University of Southern Queensland

POLYPHOSPHORAMIDES AS HIGHLY EFFECTIVE FIRE RETARDANTS FOR POLYLACTIDE: GREEN SYNTHESES, PROPERTIES AND MECHANISMS

A Thesis submitted by

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For the award of

Doctor of Philosophy

2022

ABSTRACT

Renewable Polylactide (PLA) suffers from a high flammability that limits in its practical applications in many industrial settings. Therefore, it is imperative to develop flame-retarding PLA. Polyphosphoramides have shown a high fire-resistant efficiency in PLA, but nearly all of their existing synthesis methods involve a large volume of toxic solvents. Meanwhile, there has been a lack of in-depth understanding of their modes of actions and how they affect comprehensive properties of PLA. For these reasons, this thesis focuses on developing solvent/catalyst-free synthesis approaches for polyphosphoramides, then unveiling their modes of actions, and then investigating how the physical properties of PLA are impacted by polyphosphoramides. We pioneered developed a green strategy to synthesize three types of polyphosphoramides fire retardants (DM-H, DM-Si and DM-OHn) without use of any solvents and catalysts. DM-H and DM-Si show very high fire-retardant efficiency in PLA, only 2 and 3 wt%, respectively, enable PLA to achieve a desired UL-94 V-0 rating and a high LOI, but reduce its thermal stability. In comparison, DM-OHn makes PLA show both desired flame retardancy and enhanced thermal stability. The polyphosphoramides fire retardants mainly function in the gas phase. Moreover, they have limited impact on the mechanical strength of PLA. This work provides one new eco-benign strategy for synthesizing polyphosphoramides fire retardants and the results and findings of this work will significantly promote the green development of next-generation eco-friendly effective fire retardants and fire-retardant PLA bioplastics, thus enabling PLA to find more applications in industries.

CERTIFICATION OF THESIS

I Jiabing Feng declare that the PhD Thesis entitled Polyphosphoramides as Highly Effective Fire Retardants for Polylactide: Green Synthesis, Property and Mechanism is not more than 100,000 words in length including quotes and exclusive of tables, figures, appendices, bibliography, references, and footnotes. This thesis is the work of Jiabing Feng except where otherwise acknowledged, with the majority of the contribution to the papers presented as a Thesis by Publication undertaken by the Student. The work is original and has not previously been submitted for any other award, except where acknowledged.

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STATEMENT OF CONTRIBUTION

Paper 1:

Jiabing Feng, Xiaodong Xu, Zhiguang Xu, Hongyan Xie, Pingan Song*, Lujuan Li, Guobo Huang and Hao Wang. (2020). One-pot, solvent- and catalyst-free synthesis of polyphosphoramide as an eco-benign and effective flame retardant for poly(lactic acid). *ACS Sustainable Chemistry & Engineering*, *8,* 16612-16623. https://doi.org/10.1021/acssuschemeng.0c05931

The student **Jiabing Feng** contributed 65% to this paper. Collectively Xiaodong Xu, Zhiguang Xu, Hongyan Xie, Pingan Song, Lujuan Li, Guobo Huang and Hao Wang contributed the remainder.

Paper 2:

Jiabing Feng, Zhewen Ma, Zhiguang Xu, Hongyan Xie, Yixia Lu, Christian Maluk, Pingan Song, Serge Bourbigot and Hao Wang. (2022). A Si-containing polyphosphoramide via green chemistry for fire-retardant polylactide with well-preserved mechanical and transparent properties. *Chemical Engineering Journal, 431,* 134259. https://doi.org/10.1016/j.cej.2021.134259

The student **Jiabing Feng** contributed 65% to this paper. Collectively Zhewen Ma, Zhiguang Xu, Hongyan Xie, Yixia Lu, Christian Maluk, Pingan Song, Serge Bourbigot and Hao Wang contributed the remainder.

