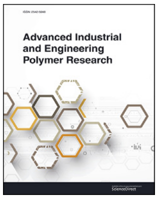
Advanced Industrial and Engineering Polymer Research 6 (2023) 156–164

Contents lists available at ScienceDirect

Advanced Industrial and Engineering Polymer Research

journal homepage: http://www.keaipublishing.com/aiepr



Recent advances for flame retardant rubber composites: Mini-review

Liangqing Lai [a], Jia Liu [a], Zhen Lv [b], Tianming Gao [d, **], Yongyue Luo [b, c, *]

[a] Baimtec Material Co., Ltd., Beijing 100095, China
[b] Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001 China
[c] Leibniz-Institut Für Polymerforschung Dresden e.V., 01069 Dresden, Germany
[d] School of Chemistry and Chemical Engineering, Lingnan Normal University, Zhanjiang 524001 China

ARTICLE INFO

Article history:
Received 25 October 2022
Received in revised form
6 December 2022
Accepted 12 December 2022

Keywords:
Flame retardancy
Natural rubber
Silicon rubber
Artificial rubber
Polyurethane elastomer

ABSTRACT

Flame retardant rubber composites have attracted a great attention during the past decades owing to their irreplaceable roles in complex industrial systems. Large amounts of efforts have been made to improve the flame retardant ability, developing high efficiency flame retardant systems which can reduce the release of heat, smoke and toxic gases while not deteriorate overall properties is becoming more and more important. This review briefly outlines the recent developments of flame retardant natural rubbers, silicon rubbers, some kinds of artificial rubbers and polyurethane elastomer composites, focuses on the design, development, mechanism and applications of advanced high-performance flame-retardant methods. Finally, outlooks the future tendency including more environmental-friendly strategies, higher flame-retardant efficiency and development of multifunctional flame-retardant rubber composites are proposed.

1. Introduction

Rubbers and elastomer as one of the most important inventions play irreplaceable roles in tires, dampers, suspension elements, etc., their unique overall performances make them indispensable in daily life, transportation and industrial systems [1–4]. Based on the data from *International Rubber Research Group*, the rubber consumption is expected to beyond 30 million tons every year around the world [5]. Natural rubber which directly from plants has been widely used for hundreds of years owing to their excellent overall performances, while a large number of synthetic rubber composites have also been developed for various fields owing to their adjustable structure and properties [6,7]. In recent decades, different kinds of advanced rubber composites including high-performance rubbers, bio-sourced rubbers, functional rubbers and easily-recycled/reprocessing rubbers have been developed, which further expanded the application of rubber composites [8–10].

However, since most widely used rubber composites are flammable their quickly incineration while being ignited would significantly speed up the destroy of the whole system, while the toxic smoke could also be a great threat to the life (Fig. 1) [11–14]. According to the data of European fire safety alliance, in Europe there are more than 5000 people die each year from fires, while the economic loss may reach a really high value at about 1% of the GDP [15]. Hence, a great attention has been paid to the flame retardation of rubber composites in the past decades [16]. At present, owing to the increasing requirement of advanced applications and environment-protect conception, how to design and fabricate high performance flame-retardant rubber composites based on green and efficient materials and process is highly attractive all over the world [17–20].

This mini review mainly focuses on the recent efforts for the design, performances and applications of high-performance flame-retardant natural rubbers, silicon rubbers, some kinds of artificial rubbers and polyurethane (PU) elastomer, demonstrate the achievements enabled by additive-type flame retardants including intumescent flame retardants, nano flame retardants and other advanced flame retardants. The development of efficient bio-inspired and bio-sourced flame retardants which endow the rubber composites matrix with desired flame-retardant ability in a green way without degrading other performance may open up new opportunities in high-valued applications of advanced rubber composites. Finally, the conclusions and outlooks are discussed.

---

* Corresponding author. Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001 China.
** Corresponding author.
E-mail addresses: gaotmcat@163.com (T. Gao), lyy6226@hotmail.com (Y. Luo).

https://doi.org/10.1016/j.aiepr.2022.12.002

Acronyms

PU	Polyurethane
GDP	Gross Domestic Product
EG	Expandable Graphite
UL-94	Standard for Safety of Flammability of Plastic Materials for Parts in Devices and Appliances Testing
NR	Natural Rubber
CO_2	Carbon Dioxide
SiO_2	Silicon Dioxide
LOI	limiting Oxygen Index
MARHE	Peak Heat Release Rate
FPI	Fire Performance Index
FGI	Fire Growth Index
FeOOH	Hydroxyl Oxidize Iron
Fe_2O_3	Iron (III) Oxide
$CuMoO_4$@h-BN	$CuMoO_4$-Hexagonal Boron Nitride
EPDM	Ethylene–Propylene–Diene Rubber
LDH	Layered Double Hydroxide

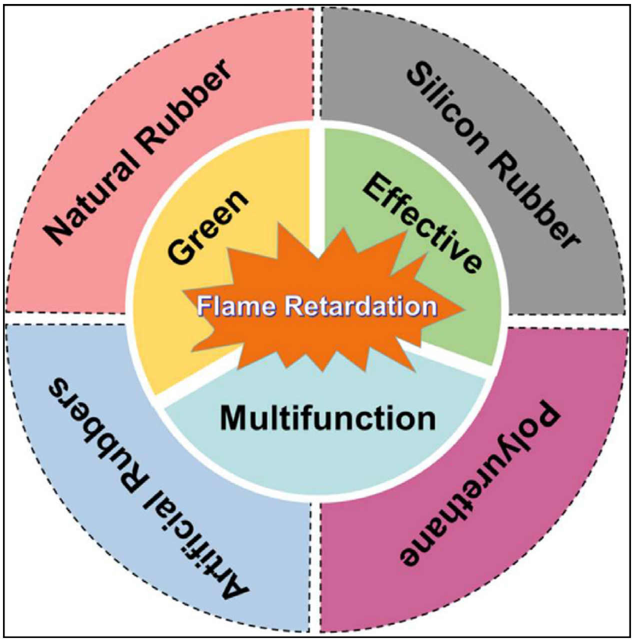


Fig. 2. Schematic diagram of the recent development of flame retardant rubbers.

2. Recent advances

The molecular structures of most rubber composites are consisting of carbon and hydrogen elements, which may lead to a highly flammable performance while the flame would spread quickly with a large amount of toxic smoke. The burning behaviors are based on a free radical chain reaction in which the oxidation reaction is an automatic catalytic process, resulting in the uncontrollable destroy. Traditional halogen-based flame retardants always generate toxic gas which may cause serious pollution have been widely forbidden these yeas. Bio-inspired strategies, halogen-free and sustainable-sourced flame retardants have attracted more and more attentions, however, owing to their limited flame-retardant t efficiency the large addition amount usually affect the overall performances of the composites. Hence, how to design green and efficient flame-retardant system to expand the advanced application of rubber composites still remains great challenges.

