performance is diminished, and electrical conductivity is increased though the solid phase of conductivity of EG.

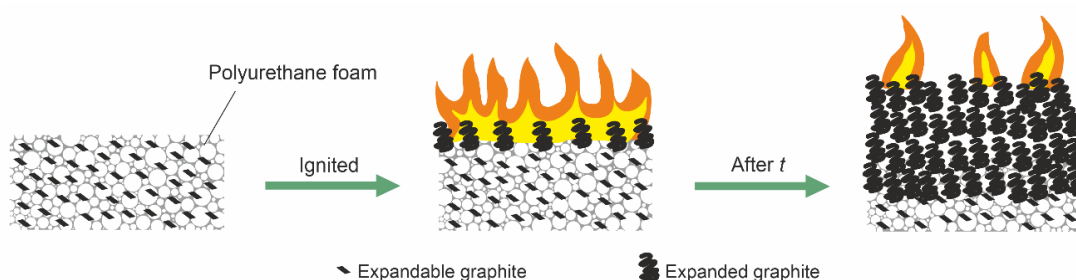


Figure 6. Burning behavior of PUFs with expandable graphite.

The burning processes of FPUFs and FPUFs with 10 wt.% EG (FPUF-10EG) are described by the heat release rate (HRR) and total heat release (THR) curves in Figure 8a,b, respectively, via cone calorimeter measurement. With 10 wt.% EG, the HRR is greatly reduced, and the sharp peak appears at the beginning of burning [42,68]. The very top surface of the polymer matrix is exposed to the heat flux, initially without any protection, so that the HRR reaches the highest value within a very short time. Since the FPUF with 10 wt.% EG in the pyrolysis front region is continuously subjected to the pyrolysis temperature, the polymer matrix starts to decompose. After accumulating a certain amount of

expanded graphite at the pyrolysis front, it acts as a protective layer for the underlying material. The HRR keeps gradually decreasing, and the burning time is prolonged. The presence of 10 wt.% EG results in a lower PHRR and a flatter HRR curve. Only minor second and third peaks following the PHRR are shown in the HRR curve of FPUF-10EG, which proves that a sufficient amount of EG significantly reduces the fire hazard.

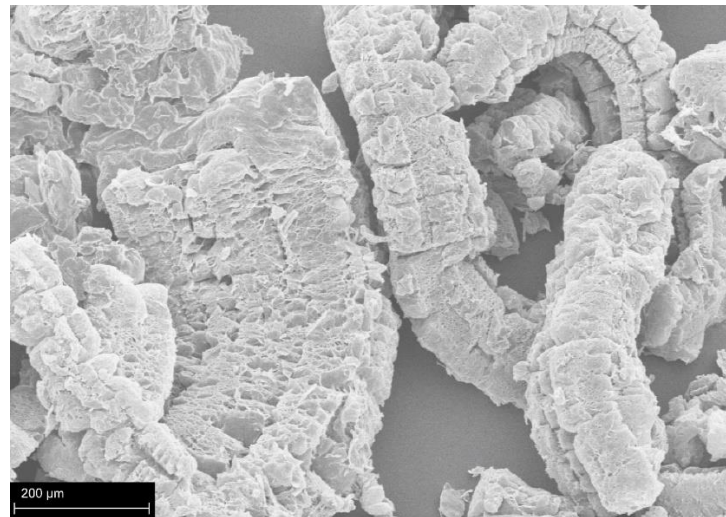


Figure 7. Scanning electron microscope (SEM) image of expanded graphite.

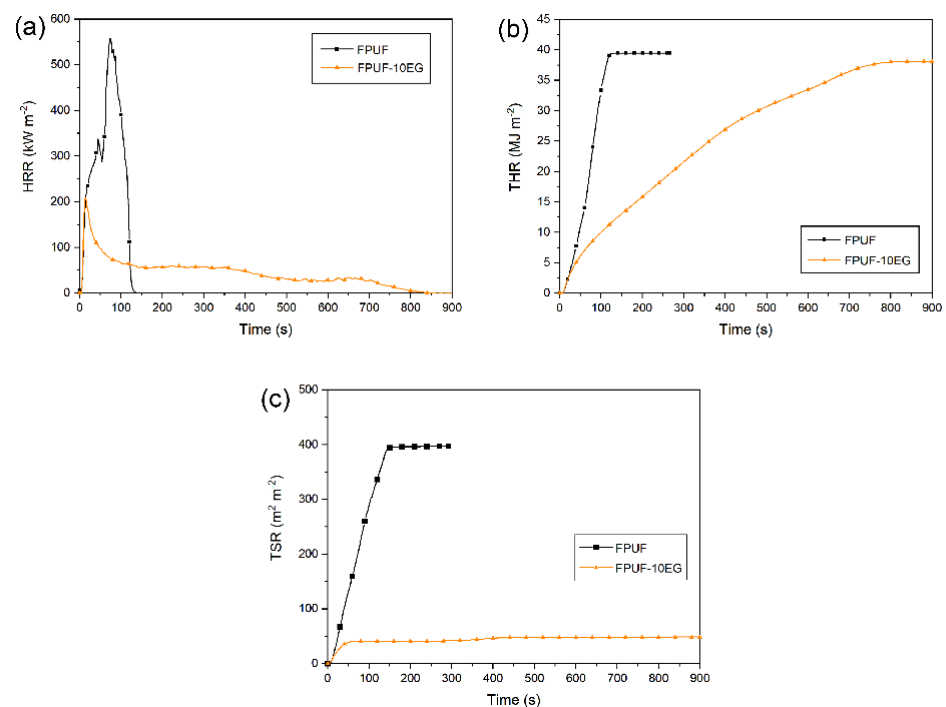


Figure 8. (a) Heat release rate (HRR), (b) total heat release (THR), and (c) total smoke release (TSR) of FPUFs and FPUF-10EG.