Paper 3:

Jiabing Feng, Yixia Lu, Hongyan Xie, Zhiguang Xu, Chengfei Cao, Pingan Song, and Hao Wang. Solvent-free synthesis of organic-inorganic polyphosphoramide-halloysite nanohybrids for thermally stable and fire-resistant polylactide. *Green Chemistry.* (Under review)

The student **Jiabing Feng** contributed 60% to this paper. Collectively Yixia Lu, Hongyan Xie, Zhiguang Xu, Chengfei Cao, Pingan Song, and Hao Wang contributed the remainder.

ACKNOWLEDGEMENTS

The Ph.D. program was a very interesting yet tough journey for me, and I believe this experience will benefit my entire life. First, I would like to express gratitude to my supervisory team, Prof. Pingan Song and Prof. Hao Wang who accepted my application of this Ph.D. program. They support me during this whole journey. At the beginning, their profound knowledge and keen insight gave me key inspiration in the topic selection. Then, after I commenced with my experiments, I met many technical issues that confuse me so much. Prof. Pingan Song gave me much lab resource and sent me to other labs to learn how to solve these problems. At the stage of paper writing, he taught me many important academic writing skills including language express and the style for figures display. Prof. Hao Wang provided me much instruction concerning how to think the academic questions in a big perspective. He always helps me to connect the academic program to industrial products. Thanks to their valuable advice, I was able to complete my program successfully.

I would like to acknowledge the financial support received from the USQ International Fees Research Scholarship.

I am so appreciated for the help from Prof. Zhiguang Xu team in Jiaxing University, for helping me with the experiments. Dr. Hongyan Xie and PhD candidate Yixia Lu gave me much instruction and helps during my program.

Finally, I feel so grateful to my family for their support mentally and financially. Each time I felt frustrated by difficulties or obstructions in my program, they would give me consolation and confidence, to help me get out of a predicament and continue my work.

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ABBREVIATIONS

ABS: acrylonitrile-butadiene-styrene

AIP: aluminum diethlyphosphinate

APP: ammonium polyphosphate

ACN: acetonitrile

BATMDS: 1,3-Bis(3-aminopropyl) tetramethyl-disloxane

DCM: dichloromethane

DEE: diethyl ether

DMF: N,N-dimethylformamide

DMMP: dimethyl methylphosphonate

DOPO: 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide

DOX: dioxane

EHC: effective heat of combustion

EP: epoxy

FRs: flame (or fire) retardants

EVA: ethylene-vinyl acetate

GF: glass fiber

HDA: 1,6-diaminohexane

HNTs: halloysite nanotubes

LDPE: low density polyethylene

LLDPE: linear low density polyethylene

LOI: limited oxygen index

OMMT: montmorillonite

PBT: polybutylene terephthalate

PC: polycarbonate

pHRR: peak of heat release rate

PLA: polylactide

POSS: polyhedral oligomeric silsesquioxane

PP: polypropylene

PX: para-xylene

Py-GC/MS: pyrolysis-gas chromatography/mass spectrometry

TCM: trichloromethane

TEA: triethylamine

TGA: thermogravimetric analysis

TG-IR: thermogravimetry-infrared

THF: tetrahydrofuran

THR: total heat release

TL: toluene

TSP: total smoke production

$T_{0.1}$: temperature at 0.1 wt% weight loss

T_5: temperature at 5 wt% weight loss

$T_{\max}$: temperature at maximum weight loss rate

(W)PU: (waterborne) polyurethane

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

The proliferation of polymeric materials in our daily life has significantly improved the quality of life. The polymers, e.g., polyolefin, polyester, polyamide and polyurethane, enable us to make films, clothing, vehicles, and even medical applications, to enrich and reform the human beings' life. Most polymers are derived from petrochemical resources, but petrochemical extraction tends to cause environment concerns (Hillmyer, 2017), which impeding the sustainable development of materials. As a result, polymers made from biomass are increasingly favored due to their nature of sustainability (e.g., renewability and eco-benign manufacturing).