2.1. Flame retardation natural rubber

Natural rubber and corresponding composites possess a great strategic importance in human society, as one of the most important bio-polymer with a series of unique properties such as elasticity, abrasion, impact resistance and malleability at cold temperatures. To meet the stringent requirements of the developing rubber industry, expandable graphite (EG) intumescent additive for flame retardant natural rubber composites is attracting more and more interests based on its high flame retardant efficiency and environmental-friendly characterization [21]. Cheng and co-workers reported a new kind of EG microcapsule doped by nitride which possesses an organic shell with high compatibility and thermal conductivity. Owing to the presence of organic silicone shell the composites exhibit better flame-retardant and mechanical properties, the UL-94 ratings was reported increase to V-0 [22]. Aksam and partners proposed a melamine salt of pentaerythritol phosphate/graphite mixture to further improve the flame retardant properties by combining the acid source, carbon source, and blowing agent in one system. The developed addictive decreased total heat release, mean effective heat of combustion and maximum average rate of heat emission (FGI 6.9 kW/m^2 s, and FPI 0.06 $m^2 s\ kW^{-1}$), and can help the formation of a coherent char after calorimeter test [23].

Similar to EG additive, inorganic modified organoclay is also reported in the flame-retardant high performance natural rubber composites (see Fig. 2). For example, Zhang and co-workers prepared a flame-retardant montmorillonite to obtain highly branched polymer chains. As shown in Fig. 3a, the obtained organoclay materials were used in natural rubber composites which can improve the tensile strength (22.2 MPa, 764% elongation at break) and elongation compared while improving the thermal stability and increasing the burning time by about 69% (218 s) [24]. A series of flame-retardant composites based on dendrimer modified organic montmorillonite have also been established, which possess better mechanical (from 15.2 MPa to 17.3 MPa and from 771% to 796%),

Fig. 1. Applications of rubbers and elastomer, and the photo of the fire scene.

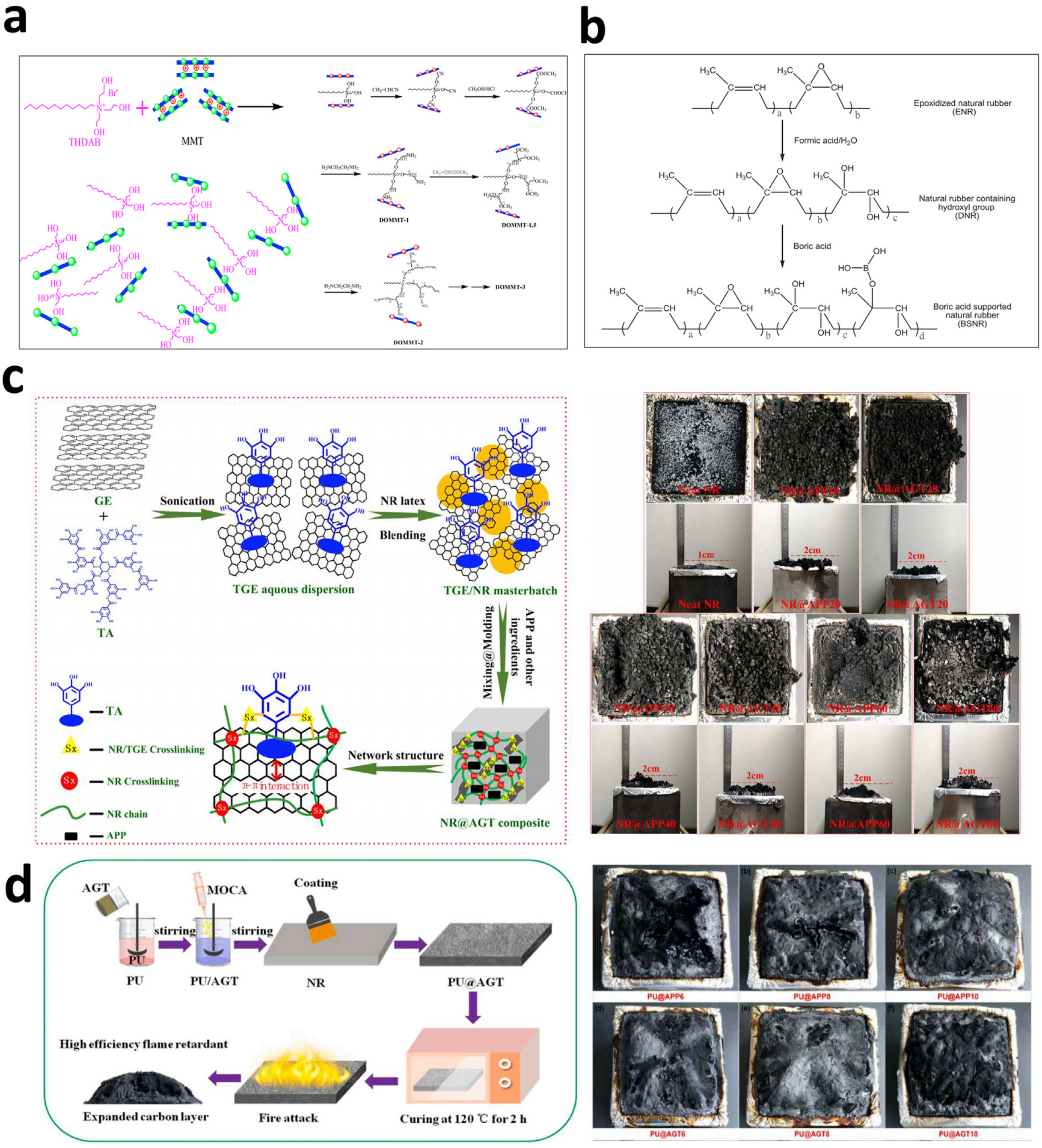


Fig. 3. Schematic diagrams of the flame-retardant natural rubber composites based on (a) modified organoclay [24], Copyright 2018, Elsevier (b) reactive flame retardants [26], Copyright 2016, Elsevier, and natural inspired strategy of different reported works (c) [28], (d) [30]. Copyright 2020, Elsevier.

flame-retardant properties, and efficiently reduce the heat release rate, smoke evolution area and carbon monoxide concentration [25].

As another important kind of additives, the reactive flame retardants also show superiors to improve efficiency by inhibiting or suppressing the combustible process. Intharapat described a reactive flame retardant carried out by introducing boric acid into natural rubber matrix with hydroxyl groups. In Fig. 3b, the obtained composites exhibit higher Mooney viscosity, thermal stability and improved flammability behaviors (owing to the reduction of CO_2 and burning rate, the LOI value reaches 25, PHRR 674 kW/m^2 and FGI 2,87 kW/m^2 s), which expanded its future applications [26]. Wu et al. reported a novel microencapsulated ammonium polyphosphate with a triallyl cyanurate/SiO_2 shell, benefit from the shell the flame retardant additives can be well dispersed in the natural rubber matrix, achieve excellent flame-retardant performances (UL-94 reaches V-0) while improve mechanical properties (21.4 MPa) at the same time [27].

Although the above-mentioned strategies have achieved desired performances, the complex synthetic processes and sometimes toxic materials still limit their future applications. To develop advanced green strategies, inspired by natural fire-protecting strategy, Li et, al. reported an efficient natural tannic acid based intumescent flame-retardant system, in which the ammonium polyphosphate as acid source and gas source, tannic acid as acid source and carbonization agent, graphene as

Table 1
Comparison of the reported flame-retardant ability of natural rubber composites.