Apart from enhancing the flame retardancy of PU foams, EG performs through smoke suppression, as shown in Figure 8c [69]. The higher the amount of EG added is, the less smoke is released. EG reduces the smoke generated during the burning process because expanded graphite prolongs the residence time of smoke precursors in the pyrolysis zone, charring more aromatics, while expanded graphite protects the underlying materials, thus causing less polymer matrix to be consumed [70–72].

According to the UL 94 test, there are two common modes regarding dripping: (1) dripping with flame and (2) dripping without flame. The former may propagate the fire to the flammable materials nearby, enhancing the fire. The latter mode is achieved by removing the heat and fire load to cause dripping without any flame and prevent the propagation of the fire, diminishing the fire due to less heat and fewer flammable components in the burning material. However, a sufficient amount of EG uses a different mode from the above. It reduces the melt drips throughout the test to limit flame spread [61,73]. Because the intumescent structure of expanded graphite provides many tiny openings to keep the melt from dripping and because the char residue is not combustible, EG functions as an anti-dripping agent [73–76].

Flame-Retardant Performance Optimization of Expandable Graphite

The properties of EG, such as expansion volume, particle size, and type of intercalant, determine its effectiveness as a flame retardant in PUFs. Acuña et al. [61] showed that a higher expansion volume of EG improved flame retardancy and reduced smoke production because the larger particle size of expanded graphite provided a compact protective layer to reduce the heat flux passing through to the material underneath. They concluded that the particle size of EG is a key parameter affecting flame retardancy. Pang et al. [77] studied how the EG size affects the flame retardancy of rigid polyurethane foams with EG and ammonium polyphosphate (APP). The study shows that the size of EG had a linear relationship with the expandable volume. They proved that a greater size of EG provided greater flame retardancy, with a higher limiting oxygen index value and increased char yield. The addition of EG and APP delays the decomposition reaction and strengthens the char residue through the formation of a phosphorus-carbonaceous polyaromatic structure. Li et al. [78] confirmed that the larger particle size of EG was advantageous to the synergistic effect between EG and APP in semi-rigid polyurethane foams, as it formed a more continuous and compact protective layer that effectively shielded the transmission of heat to underlying materials during burning.

Apart from particle size, the type of intercalants between the graphite layers is a decisive criterion for enhancing the flame retardancy of PUFs. Lorenzetti et al. [38] investigated the effect of the intercalants of EG on the flame retardancy of polyurethane foams. They observed that the PUF with sulfur-intercalated EG performed better than that with phosphorus-intercalated EG in terms of flame retardancy.

3.2. Phosphorous Flame Retardant

Figure 9 shows the modes of action of phosphorous flame retardants [56]. Phosphorus usually works in the gas phase and the condensed phase [79–81]. The free phosphorous radicals, such as $\text{HPO}_2\cdot$, $\text{HPO}\cdot$, $\text{PO}\cdot$, and $\text{PO}_2\cdot$, generated in the gas phase can quench the other free radicals formed, such as $\text{H}\cdot$ and $\text{OH}\cdot$, by slowing down or interrupting the branching and chain reactions of the oxidation of hydrocarbons during burning, thus playing a role in flame inhibition [82,83]. Phosphorous radicals lead to less complete combustion in the flame zone, thereby reducing combustion efficiency (χ). As a result, increased amounts of incomplete combustion products such as smoke and carbon monoxide evolve at the same time [2,32]. Meanwhile, the heat release is reduced because phosphorus prevents the conversion from carbon monoxide to carbon dioxide, which is a highly exothermic reaction. In the condensed phase, phosphorus takes a variety of modes of action. The dehydration reaction of the polymeric structure during burning induces aromatization and graphitization, and phosphorus acts as a crosslinker to enhance charring. Bourbigot et al. [84] demonstrated that polyaromatic species are crosslinked with phosphohydrocarbonaceous bridges to form voluminous carbonaceous char with higher thermal stability. Phosphorus generally pyrolyzes under elevated temperatures, forming phosphoric acid derivatives to catalyze the carbonization of polymers. However, some phosphoric acid, instead of interacting with the charring agent, generates inorganic polyphosphate glass that acts as a barrier to reduce mass transfer and heat release [85–87]. Although phosphorous compounds are char promot-

ers, incomplete charring by phosphorus, such as aromatization without graphitization, can increase smoke release and even produce larger decomposition fragments. Phosphorous compounds are used as additive or reactive flame retardants in polyurethane foams. For the former, the flame retardancy of the material may decrease over time due to the migration of the flame retardant. Moreover, flame-retardant additives are usually detrimental to the mechanical properties of polymers. Conversely, reactive phosphorous flame retardants are chemically bonded to the main polymer chain or grafted to the backbone as branches. Therefore, using reactive flame retardants is a solution to prevent migration, providing even distribution on the polyurethane backbone and maintaining mechanical performance.