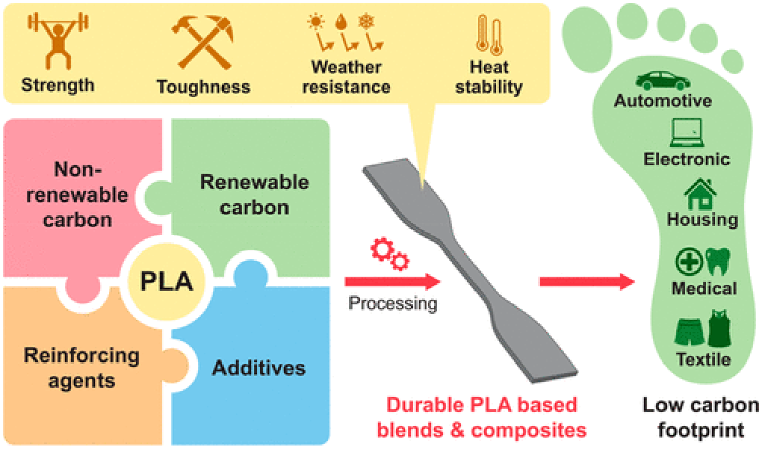


Figure 1.1 Schematic representation of features and applications of PLA (Tripathi et al., 2021).

Polylactide (PLA) offers a good example of transformation from sugar to biopolymers. PLA is produced via the fermentation of starch to lactic acid, then followed by the synthesis of lactide and its subsequent polymerization. The first attempt to synthesize PLA can date back to 1845 when Pelouze used L-lactic acid as raw material, but only leading to low molecular weight (Carothers et al., 1932). Afterwards, ring-opening polymerization of lactide facilitated the realization of high molecular weight PLA (Sosnowski et al., 1996). Currently, the relatively mature fabrication process makes PLA commercially competitive in the market.

In addition to the renewability, the biodegradability of PLA is attractive, and it enables PLA to be used in applications such as plastic bags and disposable flatware. Degradation of PLA can occur in biological environment such as soil or compost. The two main stage during the degradation are hydrolysis and enzymolysis. Firstly, water diffuses into the polymer and this leads to random non-enzymatic chain scissions of ester group. The cleavage of chains results in the formation of oligomers that can be absorbed by microorganisms (Fukushima et al., 2009). The biodegradable feature brought by PLA is promising to address the concern of white pollution caused by traditional petrochemicals-based polymers such as polyethylene and polystyrene.

Additionally, the excellent mechanical performance, particularly the Young's modulus (~3 GPa), offers PLA opportunities to take place of traditional engineering plastics (e.g., polyethylene terephthalate and polyamide 6) used in automobiles and electric appliances (Armentano et al., 2013). Another advantage of PLA is ease of process. PLA can be fabricated by variety of transformation methods including extrusion and injection moulding, stretch blow moulding, foaming and fiber spinning, as well as 3D printing. More excitingly, PLA is capable of being reprocessed due to its thermoplasticity, which makes the recycling of PLA possible. All these features make PLA a promising alternative to petroleum-based polymer, to foster and encourage a sustainable society.

Unfortunately, PLA still suffers from some drawbacks, including inherent flammability, poor toughness, low thermal deformation temperature, and low degree of crystallization. Among these shortcomings, the intrinsic high flammability of PLA significantly limits its industrial applications, especially in the sectors where stringent fire retardancy is required (Feng et al., 2017), such as in textile, automobile, and electronics industries. Pure PLA is quite easy to be ignited with a low limiting oxygen index of only ~ 19 vol% and have a tendency to drip when burning. Therefore, it would be very dangerous for PLA to be applied in household goods such as textile furniture and appliances. It will also risk the fire safety of vehicles or buildings if unmodified PLA is used in these areas. For this reason, it is imperative to develop effective fire-retarding strategies for creating fire-retardant PLA without compromising its other physical properties, to ensure its safe application in the industrial settings.