Achieved approach	Ref.	Brief introduction	Flame retardant ability					
			UL-94	LOI (%)	PHRR (kW/m^2)	FGI (kW/m^2 s)	FPI (m^2s kW^{-1})	Burning time (s)/rate (mm/min)
Expandable graphite	[21]	Organic modified boron nitride and intumescent flame retardant	V-0	26.8	410	–	–	–
	[22]	Double-shell co-microencapsulated ammonium polyphosphate and expandable graphite	V-0	29.9	501	2.5	0.07	–
	[23]	Melamine salt of pentaerythritol phosphate/graphite	–	–	415	6.9	0.06	–
Modified organoclay	[24]	Flame-retardant montmorillonite	–	–	–	–	–	218 s
	[25]	Dendrimer modified organic montmorillonite	–	–	1054	–	–	208 s
Reactive flame retardants	[26]	Boric acid supported natural rubber	–	25	674	2.87	–	–
	[27]	Microencapsulated ammonium polyphosphate with a triallyl cyanurate/SiO_2 shell	V-0	32.5	1118	–	–	–
Natural inspired fire-protecting strategy	[28]	Tannic acid based intumescent flame-retardant system	V-0	32.1	443	2.76	0.13	–
	[29]	Combining phosphoric acid, tea saponin (TS) and melamine structures into a single structure	V-1	25.7	460	–	–	–
	[30]	Highly efficient natural tannic acid (TA)-based intumescent flame-retardant system	V-0	32	171.9	0.5692	0.2966	–
Environment-friendly Flame retardant natural rubber composites	[31]	Sugarcane bagasse mixed with natural rubber compound	–	–	–	–	–	16.78 mm/min
	[32]	Watermelon peels powder and crumb rubber as alternatives to fillers flame retardant chemicals	–	20.6	–	–	–	23 mm/min

carbonization agent and carbon layer reinforcing agent. It was demonstrated that the developed system can provide both flame retardant ability (UL-94 reaches V-0, and LOI value is up to 32.1) and enhanced mechanical properties (>24 MPa, as shown in Fig. 3c), while which possesses a synergistic ability of both flame retardant and smoke suppression due to the dual flame retardant functions of each component [28]. An efficient flame retardant system combining phosphoric acid, tea saponin and melamine structures was also reported which can improve both the mechanical properties and flame retardant performances of natural rubber composites. The mechanical properties (26.2 MPa and 523%) and flame retardant behavior (LOI 25.7) were efficiently improved owing to the strong interfacial interaction and effective dispersion [29]. Recently researchers also developed natural tannic acid-based intumescent flame-retardant system combined with polyurethane coating as a carbon forming agent, which can minimize the influence of flame retardant additives on the desirable intrinsic properties (Fig. 3d). The coating method requires just less flame retardant additives to achieve high flame retardant effect (UL-94 reaches V-0, and LOI is 32), which may benefit the flame retardant natural rubbers in industry [30].

Obviously, to meet the increasing requirements of green and environmental-friendly conceptions, a number of efforts have been made to achieve the green and high-performance flame retardant natural rubber composites. Although the inorganic fillers and reactive flame retardant additives achieved a desired performances, the complex synthetic processes and sometimes toxic materials still limit their future applications, and for bio-inspires and bio-sourced strategies, their flame retardant ability is sometimes not excellent enough. Besides the design and fabrication of advanced green flame-retardant additives, researchers also studied their influence on environment-friendly natural rubber composites to better direct the future development. Yotkuna and co-partners utilized sugarcane bagasse mixed with natural rubber compounds to enhance the mechanical properties and improve their flame-retardant properties, and most importantly, the influence of magnesium hydroxide and aluminum hydroxide was also described [31]. Younis and co-workers investigated the suitability of watermelon peels powder and crumb rubbers as alternatives of flame retardant chemicals to reduce the cost [32]. These works give excellent demonstrations about high performance flame retardant natural rubber composites, which can be important steps toward future advanced applications. In the future, how to design and fabricate high-performance flame retardant additives based on green and sustainable strategies is still highly attractive. A detailed comparison of these mentioned advances, including UL-94, limiting oxygen index (LOI), maximum rate of heat emission (MARHE), fire performance index (FPI) and the fire growth index (FGI), is demonstrated in Table 1.

2.2. Flame retardation silicon rubber

Since the commercialization of silicone rubbers which possess outstanding bio-compatibility, high temperature resistance and excellent electrical properties, corresponding researches and applications have attracted interests all over the world. However, since the silicon rubbers are considerably flammable, it's also very important to improve their flame-retardant ability and develop high performance composites. It has also been widely demonstrated that synthesized reactive flame retardant additives possess desired performances. Zhu et al. reported poly [N,N,N′,N′,N″,N″-hexakis-cyclotriphosphazene-[1,3,5]triazine-2,4,6-triamine as an new kind of efficient flame retardant additive for flame retardant silicon rubber composites (Fig. 4a). Benefiting from the designed structure the heat release rate and smoke production rate were significantly reduced (a LOI value of 31.8% and UL-94 V-0), which is attributed to the formation of compact and stable char layer during thermal decomposition [33]. Similar research has been reported that efficient cyclophosphazene derivative Hexa (*p*-acetamidophenoxy) cyclotriphosphazene can be prepared by one-step reaction for highly flame-retardant silicon rubber composites (UL-94 V-0 rating, the total heat release and total smoke release decreased by 26.9% and 41.5%) [34]. Phosphaphenanthrene structure was also synthesized and exhibited advantages like quicker self-extinguishment, lower heat release rate, higher thermal stability and better charring capacity (UL-94 V-0 and LOI reaches 42.3) [35]. These synthetic additives have been demonstrated effective in high efficiency flame retardant silicon rubbers, however the complex synthesis process, related potential high cost and sometimes toxic raw materials may limit their further application.

Beside the synthetic reactive flame retardant additives, efficient additives based on green and more environmental friendly materials and process have also been widely studied. Consist with natural rubber composites, the utilization of intumescent flame