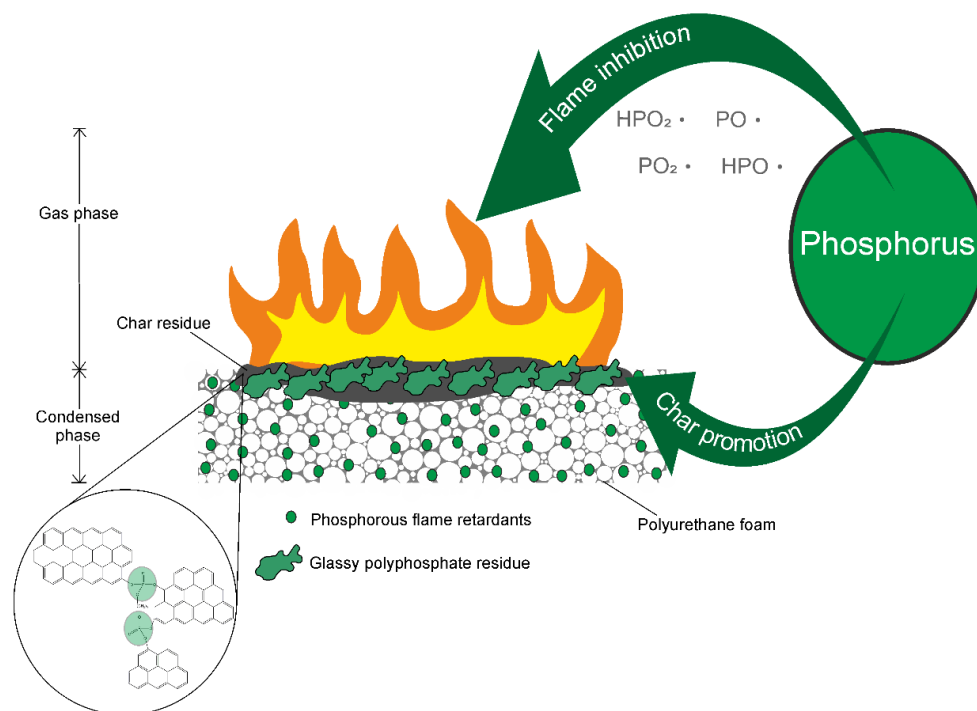


Figure 9. Modes of action of phosphorous flame retardants.

Flame-Retardant Performance Optimization of Phosphorus

Beyond decomposition and evaporation temperatures, the phosphorus oxidation state of phosphorous flame retardants determines their reaction rates with the carbon source and plays an important role in the flame-retardant efficiency of PUFs [4]. Phosphorous flame retardants with different phosphorus valence behave differently in various modes of action. Lorenzetti et al. concluded that the lowest phosphorus valence (+1) was active in both the gas and condensed phases, while the highest phosphorus valence (+5) only worked in the condensed phase [88]. Lenz et al. compared phosphorous flame retardants with different phosphorus oxidation states (+1, +3, +5) [89]. They observed that the phosphorous flame retardants with the lowest phosphorus valence (+1) were more effective in the gas phase. Chen et al. also reported that phosphorous flame retardants with the lowest phosphorus valence (+1) were likely to function in the gas phase and provided better flame retardancy than those with higher phosphorus valence [90]. The mode of action of phosphorous flame retardants during decomposition can be predicted, and the flame retardancy of PUFs can be optimized by choosing the phosphorous flame retardants according to their decomposition and phosphorus oxidation state. The concentration of P-FR used is also a key to optimize the flame-retardant performance of PUFs. With the increase in the concentrations of P-FRs used in the polymer, flame retardancy is significantly improved. Over a certain amount of P-FR concentration, flame retardancy tends to be stable or even decline [91,92]. Thus, flame retardancy is somewhat limited when a P-FR is used alone. Synergy in multicomponent systems is one way to improve the flame retardancy of polymers [93,94].

4. Mechanism of Synergistic Effect between Phosphorus and Expandable Graphite

The combination of phosphorus and EG is an advantageous approach to obtain efficient flame retardancy, and at the same time, the flame-retardant content can be kept as low as possible to reduce the worsening of the mechanical properties [95]. As both EG and phosphorous flame retardants have their own strengths in flame retardancy, they can complement each other. General synergy between phosphorus and EG occurs when flame inhibition and the protective layer are combined [43]. Combustion in the flame and pyrolysis can be understood as two strongly coupled chemical reactions [96]. In addition, at the beginning of burning, when the protective layer is still built up, flame inhibition can delay ignition and/or reduce the first pHRR [18,73,97].

Many contributions to the literature have stated that distinct synergistic effects occur between EG and phosphorus, especially regarding the weight and the morphology of char residue [98–100]. Any synergistic interaction between FRs active in the condensed phase is not straightforward [101] but only occurs when specific mechanisms enhance their efficiency [102]. Figure 10 depicts the burning behavior of PUFs with EG and a phosphorous compound. After ignition, the top layer of EG expands, and the phosphorous compound decomposes to form glassy polyphosphate. The cohesion of the fluffy expanded graphite increases because char is glued together by this polyphosphate. It strengthens the char structure and provides a superior protective layer against the external heat flux for the unburned underlying material [103–105]. Figure 11a,b are SEM images showing that expanded graphite is surrounded by the phosphorous residue, which strengthens the char layers. The phosphorous residue acts a binder to maintain the integrity of the carbonaceous char by linking the expanded-graphite particles. The adhesion of carbonaceous char effectively prevents the formation of cracks during burning to protect the underlying materials. Thus, the total heat release (THR) decreases crucially because of incomplete burning. Figure 12 displays the HRR and THR of FPUF samples with phosphorus (FPUF-P), EG (FPUF-EG), and phosphorus/EG (FPUF-P-EG). FPUF-EG and FPUF-P-EG significantly reduce the peak heat release rate (PHRR) and the THR when compared with FPUF-P. FPUF-P-EG shortens the burning time of FPUF-EG even further, because the combination of phosphorus and EG creates a better protective layer for the underlying material. The underlying material undergoes incomplete pyrolysis or even stops decomposing due to less heat transfer, thus simultaneously reducing the THR.