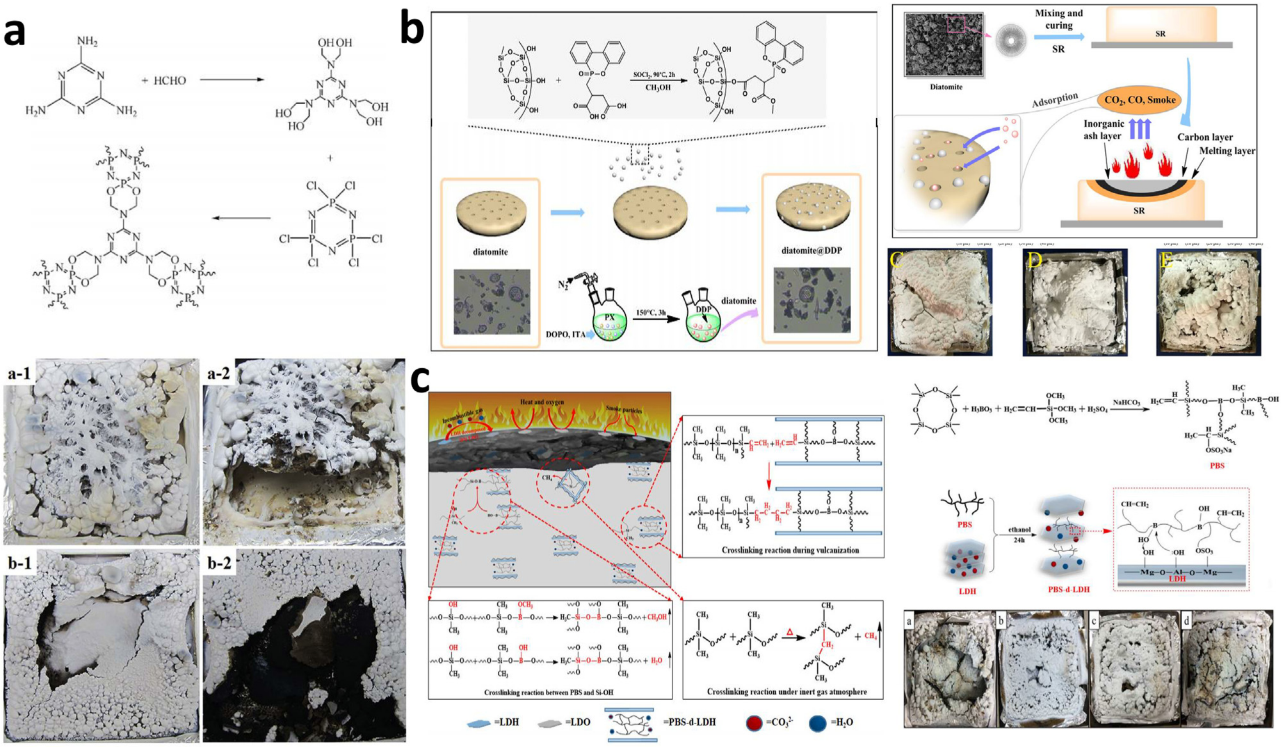


Fig. 4. Schematic diagrams of flame-retardant silicon rubber composites. (a) Efficient flame retardant [33], Copyright 2015, Elsevier. Diatomite based systems (b) [39],(c) [41], Copyright 2019, Elsevier.

retardant additives are also one of the most advanced approaches. An organic-inorganic hybrid functionalized expandable graphite was reported being utilized in silicone rubber composites, which can effectively enhance the flammable properties including reduce the total heat release and total smoke release, improve the thermal stability and form a more obvious intumescent char layer (LOI values up to 53.8) [36]. To further improve the flame retardant performances, Liu and co-partners reported a silicone rubbers-based hybrid material containing intumescent flame retardant additives and ferric hydroxide, the exist of FeOOH particles can enhance the thermal stability under high temperature (toward high up to 582 °C for the sample containing 4.0 mass% FeOOH), and improve the flame retardant performances by forming a condensed barrier for heat and mass transfer [37]. Recent publication also demonstrated that Fe_2O_3 particles in intumescent flame retardant system are able to further increase smoke suppression efficiency, promote early cross-linking during decomposition to increase char formation, which can restrict the diffusion of fuels into combustion zone [38].

Compared with synthetic additives, the utilization of inorganic flame retardant materials may be less efficient, but greatly simplify the design and processing of corresponding composites while decrease the risk of toxic smoke. Diatomite is also utilized in flame retardant silicon rubber composites, in Fig. 4b, Zhang er at prepared a flame retardant additive based on modified diatomite by esterification method, the obtained additive can reduce fire risk and toxicity effectively (PHRR was reduced to 185 kW/m^2 from 237 kW/m^2) [39]. A flame retardant additive based on diatomite, polyethyleneimine and multi-walled carbon nanotubes was reported, the corresponding silicone rubber composites owns better flame retardant performances (LOI 24.8 and PHRR 345 kW/m^2), and owing to the desired compatibility the tensile properties were also improved [40]. Polyborosiloxane decorated layered double hydroxide was demonstrated in Fig. 4c, which can easily exfoliated and dispersed in matrix to endow the composites with outstanding mechanical properties (11.9 MPa, 675%), thermal stability, flame retardant performances and smoke suppression performances (peak heat release rate and peak smoke production rate were reduced by 54.4% and 61.5%) [41]. These results indicate that the introduction of flame retardant fillers can improve the performance of silicon rubber composites in a simple way, while it can be found that the combination of several different additive shows a great potential.

Owing to the limitation of different flame retardant additives, to further improve the corresponding performances, the synergistic effect of the flame-retardant elements may lead to desired excellent flame-retardant performances. Ye and co-partners reported a synergistic system based on 9,10-dihydro-9-oxa-10-phenanthrene-10-oxide, vinyl trimethoxysilane, and (3-aminopropyl) triethoxysilane, phytic acid and oxidized multi-walled carbon nanotubes, the silicon rubber composites with a small amount of obtained additive exhibit desired flame retardant effect (UL-94 V-0) benefit from the synergistic effect [42]. The synergistic effect of expandable graphite and aluminum hypophosphite for flame retardant silicone rubber composites was also reported, which can effectively reduce the flammable properties and improve thermal stability (smoke factor can be 245 kW m^{-2} contrast to pure silicon rubber 1058 kW m^{-2}) [43]. The antimony trioxide and melamine cyanurate hybrid additive which can uniformly dispersed in silicone rubber matrix indicated a reduced heat release rate and total heat release values while the mechanical properties keep good behavior (a 31.5% LOI of the composite was achieved) [44]. The synergistic effects have been indicated as a good approach to prepare highly effective flame retardant additives, which may open up new opportunities in high performance flame retardant silicon rubber composites. In conclusion, develop high performance additives based on synergistic effect for silicon rubber composites can be regarded as one of the most attractive trends in corresponding areas.

2.3. Flame retardation polyurethane elastomer

Thermoplastics polyurethane elastomer have been widely accepted in a series of different applications owing to their excellent physical properties, oil and water resistance, and the adjustable molecular design. Through precise structural design and controlled composite, high-performances flame retardant PU composites are expected to meet the increasingly diversified market demands. Recent decades a large amount of efforts have been made to achieve the flame retardant ability, reduce the toxic gases and prevent severe droplet [14]. Synthetic high-efficient additives are demonstrated that can be significantly improve the flame retardant performances. For example, 1-aminoethyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium hexafluorophosphate has been developed as advanced flame retardant additive for PU composites, which can promote the formation of carbon layer in the early stage of fire, and the peak heat release rate can be reduced by 32.97% [45]. Wang et al. reported an inherently flame-retardant polyester diol based on 9,10-dihydro-10-[2,3-di (hydroxycarbonyl)propyl]-10-phosphaphenanthrene-10-oxide, adipic acid, ethylene glycol, and 1,4-butanediol, the synthesized composites exhibit higher residual char yield (Fig. 5a), higher limiting oxygen index and tensile strengths and most importantly, reduces the total heat release at the same time [46]. Aromatic acetylene compound 4-(phenylethynyl) di(ethylene glycol) phthalate was also reported as a chain extender to synthesize intrinsic flame-retardant PU composites which can form foaming char structure after being burned, endow the composites with improved flame retardant ability (peak heat release rate and total heat release declined by 46.2% and 24.5%, respectively) and improved mechanical properties (39.2 MPa, almost twice as much as neat PU) [47]. Other synthesized systems including aluminum monomethylphosphinate [48], ammonium polyphosphate with dopamine and cobalt ions (Fig. 5b) [49] have also been reported and demonstrated efficient in high performance PU composites.

Beside the achievement of synthesized molecules, high-performance flame retardant additives based on inorganic materials have also attracted great interests owing to their easily processing properties. Xu et al. reported a flame retardant ($CuMoO_4$@h-BN) through co-precipitation method, only 2 wt%

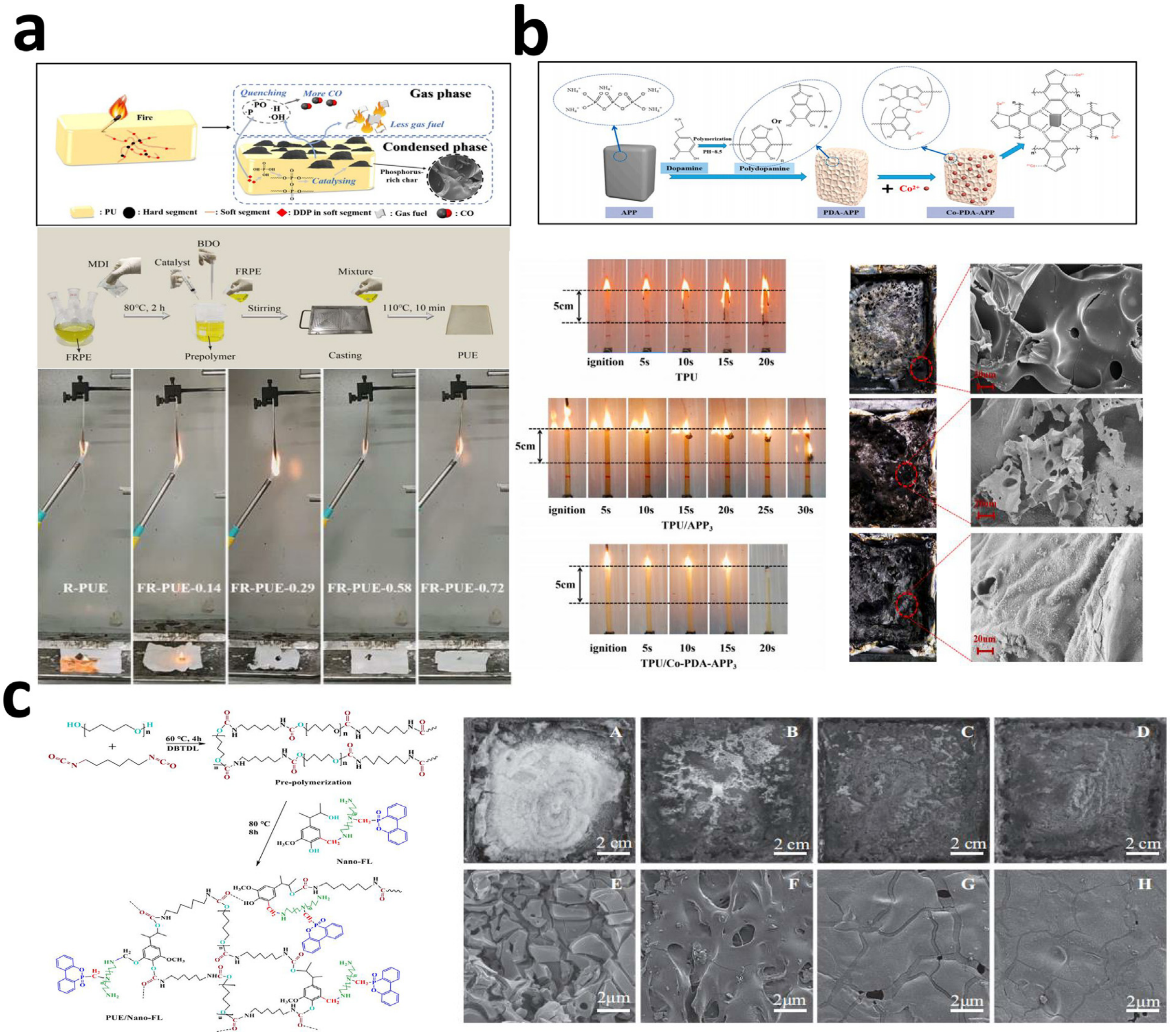


Fig. 5. (a) Fabrication process of high-performance flame retardant PU composites [46], Copyright 2021, Elsevier. (b) Molecular design of ammonium polyphosphate with dopamine and cobalt ions [49], Copyright 2022, Elsevier. (c) Design of functionalized lignin nanoparticles [56], Copyright 2022, Elsevier.

amount of additives can decrease the peak heat release rate, total heat release and smoke density by 73.6, 52.4 and 28.2%, which is expected to expand the fire safety applications of the material in a simple and inexpensive way [50]. Similarly, two-dimensional nanoplates including zinc zeolite imidazole frameworks-L, cobalt zeolite imidazole frameworks-L, and Zinc–Cobalt hybrid zeolite imidazole frameworks-L have also been studied and showed good flame retardant performances (the LOI values increased from 23.2% to 25.7%, total heat release decreased by 11.4%, peak heat release rate decreased by 43.8% and peak smoke production rate reduced by 51.5%) [51]. Synergistic flame retardant systems have been demonstrated that can further improve the performances, Chen and co-partners proposed a copper metal-organic framework with ammonium polyphosphate, the good synergistic flame-retardant effect is able to form char residue layers with high graphitization and expansion degree [52]. More complex system like cobalt citrate/copper citrate/yttrium citrate/ammonium polyphosphate hybrids has also been developed and exhibit a desired high flame retardant ability [53].

It can also be easily found that to further expand the application of flame-retardant PU composites, how to design and fabric high efficiency additives based on low-cost wastes or bio-sourced materials is also an important issue. Jiao et al. reported a flame-retardant and smoke-suppressant agent based on abandoned molecular sieve, which also exhibit a good application prospect in flame retardant and smoke suppressant of PU composites (PHRR declined by 55.0%) [54]. Carretier and co-partners studied the influence of sepiolite and lignin as potential synergists for fire retardant systems, the results indicated that sepiolite can acts as char reinforcement and lignin exhibit complementary effects on flame retardant performances [55]. Functionalized lignin nanoparticles with nitrogen and phosphorus moieties have been developed as both crosslinking agents and flame retardants for PU composites, as can be seem in Fig. 5c. By overcoming the weakening effect of traditional lignin on the mechanical properties the composites exhibit strong tensile properties and desired flame retardant ability (LOI as high as 29.8% and it also passed the UL-94 V-0 rating), greatly benefit the future application of high performance PU composites (48.7 MPa, and the elongation at break 1128%) [56]. In conclusion, although the synthetic reactive flame retardant additives and inorganic fillers have been developed and achieved desired performances, to meet the sustainable goal of future, high-efficient additives based on recycled wastes and bio-source materials is highly desired while which still remains challenge.

2.4. Recent advances of other artificial rubbers

Researchers all over the world also paid great attention to different kinds of flame-retardant artificial rubbers, owing to their unique properties and potential applications. For example, chlorinated acrylonitrile butadiene rubber composites prepared by alkaline hydrolysis of chloroform have been demonstrated as high performance rubbers with superior tensile strength, high oil resistance and excellent flame resistant property [57]. Guo and group reported alternating multi-layered damping composites consisted of chlorinated butyl rubber layers and poly (vinyl chloride) layers, it was demonstrated that the flame-retardant properties (LOI values can up to almost 40%) were enhanced with increasing the layer number which can effectively retard the combustion of the material [58].