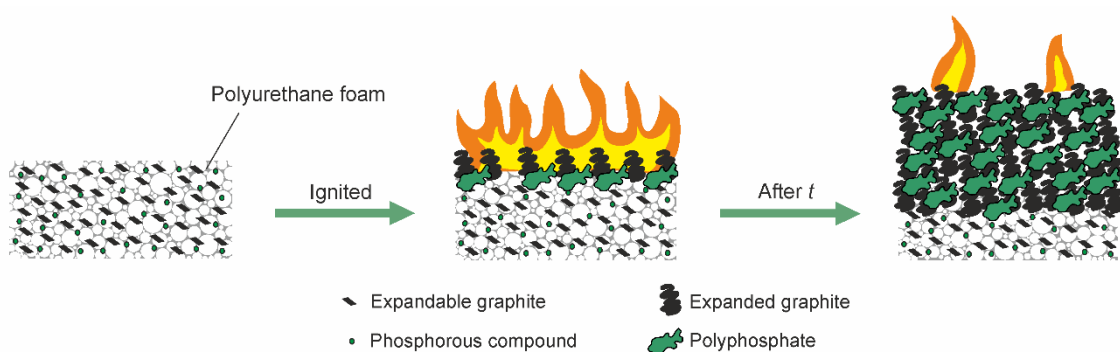


Figure 10. Burning behavior of PUF with expandable graphite and phosphorous compound.

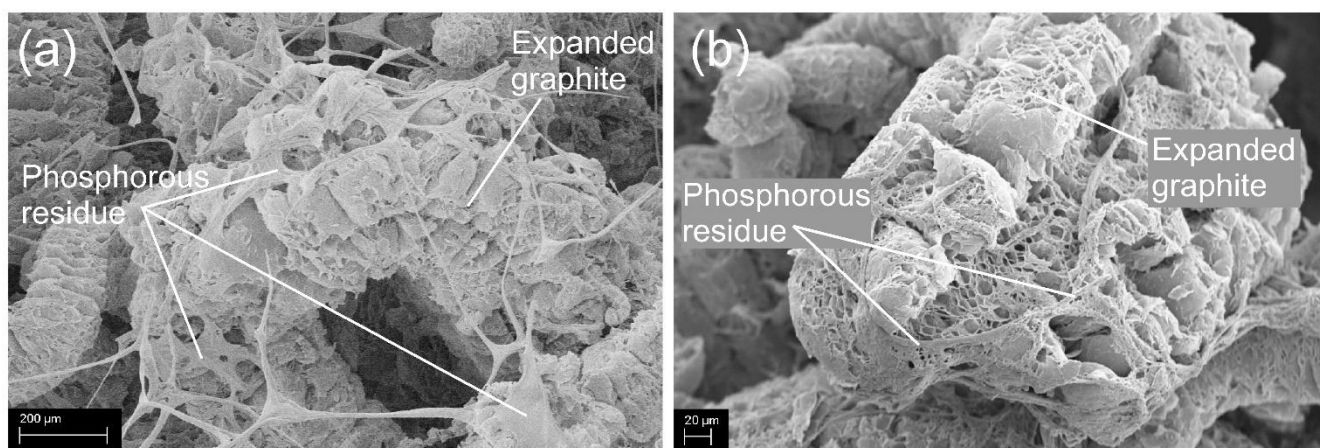


Figure 11. Phosphorous residue acts as a binder for expanded graphite in FPUFs.

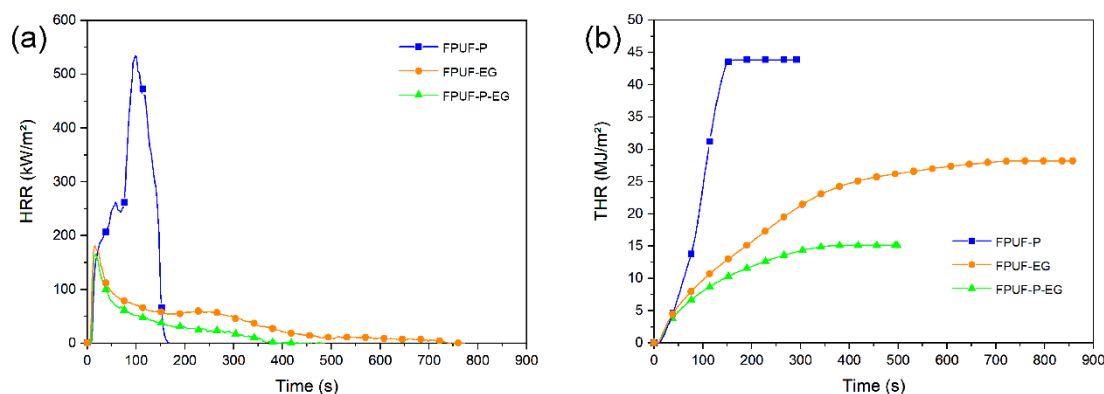


Figure 12. (a) Heat release rate and (b) total heat release of FPUF-P, FPUF-EG, and FPUF-P-EG.

5. Current and Future Tasks

Due to the current general trend and upcoming environmental regulations, further breakthroughs are still ahead, both in the manufacture of PUFs and with regard to the flame retardants used in PUFs.

5.1. Green Solutions for Flame Retardants

Inventing various novel halogen-free chemical flame retardants, using solid waste-based fillers [106–108], and developing environmentally friendly flame-retardant additives in polymeric materials are the current trends in sustainable development. Surprisingly, flame retardants not only exist in laboratories but can also be found in nature. The use of natural flame retardants is an environmentally friendly approach. Some of the natural compounds can be used directly, while others require certain modifications before they can be used as flame retardants.

5.1.1. Natural Renewable Resources as Flame-Retardant Additives

Some biological resources can be added to polymeric materials to enhance flame retardancy due to their special chemical structure and/or content of flame-retardant moieties. One of the natural flame retardants is deoxyribonucleic acid (DNA). DNA is responsible for the storage of genetic information about organisms. The chemical structure of DNA shown in Figure 13a exhibits a carbon backbone that connects with phosphate groups and nitrogen-rich nucleobases (adenine, guanine, cytosine, and thymine). As shown in Figure 13b, phosphodiester linkages form the backbone of DNA, linking nucleotides together. DNA can be used as an intumescent flame retardant because the three main constituents of DNA (phosphate, pentose, and nitrogenous base) are similar to the three

chemical components of a traditional intumescent system: a char promoter, a char source, and a blowing agent [109]. During the combustion process, a foamed carbonaceous protective layer is formed, providing thermal insulation to limit the transfer of heat and fuel between the flame and the polymer. By studying the thermal decomposition process, Alongi et al. [110] found that the ceramic-like intumescent protection layer formed by DNA had higher thermal stability than the intumescent char formed by traditional intumescent flame retardants. Li et al. [111] used DNA-based nanocomposites as a bio-coating to increase the flame retardancy of FPUFs.

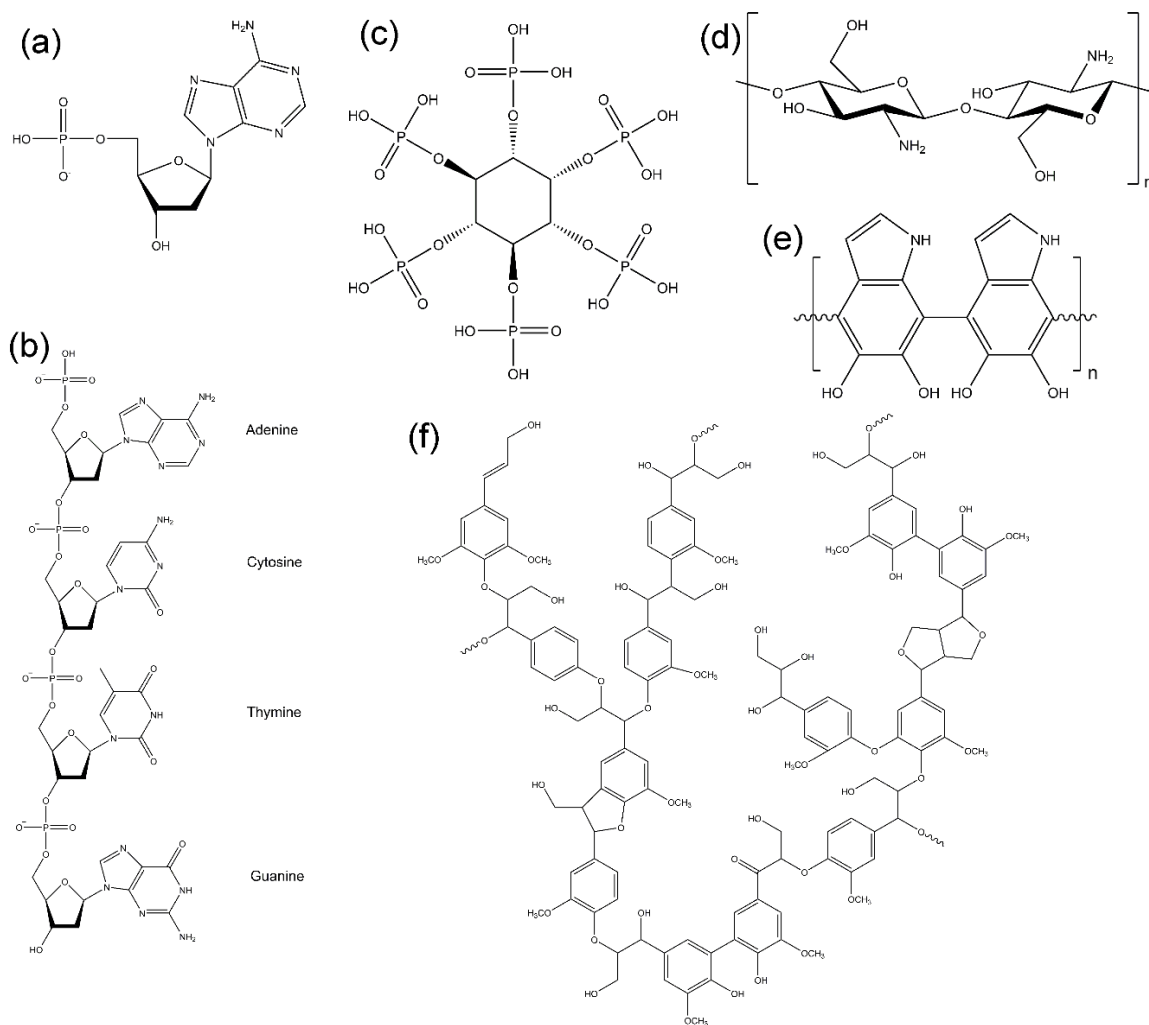


Figure 13. Natural flame-retardant additives: (a) deoxyribonucleic acid (DNA), (b) chain of DNA, (c) phytic acid, (d) chitosan, (e) polydopamine, and (f) lignin.