Ethylene–propylene–diene rubbers (EPDM) as a kind of important product have also been widely studied. Andreas and co-partners reported layered double hydroxide (LDH) [59], known as naturally occurring hydrotalcite for flame retardant EPDM composites, which demonstrated a peak heat release rate value of 654 kW/m^2 [60]. Also, a high-performance flame retardant EPDM composites have been designed and prepared based on one-step synthesized LDH and an intumescent flame retardant comprised of pentaerythritol, ammonium polyphosphate and methyl cyanoacetate, while the authors also proposed the flame retardant mechanism [61]. Wang et al. prepared intumescent flame retardant additives based on ammonium polyphosphate/pentaerythritol and expandable graphite particles which exhibit excellent synergistic flame retardant effects for EPDM applications [62]. Researchers also studied the influence of aluminum hypophosphide and nano-sized silica on the flame-retardant and mechanical properties of EPDM rubber composites, the synergistic effect was demonstrated effective in improving both flame retardant ability and mechanical ability [63]. Moreover, the potential char precursor polyaniline was also reported in high performance EPDM rubber composites [64].

Halogen-free flame retardant additives are absolutely an important issue in different kind of artificial rubber composites. For ethylene vinyl-acetate co-polymer rubber composites, researchers have developed new flame retardant additives containing phosphorus and silicon elements at the same time, which can significantly improve the flame retardant performances and thermal stability [65]. For styrene-butadiene rubber composites, a facile method has been developed for cost-effective, green and smart flame-retardant additives based on rice husk silica nanoparticles coated with organic green molokhia extract, the thermal stability was enhanced by 55 °C and the flame retardant properties were improved 31% and 33% reduction in peak heat release rate and average heat release rate [66]. Thermoplastic vulcanizate based on ethylene vinyl acetate rubbers and ethylene-vinyl acetate copolymers has been composited with aluminum hydroxide, which shows desired flame retardant ability, good stretchability, nice elasticity, high strength and flexibility at the same time [67]. Obviously, design and fabrication of new high-performance flame retardant additive is expected further improve the overall properties of rubber composites, which lead to more advanced applications in the future.

3. Conclusion

As the key part of industrial systems, flame-retardant rubber composites show their importance in different applications and have attracted great attentions worldwide. Recent advances about flame retardant natural rubber composites, silicon rubbers, PU composites and other artificial rubbers have achieved some desired progresses. The development of advanced flame retardant additives including synthesized reactive molecules, modified functional fillers and designed synergistic hybrids have been demonstrated efficient in improving the performances of rubber composites. Moreover, it can be easily found that flame retardant systems based on low-cost wastes, bio-sourced materials, advanced functional nanoparticles with green and efficient fabricated process are attracting increasing attentions. Corresponding researches are expected to significantly improve the overall properties of rubber composites, which greatly expand their potential applications in complex and advanced situation in the future.

4. Outlooks

Environmentally friendly flame-retardant technologies are highly desirable for decades owing to the increasing attentions of environment and health. More and more attentions have been paid to reduce the toxic smoke and harmful wastes. Introducing green flame retardant additives including bio-sourced agents and low-cost inorganic fillers, reducing the usage of complex solvents and potential by-product emission would be crucial steps to desired green lifestyles. Moreover, scientists have been chasing for further improvement of flame retardant ability, endow the rubber composites with higher performances including higher LOI value, lower burning rate, lower smoke release and so on. Elaborately designed high efficiency flame retardant systems based on synergistic effect is of great interests of future high-performance rubber composites, which obviously is one of the most important directions.

Furthermore, it's also desirable to develop flame retardant systems in advanced functional rubber materials, as multifunctional materials are one of the most attractive topics of future. Combining excellent flame retardant ability with other outstanding functions such as stimulus-response ability, antistatic ability and fatigue resistance will be more attractive. Such combination not only expands the application of flame retardant systems in high value-added products, but also significantly improves the robust of complex systems to protect lives.

Declaration of competing interests

The authors declare no competing interests.

Acknowledgements

The authors would like to acknowledge the financial support from the Natural Science Foundation of Hainan Province, China (Grant No. 521MS0798, 521MS080) and the China Scholarship Council (201903260015).