Phytic acid is a bio-based flame retardant rich in phosphorus. The chemical structure is shown in Figure 13c. Relative to its molecular weight, it contains around 28 wt.% phosphorus. The phosphate group acts as a char promoter upon burning. Sykam et al. [112] reviewed different research papers, focusing on the flame retardancy of phytic acid applied to cotton and wool fabrics. Phytic acid catalyzes the carbonization of cellulose fibers to form a dense carbonaceous layer, which protects the heat transfer within the unburned material below the flame. Phytic acid not only works in the condensed phase, but also in the gas phase. When phytic acid combines with blowing agents such as ammonium ions and amine compounds, an expanded char foam is formed, providing stronger thermal insulation. Lin et al. [113] conducted research on layer-by-layer (LbL) coatings of Ti_3C_2 , phytic acid, and chitosan for FPUFs. They found that the FPUF coated with Ti_3C_2 /phytic

acid/chitosan had better flame retardancy than that with only Ti_3C_2 /chitosan. Compared with the FPUF coated with Ti_3C_2 /chitosan, the peak HRR and total smoke release (TSR) of the FPUF coated with Ti_3C_2 /phytic acid/chitosan were reduced by 51.1% and 84.8%, respectively. The phosphorus in phytic acid acts as a char promoter in the polymer matrix to increase the char yield.

Chitosan, shown in Figure 13d, is a fibrous compound extracted from crustacean shells. Wong et al. [114] coated FPUFs with chitosan and EG using single-step coating. In the cone calorimeter measurements, the combination of chitosan and EG in FPUFs significantly reduced the PHRR, THR, and TSR. Compared with uncoated foam, the char yield of the FPUF containing chitosan and EG was increased by more than six times. Chitosan is also commonly used as a layer-by-layer (LbL) coating material. Nabipour et al. [115] coated FPUFs with nine bilayers of alginate, chitosan, and hydroxyapatite. The nine-bilayer-coated PUF showed reductions in PHRR and smoke production rate (SPR) of 77.7% and 53.8%, respectively. Lin et al. [116] coated FPUFs with eight bilayers of Ti_3C_2 and chitosan. The coated foam reduced the PHRR and TSR by 57.2% and 71.1%, respectively. Coating containing chitosan provides excellent flame retardancy for FPUFs.

Polydopamine (PDA), illustrated in Figure 13e, is a polymeric product yielded by the self-polymerization of dopamine, which is a hormone and neurotransmitter found in various organisms [117]. The advantage of using PDA as a coating material is that it has high adhesion to the surface of various materials. Cho et al. [118] conducted a study on the flame retardancy of PDA-coated FPUFs. They found that the PHRR of the PDA-containing FPUF with a PDA coating thickness of 240 nm (PDA coating for 72 h) was 67% lower in cone calorimeter measurements than that of the uncoated FPUF. PDA works in both the gas phase and condensed phase because it contains nitrogen and is composed of aromatic rings [119].

Lignin, displayed in Figure 13f, mainly provides structural support to plants and is found in cell walls. Lignin is used as a charring agent or flame retardant, because it produces high char yield during burning due to its high weight percentage of aromatic structure with respect to molecular weight [120,121]. Unmodified lignin was added directly to RPUFs and FPUFs [122,123]. Lignin is a polyol typically used as a filler in FPUFs to increase the viscosity of the pyrolysis products to prevent dripping [46]. However, attention must be paid to the amount of lignin added to PUFs, because there are functional hydroxyl groups on lignin that may react with isocyanates during the foaming process, thereby increasing the proportion of hard segments and causing the PUF structure to become brittle, affecting the mechanical performance.

It is noteworthy that pure lignin is composed of functional hydroxyl groups that can be modified to improve flame retardancy and compatibility with polymer matrices [124]. Phosphorylated lignin is a typical example of combining phosphorus and a charring agent in one flame retardant [8]. Xing et al. modified lignin with phosphorus for RPUFs, replacing the petroleum polyol with phosphorylated lignin [125]. Their research study proved that the combination of modified lignin and phenolic encapsulated ammonium polyphosphate in RPUFs reduced the HRR and THR and increased the char yield. Zhang et al. [126] synthesized 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-based lignin to improve the flame retardancy of polyurethane. They demonstrated that the formation of expanded carbonaceous char in the condensed phase by the DOPO-based flame retardant was indicative of an improved flame retardancy of polyurethane. More examples on the modification of renewable resources into functional flame retardants are discussed in Section 5.1.2.

5.1.2. Modification of Renewable Resources into Functional Flame Retardants

Material scientists are seeking different bio-based flame-retardant solutions. Due to the excessive exploitation of fossil fuels, the use of renewable resources is a hot topic at present. More and more countries are aware of this problem and are introducing regulations to deal with the excessive use of non-renewable resources. It is environmentally friendly to modify

bio-based resources into functional flame retardants in polymeric materials to improve flame retardancy and lighten the burden on the Earth.

The most common method for preparing bio-based flame retardants is to take advantage of the chemical similarity between petroleum polyols and plant oils. Plant oils are used in PUF formulations to increase the bio-content of the material from an environmental perspective. Most plant oils, for example, soybean oil [127,128], palm oil [129], and linseed oil [130], are composed of fatty acids that can be directly chemically modified into polyols by introducing hydroxyl groups at the position of the double bonds. The functional groups can be modified by hydroformylation, hydrolysis, ozonolysis, and epoxidation [131]. Among them, epoxidation is a common way to modify functional groups. Fatty acids in plant oils are mostly unsaturated and are reactive to form epoxy rings through epoxidation [132]. The hydroxyl group can then be formed by opening the epoxy ring on the epoxidized oil [133,134]. Therefore, plant oils may react with isocyanates to form urethane bonds. However, plant-oil-based polyols are usually more flammable than their petrochemical counterparts, because the hydroxyl groups formed are usually located in the middle of the fatty acid, with the remaining fatty acid chain treated as a dangling chain [135]. These dangling aliphatic chains serve as a fuel source to support combustion. Considering ways to improve the flame retardancy of PUFs by using plant oil, many scientists have introduced flame-retardant elements, such as phosphorus and nitrogen, onto the backbone of plant oil to obtain flame-retardant polyols, thereby effectively preventing the migration of flame-retardant moieties. Tang et al. [136] synthesized phosphorous soybean-oil-derived polyols for RPUFs. Compared with neat RPUF, the RPUF with 12.3 wt.% synthesized polyols significantly reduced the PHRR, THR, and total smoke production (TSP) by 40%, 35%, and 49%, respectively. The charring performance of RPUFs was improved by introducing the synthesized polyol, and the carbonaceous residue acted as a stronger thermal barrier. Some studies have also combined the advantages of EG and phosphorylated plant oil to simultaneously improve the flame retardancy and bio-based contents of polyurethane foams [137]. In another study of ours [97], petrochemical polyols were partially replaced with novel phosphorus-grafted soybean-oil-based polyols in the formulation of FPUFs with additional EG. The results showed that the synergistic effect between phosphorus and EG increased the char yield by three times and effectively reduced the HRR and THR. Acuña et al. [138] modified castor oil with nitrogen and phosphorous compounds into flame-retardant polyols combined with EG and graphene oxide (GO), which provided superior flame retardancy for RPUFs. Zhang et al. [139] synthesized phosphorous bio-based polyols using castor oil and diethyl phosphate as raw materials. EG was blended into the RPUF formulation. The result showed that the system with EG and phosphorus-grafted castor oil exhibited a large reduction in PHRR compared with the one with EG and glycerolysis castor oil. Chen et al. [140] fully substituted the petroleum-derived polyols in polyisocyanurate foams with phosphorous soy-based polyols they synthesized themselves, also adding EG and a commercial phosphorous liquid flame retardant. Flame retardancy was strongly enhanced by the combination of gas-phase and condensed-phase actions.

5.2. Green Solutions for Polyurethane Foams

Conventional polyurethane foams are mainly produced from petrochemical ingredients, polyols and diisocyanates. Due to increasing concerns about environmental protection, there is great demand for environmentally friendly products. Isocyanates, especially, cause environmental hazards and are highly toxic to human health. Thanks to scientific research regarding green solutions for PUFs, sustainable alternatives to polyols and isocyanates have been found, as well as different reactions to obtain urethane bonds.

CO₂ has always been regarded as the chief culprit of global warming. The Covestro chemical company has capitalized on this waste. They have been researching and successfully producing CO₂-based polyols for polyurethane via catalytic copolymerization [141]. They prepared FPUF from a 3-functional polyethercarbonate polyol and toluene diisocyanate. The apparent density, morphology, mechanical properties, and thermal stability of

the CO₂-based FPUF were comparable to those of the conventional variety. A starch unit was used to construct the structure of the soft segment by Lubczak et al. [142].

Most isocyanates on the market are derived from petroleum. To cope with the problem of non-renewable resources, bio-based alternatives to isocyanates have become available for PU. Konieczny et al. [143] reported that ethyl ester L-lysine diisocyanate and ethyl ester L-lysine triisocyanate were used to produce PU films. Hojabri et al. [144] synthesized fatty acid-derived diisocyanate to replace the petrochemical one for PU.

Conventional PU manufacturing processes use isocyanates, which are highly toxic to living organisms and unsustainable. In addition to the highly toxic isocyanates themselves, colorless toxic gas phosgene is used as a raw material in the manufacturing process of isocyanates [145]. Due to the health and environmental concerns about isocyanates, the synthesis of non-isocyanate polyurethane is a way to eliminate highly toxic compounds from the manufacturing process and final products. Non-isocyanate polyurethane can be synthesized through several reactions, polyaddition, rearrangement, polycondensation, and ring opening. The most general approach is cyclic carbonate–primary amine addition reaction [146,147]. During the formation of every urethane linkage, a primary or secondary hydroxyl group is also formed. This reaction yields polyhydroxyurethanes [148]. The reaction does not require the use of isocyanates. Cyclic carbonate can be directly synthesized by the reaction between the unsaturated bond and hydrogen peroxide to form an epoxy ring and subsequently react with carbon dioxide. However, certain carbonate–amine systems are less reactive, except at elevated temperatures and/or in the presence of a catalyst.

6. Challenges and Conclusions

The recyclability of PUFs is an important issue that needs to be addressed. Pure PUFs can be recycled and recovered through mechanical, physical, chemical, and thermo-mechanical processes. The main challenge is that PUFs containing traditional flame retardants cannot easily be recovered via pyrolysis. Flame retardants in PUFs change the decomposition temperature and may hinder the thermal decomposition of the material by charring [149]. Therefore, incineration is a common disposal method for flame-retardant PUFs. However, incineration has adverse effects on global warming due to the high emission of greenhouse gases. The recyclability of PUFs containing traditional flame retardants remains a challenge in practice.

Biodegradation is an eco-friendly way to break down polymers. However, the bacterial degradation of PUFs takes an exceedingly long time because it largely depends on the structure and crosslink density of the materials [150]. The use of renewable resources continues to expand due to growing interest from the industry and academia. The trend is towards a safer, non-toxic, sustainable, and economical way to produce PUFs. Flame-retardant PUFs composed of fully sustainable ingredients, along with sustainable production methods, would also improve biodegradability as a solution for natural decomposition in the environment.

In addition to focusing on the environmental impact of the end-of-life disposal of PUFs themselves, the potential hazards of phosphorus-based flame retardants used in PUFs are also noteworthy. Since many small-molecule phosphorous flame retardants are not chemically bonded to the polymeric products, they can be released into the living environment through volatilization, leaching, and/or abrasion over time, and people can easily be exposed to them [151]. The potential health concerns phosphorous flame retardants present for human beings are considerable. Numerous studies have been conducted on the toxicity of phosphorous flame retardants for human health. Araki et al. investigated the impact of phosphorous flame retardants in residential dust on human health and reported that their level was positively correlated with the prevalence of asthma and allergies [152]. Bruchajzer et al. found that phosphorous compounds affect reproduction in humans [153]. Nevertheless, phosphorous flame retardants have relatively low environmental toxicity compared with their halogenated counterparts [154,155]. In order to reduce the health hazards of phosphorous flame retardants for human beings, it is suggested to use reactive

phosphorous flame retardants that are chemically bonded to the final products to avoid the leakage of phosphorus in the environment. In an environmentally friendly way, using the natural FRs mentioned in Section 5.1 instead of synthetic ones solves the problem of the chemical contamination of the environment.