References

[1] L. Bokobza, Natural rubber nanocomposites: a review, Nanomaterials 9 (1) (2018) 12.
[2] B.P. Chang, A. Gupta, R. Muthuraj, T.H. Mekonnen, Bioresourced fillers for rubber composite sustainability: current development and future opportunities, Green Chem. 23 (15) (2021) 5337–5378.
[3] Y. Fan, G.D. Fowler, M. Zhao, The past, present and future of carbon black as a rubber reinforcing filler – a review, J. Clean. Prod. 247 (2020), 119115.
[4] H. Patel, S. Salehi, R. Ahmed, C. Teodoriu, Review of elastomer seal assemblies in oil & gas wells: performance evaluation, failure mechanisms, and gaps in industry standards, J. Petrol. Sci. Eng. 179 (2019) 1046–1062.
[5] Y. Li, X. Zhang, R. Wang, Y. Lei, Performance enhancement of rubberised concrete via surface modification of rubber: a review, Construct. Build. Mater. 227 (2019), 116691.
[6] S. Tang, J. Li, R. Wang, J. Zhang, Y. Lu, G.H. Hu, Z. Wang, L. Zhang, Current trends in bio-based elastomer materials, SusMat 2 (1) (2022) 2–33.
[7] Y. Guo, L. Liu, Y. Liu, J. Leng, Review of dielectric elastomer actuators and their applications in soft robots, Adv Intelligent Sys 3 (10) (2021), 2000282.
[8] K. Roy, S.C. Debnath, P. Potiyaraj, A review on recent trends and future prospects of lignin based green rubber composites, J. Polym. Environ. 28 (2) (2019) 367–387.
[9] A. Mohajerani, L. Burnett, J.V. Smith, S. Markovski, G. Rodwell, M.T. Rahman, H. Kurmus, M. Mirzababaei, A. Arulrajah, S. Horpibulsuk, F. Maghool, Recycling waste rubber tyres in construction materials and associated environmental considerations: a review, Resour. Conserv. Recycl. 155 (2020), 104679.
[10] K. Roy, S.C. Debnath, A. Pongwisuthiruchte, P. Potiyaraj, Up-to-date review on the development of high performance rubber composites based on halloysite nanotube, Appl. Clay Sci. 183 (2019).
[11] S. Lu, Y. Feng, P. Zhang, W. Hong, Y. Chen, H. Fan, D. Yu, X. Chen, Preparation of flame-retardant polyurethane and its applications in the leather industry, Polymers 13 (11) (2021) 1730.
[12] E. Jasinski, V. Bounor-Legaré, A. Taguet, E. Beyou, Influence of halloysite nanotubes onto the fire properties of polymer based composites: a review, Polym. Degrad. Stabil. 183 (2021), 109407.
[13] L. Wan, C. Deng, Z.Y. Zhao, H. Chen, Y.Z. Wang, Flame retardation of natural rubber: strategy and recent progress, Polymers 12 (2) (2020) 429.
[14] L. Wan, C. Deng, H. Chen, Z.-Y. Zhao, S.-C. Huang, W.-C. Wei, A.-H. Yang, H.-B. Zhao, Y.-Z. Wang, Flame-retarded thermoplastic polyurethane elastomer: from organic materials to nanocomposites and new prospects, Chem. Eng. J. (2021) 417.
[15] R.A. Mensah, V. Shanmugam, S. Narayanan, J.S. Renner, K. Babu, R.E. Neisiany, M. Forsth, G. Sas, O. Das, A review of sustainable and environment-friendly flame retardants used in plastics, Polym. Test. (2022), 107511.
[16] Y.-T. Li, W.-J. Liu, F.-X. Shen, G.-D. Zhang, L.-X. Gong, L. Zhao, P. Song, J.-F. Gao, L.-C. Tang, Processing, thermal conductivity and flame retardant properties of silicone rubber filled with different geometries of thermally conductive fillers: a comparative study, Compos. B Eng. 238 (2022), 109907.
[17] M. Dogan, S.D. Dogan, L.A. Savas, G. Ozcelik, U. Tayfun, Flame retardant effect of boron compounds in polymeric materials, Compos. B Eng. 222 (2021), 109088.
[18] Y. Yang, J.L. Diaz Palencia, N. Wang, Y. Jiang, D.Y. Wang, Nanocarbon-based flame retardant polymer nanocomposites, Molecules 26 (15) (2021) 4670.
[19] N.F. Attia, S.E.A. Elashery, A.M. Zakria, A.S. Eltaweil, H. Oh, Recent advances in graphene sheets as new generation of flame retardant materials, Mater. Sci. Eng., B 274 (2021), 115460.
[20] S.T. Lazar, T.J. Kolibaba, J.C. Grunlan, Flame-retardant surface treatments, Nat. Rev. Mater. 5 (4) (2020) 259–275.
[21] N. Wang, M. Zhou, J. Zhang, Q. Fang, Modified boron nitride as an efficient synergist to flame retardant natural rubber: preparation and properties, Polym. Adv. Technol. 31 (9) (2020) 1887–1895.
[22] N. Wang, G. Xu, Y. Wu, J. Zhang, L. Hu, H. Luan, Q. Fang, The influence of expandable graphite on double-layered microcapsules in intumescent flame-retardant natural rubber composites, J. Therm. Anal. Calorim. 123 (2) (2015) 1239–1251.
[23] A. Abdelkhalik, G. Makhlouf, A. Abdel-Hakim, Fire behavior of natural rubber filled with intumescent flame retardant containing graphite, J. Vinyl Addit. Technol. 26 (2) (2019) 155–164.
[24] G. Zhang, J. Wang, Preparation of novel flame-retardant organoclay and its application to natural rubber composites, J. Phys. Chem. Solid. 115 (2018) 137–147.
[25] C. Zhang, J. Wang, Natural rubber/dendrimer modified montmorillonite nanocomposites: mechanical and flame-retardant properties, Materials 11 (1) (2017) 41.
[26] P. Intharapat, C. Nakason, A. Kongnoo, Preparation of boric acid supported natural rubber as a reactive flame retardant and its properties, Polym. Degrad. Stabil. 128 (2016) 217–227.
[27] C. Wu, X. Wang, J. Zhang, J. Cheng, L. Shi, Microencapsulation and surface functionalization of ammonium polyphosphate via in-situ polymerization and thiol–ene photograted reaction for application in flame-retardant natural rubber, Ind. Eng. Chem. Res. 58 (37) (2019) 17346–17358.
[28] L. Li, X. Liu, X. Shao, L. Jiang, K. Huang, S. Zhao, Synergistic effects of a highly effective intumescent flame retardant based on tannic acid functionalized graphene on the flame retardancy and smoke suppression properties of natural rubber, Compos. Appl. Sci. Manuf. 129 (2020), 105715.
[29] N. Wang, L. Hu, H.V. Babu, J. Zhang, Q. Fang, Effect of tea saponin-based intumescent flame retardant on thermal stability, mechanical property and flame retardancy of natural rubber composites, J. Therm. Anal. Calorim. 128 (2) (2016) 1133–1142.
[30] L. Li, X. Liu, K. Huang, Y. Wang, X. Zheng, J. Wang, Y. Du, L. Jiang, S. Zhao, A facile strategy to fabricate intumescent fire-retardant and smoke suppression protective coatings for natural rubber, Polym. Test. 90 (2020), 106689.
[31] K. Yotkuna, R. Chollakup, T. Imboon, V. Kannan, S. Thongmee, Effect of flame retardant on the physical and mechanical properties of natural rubber and sugarcane bagasse composites, J. Polym. Res. 28 (12) (2021) 1–13.
[32] A.A. Younis, A.A. El-Wakil, Improvement of mechanical and flame retardant properties of natural rubber by eco-friendly watermelon peel and crumb rubber, Fibers Polym. 22 (5) (2021) 1237–1246.
[33] C. Zhu, C. Deng, J.-Y. Cao, Y.-Z. Wang, An efficient flame retardant for silicone rubber: preparation and application, Polym. Degrad. Stabil. 121 (2015) 42–50.
[34] J. Yang, W. Ma, D. Hu, D. Zhang, L. Wu, B. Yang, S. Zhang, Facile preparation and flame retardancy mechanism of cyclophosphazene derivatives for highly flame-retardant silicone rubber composites, J. Appl. Polym. Sci. 138 (17) (2020).
[35] W. Chen, Y. Liu, C. Xu, Y. Liu, Q. Wang, Synthesis and properties of an intrinsic flame retardant silicone rubber containing phosphaphenanthrene structure, RSC Adv. 7 (63) (2017) 39786–39795.
[36] X. Chen, J. Zhuo, W. Song, C. Jiao, Y. Qian, S. Li, Flame retardant effects of organic inorganic hybrid intumescent flame retardant based on expandable graphite in silicone rubber composites, Polym. Adv. Technol. 25 (12) (2014) 1530–1537.
[37] L. Liu, J. Zhuo, X. Chen, C. Jiao, S. Li, Y. Gu, Influence of ferric hydroxide on smoke suppression properties and combustion behavior of intumescent flame retardant silicone rubber composites, J. Therm. Anal. Calorim. 119 (1) (2014) 487–497.
[38] X. Chen, M. Li, J. Zhuo, C. Ma, C. Jiao, Influence of Fe_2O_3 on smoke suppression and thermal degradation properties in intumescent flame-retardant silicone rubber, J. Therm. Anal. Calorim. 123 (1) (2015) 439–448.
[39] C. Zhang, J. Wang, S. Song, Preparation of a novel type of flame retardant diatomite and its application in silicone rubber composites, Adv. Powder Technol. 30 (8) (2019) 1567–1575.
[40] L. Yao, W. Jincheng, Z. Chenyang, Preparation of a novel flame retardant based on diatomite/polyethyleneimine modified MWCNT for applications in silicone rubber composites, J. Rubber Res. 24 (1) (2021) 137–146.
[41] J. Qiu, X. Lai, H. Li, J. Gao, X. Zeng, X. Liao, Facile fabrication of a novel polyborosiloxane-decorated layered double hydroxide for remarkably reducing fire hazard of silicone rubber, Compos. B Eng. 175 (2019), 107068.
[42] P. Ye, L. Cheng, W. Jincheng, S. Shiqiang, Preparation of a novel synergistic flame retardant and its application in silicone rubber composites, Fire Mater. 44 (8) (2020) 1135–1148.
[43] X. Chen, W. Song, J. Liu, C. Jiao, Y. Qian, Synergistic flame-retardant effects between aluminum hypophosphite and expandable graphite in silicone rubber composites, J. Therm. Anal. Calorim. 120 (3) (2015) 1819–1826.