In addition to environmental and health concerns, meeting fire safety regulations is a major challenge in practical applications. The development of flame-retarded PUFs, especially FPUFs used in railway vehicles, which must fulfill the high requirement of a maximum average of the rate of heat emission (MARHE) value below 90 kW m^{-2} or even lower (based on the various sets of requirements) according to European standard EN 45545 “Fire Protection on Railway Vehicles”, is a particular challenge.

Although the above-mentioned challenges question the application scope of PUFs, both academia and the industry are actively addressing them with successful and promising efforts. In terms of fire safety regulations for PUFs, the synergistic effects between phosphorus and EG provide impressive flame retardancy to PUFs and achieve a perfect balance between the mechanical properties and flame retardancy of PUFs. This feature article describes the fundamental mechanism of the synergistic effect between P-FRs and EG in PUFs. In further development, this synergy can create higher flame retardancy for PUFs with the right kinds and appropriate amounts of P-FRs and EG. In addition to the combination of P-FRs and EG, adding other flame-retardant elements, as well as cleverly adjusting the PUF chemistry to this combination, may be a further solution to provide PUFs with unexpectedly high flame retardancy through complicated interactions in the gas phase and the condensed phase [156–158]. The synergistic halogen-free combination of EG and P-FRs is posed as one of the current champions in the flame retardancy of PUFs and also offers the potential for a sustainable solution in future PUFs based on renewable polyurethane or with renewable flame retardants.

Author Contributions: Conceptualization, Y.Y.C. and B.S.; methodology, Y.Y.C. and B.S.; validation, Y.Y.C.; investigation, Y.Y.C.; resources, B.S.; writing—original draft preparation, Y.Y.C. and B.S.; writing—review and editing, Y.Y.C. and B.S.; visualization, Y.Y.C.; supervision, B.S.; project administration, Y.Y.C. and B.S.; funding acquisition, B.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research study was funded by DFG (Deutsche Forschungsgemeinschaft), grant number SCHA 730/19-1.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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5 Summary

Due to the high flammability of FPUF, a series of research efforts was done to enhance its flame retardancy for a wide range of applications. Furthermore, bio-based and halogen-free materials were used in this work to achieve a less toxic and more environmentally friendly solution for FPUF. Bio-based materials is a renewable resource to reduce the use of petrochemical counterpart. Halogen-free flame retardants such as P-FRs, MA and EG are used in FPUF. Moreover, two or more flame retardants were used in FPUF, and surprisingly, the combination of P-FR and EG provides excellent synergistic effect in flame retardancy. The synergistic effect of P-FR and EG was summarized comprehensively in the feature article.

In this work, various characterization methods were used to investigate comprehensively the fire behavior of materials, such as LOI, UL 94 and cone calorimeter. Since the morphology of cellular structure of FPUF is crucial to the mechanical properties of FPUF, SEM was performed to compare the modified FPUFs with the neat FPUF and to study the residue after burning to better understand the role of flame retardants in the condensed phase. The SEM images reveal that the structural integrity of FPUF residue containing EG and P-FR is retained due to glassy phosphorous residue surrounding the expanded graphite to act as a binding agent. Mechanical properties such as tensile strength, elongation at break and compression stress were measured to be ensured the modified FPUFs are comparable to the neat FPUF. Pyrolysis behavior was studied to understand the decomposition process of FPUFs under nitrogen. The two-step pyrolysis of FPUF is closely related to the difference in the decomposition temperature of the hard segment and soft segment representing the foam collapse and pool fire during burning.

Apart from flame retardancy, the smoke and toxic gases released by FPUF during burning are also a concern. Smoke and toxic gases are the leading cause of death in fire. Specific optical smoke density was measured by the SDC. And the toxic gases like HCN, NO_x and CO were measured by coupled FTIR simultaneously. These data are important for designing FPUFs to release less smoke during burning. In this work, it was recognized that EG serves as an excellent smoke suppressant for FPUF. When only 10 wt.% loading of EG was present in the polymer matrix, the smoke emission was reduced by more than 10 times. EG prolongs the residence time of the smoke precursors in the pyrolysis zone to char more stable and larger sized aromatics without escaping from the condensed phase. Hence, less smoke is emitted.

Since FPUFs are usually used in the cushioning material for vehicle seats, the fire protection standard DIN EN ISO 5659-2 requires compliance with MARHE and smoke parameters for such applications in various countries to ensure the high level of fire safety. These values are obtained from cone calorimeter and smoke density chamber measurements.

Through a series of scientific studies, it is strongly proved that the combination of P-FR and EG indeed has a synergistic effect on the flame retardancy of PUF. The polyaromatic species in the carbonaceous char are reinforced by the crosslinking with phosphohydrocarbonaceous bridge. [43] The protective layer of EG is strengthened with glassy polyphosphate as a binder. Hence, the combination of P-FR and EG forms a thermal barrier, which effectively enhances the flame retardancy of FPUF. The results were compared with and placed with the current state of the art. This work advanced the state-of-the-art and provides valuable insights to enable evidence-based development for further optimization of effective multicomponent flame retardant FPUF systems to meet the higher requirements in terms of flame retardancy and smoke emission for specific fire safety standards, such as in automobile, railway, and aircraft.

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