[44] X. Huang, Z. Tian, D. Zhang, Q. Jing, J. Li, The synergetic effect of antimony (Sb_2O_3) and melamine cyanurate (MCA) on the flame-retardant behavior of silicon rubber, Polym. Bull. 78 (1) (2020) 185–202.

[45] C. Jiao, Y. Zhang, S. Li, X. Chen, Flame retardant effect of 1-aminoethyl-3-methylimidazolium hexafluorophosphate in thermoplastic polyurethane elastomer, J. Therm. Anal. Calorim. 145 (1) (2020) 173–184.

[46] H. Wang, Q. Liu, X. Zhao, Z. Jin, Synthesis of reactive DOPO-based flame retardant and its application in polyurethane elastomers, Polym. Degrad. Stabil. 183 (2021), 109440.

[47] M. Xie, D. Jia, J. Hu, J. He, X. Li, R. Yang, Fabrication of enhanced mechanical properties and intrinsic flame-retardant polyurethane elastomer containing 4-(Phenylethynyl) Di(Ethylene Glycol) Phthalate, Polymers 13 (15) (2021) 2388.

[48] Q. Hu, L. Zou, Z. Liu, J. Chen, J. Liu, X. Liu, Flame-retardant polyurethane elastomer based on aluminum salt of monomethylphosphinate, J. Therm. Anal. Calorim. 143 (4) (2020) 2953–2961.

[49] Y.-R. Li, Y.-M. Li, W.-J. Hu, D.-Y. Wang, Cobalt ions loaded polydopamine nanospheres to construct ammonium polyphosphate for the improvement of flame retardancy of thermoplastic polyurethane elastomer, Polym. Degrad. Stabil. 202 (2022), 110035.

[50] W. Xu, A. Li, Y. Liu, R. Chen, W. Li, $CuMoO_4$@hexagonal boron nitride hybrid: an ecofriendly flame retardant for polyurethane elastomer, J. Mater. Sci. 53 (16) (2018) 11265–11279.

[51] W. Xu, Z. Cheng, D. Zhong, Z. Qin, N. Zhou, W. Li, Effect of two-dimensional zeolitic imidazolate frameworks-L on flame retardant property of thermoplastic polyurethane elastomers, Polym. Adv. Technol. 32 (5) (2021) 2072–2081.

[52] X. Chen, X. Chen, S. Li, C. Jiao, Copper metal-organic framework toward flame-retardant enhancement of thermoplastic polyurethane elastomer composites based on ammonium polyphosphate, Polym. Adv. Technol. 32 (8) (2021) 2829–2842.

[53] X. Chen, K. Wang, S. Li, C. Jiao, Effects of flame retardants integrated with citrate and ammonium polyphosphate on thermal stability and flame retardancy of thermoplastic polyurethane elastomer, Polym. Adv. Technol. 32 (8) (2021) 2866–2878.

[54] C. Jiao, H. Jiang, X. Chen, Reutilization of abandoned molecular sieve as flame retardant and smoke suppressant for thermoplastic polyurethane elastomer, J. Therm. Anal. Calorim. 138 (6) (2019) 3905–3913.

[55] V. Carretier, J. Delcroix, M.F. Pucci, P. Rublon, J.M. Lopez-Cuesta, Influence of sepiolite and lignin as potential synergists on flame retardant systems in polylactide (PLA) and polyurethane elastomer (PUE), Materials 13 (11) (2020) 2450.

[56] T. He, F. Chen, W. Zhu, N. Yan, Functionalized lignin nanoparticles for producing mechanically strong and tough flame-retardant polyurethane elastomers, Int. J. Biol. Macromol. 209 (2022) 1339–1351.

[57] A. Nihmath, M.T. Ramesan, Synthesis, characterization, processability, mechanical properties, flame retardant, and oil resistance of chlorinated acrylonitrile butadiene rubber, Polym. Adv. Technol. 29 (8) (2018) 2165–2173.

[58] F. Zhang, G. He, K. Xu, H. Wu, S. Guo, The damping and flame-retardant properties of poly(vinyl chloride)/chlorinated butyl rubber multilayered composites, J. Appl. Polym. Sci. 132 (2) (2015).

[59] A. Das, D.-Y. Wang, A. Leuteritz, K. Subramaniam, H.C. Greenwell, U. Wagenknecht, G. Heinrich, Preparation of zinc oxide free, transparent rubber nanocomposites using a layered double hydroxide filler, J. Mater. Chem. 21 (20) (2011) 7194–7200.

[60] D. Basu, A. Das, D.-Y. Wang, J.J. George, K.W. Stöckelhuber, R. Boldt, A. Leuteritz, G. Heinrich, Fire-safe and environmentally friendly nanocomposites based on layered double hydroxides and ethylene propylene diene elastomer, RSC Adv. 6 (31) (2016) 26425–26436.

[61] D.-Y. Wang, A. Das, A. Leuteritz, R.N. Mahaling, D. Jehnichen, U. Wagenknecht, G. Heinrich, Structural characteristics and flammability of fire retarding EPDM/layered double hydroxide (LDH) nanocomposites, RSC Adv. 2 (9) (2012) 3927–3933.

[62] J. Wang, L. Xue, B. Zhao, G. Lin, X. Jin, D. Liu, H. Zhu, J. Yang, K. Shang, Flame retardancy, fire behavior, and flame retardant mechanism of intumescent flame retardant EPDM containing ammonium polyphosphate/pentaerythrotol and expandable graphite, Materials 12 (24) (2019) 4035.

[63] Z. Wang, X. Zhang, C. Bao, Q. Wang, Y. Qin, X. Tian, The synergistic effect of aluminum hypophosphide and nanosilica on flame-retarded ethylene-propylene-diene monomer rubber, J. Appl. Polym. Sci. 124 (4) (2012) 3487–3493.

[64] B. Zirnstein, D. Schulze, B. Schartel, The impact of polyaniline in phosphorus flame retardant ethylene-propylene-diene-rubber (EPDM), Thermochim. Acta 673 (2019) 92–104.

[65] L. Wang, J. Jiang, P. Jiang, J. Yu, Synthesis, characteristic of a novel flame retardant containing phosphorus, silicon and its application in ethylene vinyl-acetate copolymer (EVM) rubber, J. Polym. Res. 17 (6) (2010) 891–902.

[66] N.F. Attia, B.K. Saleh, Novel synthesis of renewable and green flame-retardant, antibacterial and reinforcement material for styrene–butadiene rubber nanocomposites, J. Therm. Anal. Calorim. 139 (3) (2019) 1817–1827.

[67] K. Lu, L. Ye, Q. Liang, Y. Li, Selectively located aluminum hydroxide in rubber phase in a TPV: towards to a halogen-free flame retardant thermoplastic elastomer with ultrahigh flexibility, Polym. Compos. 36 (7) (2015) 1258–1265.