1.2 RESEARCH OBJECTIVE AND SCOPE

Phosphoramides have been demonstrated to be highly effective in enhancing the fire retardancy of PLA. However, the existing chemical synthesis involves a large volume of toxic organic solvents such as dichloromethane (DCM), acetonitrile (ACN), tetrahydrofuran (THF), and triethylamine (TEA). substantially impairing the sustainability of phosphoramides fire retardants. In addition, there is a lack of full understanding of their modes of actions in PLA and how they affect the comprehensive properties of the final fire-retardant PLA. As a result, this thesis aims to fill these knowledge gaps and three specifical objectives are: **(a)** to develop solvent/catalyst-free synthesis methods for polyphosphoramides; **(b)** to uncover their detailed modes of actions in PLA; and **(c)** to investigate how the physical properties (e.g., thermal stability, mechanical performances etc.) of PLA are impacted by polyphosphoramides.

1.3 THESIS OUTLINE

This thesis is structured as follows:

Chapter 1

This chapter briefly presents the research background, gaps and objectives and it highlights significant of this thesis.

Chapter 2

This chapter reviews the recent advances in the development of (poly)phosphoramides flame retardants, as well as their effect on polymeric materials. Then knowledge gaps in PLA/phosphoramides fire-retarding system is given and finally proposes the research aim in detail.

Chapter 3

In this chapter, a solvent-free approach for synthesis of a polyphosphoramide (DM-H) was developed and DM-H exhibits excellent fire retardancy in PLA, with detailed fire-retarding mechanisms and mechanical properties discussed. This work pioneeringly opens up a new pathway for the green synthesis of polyphosphoramides that can improve the fire safety of PLA.

Chapter 4

This chapter reported a Si-containing polyphosphoramide (DM-Si) that synthesized with no solvents. DM-Si presents higher fire-retarding efficiency than DM-H in PLA. A deep investigation into its thermal properties, as well as thermal stability was undertaken. This work offers an eco-benign yet facile approach for the synthesis of efficient flame retardants for bioplastics with balanced mechanical strength and transparency.

Chapter 5

This chapter developed a series of organic-inorganic hybridized polyphosphoramides (DM-OHn). DM-OH16 shows exceptional fire retardancy in PLA, and also improves thermal stability of PLA. This work provides a green strategy for the design of organic-inorganic polyphosphoramides nanohybrids for creating fire-retarding PLA with improved thermal stability.

Chapter 6

This chapter presents the main findings and contributions of this thesis, and also highlights an outlook for future directions of this research field.

CHAPTER 2: LITERATURE REVIEW

There exist three approaches to achieve fire retardancy in polymers, generally known as the 'additive' and the 'reactive' type (Lu and Hamerton, 2002), as well as the surface coating treatment. The reactive flame retardants (FRs) involve chemical modification of existing polymers via copolymerization with a fire-retarding unit, but this chemical bonding approach lacks sufficient versatility in manufacturing and is uneconomical for a product (Morgan, 2018). Flame-retardant coatings also have an issue concerning the poor adhesion between substrates and coatings. In contrast, incorporation of fire-retarding additives via physical blending is economically competitive and easy in processing. Therefore, addition of fire retardants (FRs) by melt blending is eco-friendly yet economical for PLA to improve its fire safety.

Although brominated chemicals are effective on enhancing the fire retardancy of polymers, the environmental and health risks of them make them confronted with more and more legislative banning. For this reason, phosphorus (P)-containing FRs have been widely explored and even been available on the market, owing to their high efficiency and low toxicity. It is generally accepted that P-based FRs can work in both the gas and condensed phase through physical and chemical mechanism. The combustion of plastics always leads to formation of radical species such as H· and OH· which provide the energy maintaining a fire. In the gas phase, phosphorus/oxygen (P/O)-containing radicals (PO·, PO_2· and HPO·) are able to trap the high-energy radicals (H· and OH·), leading to interference of radical chain reactions (see **Figure 2.1**) and termination of a flame (Dasari et al., 2013).

In the condensed phase, P-containing agents act as char promoters to accelerate char formation by dehydration and carbonization. Then, the accumulation of char protects underlying polymers from flames by isolating oxygen and reducing heat transfer, as well as blocking diffusion of gaseous products (Bauer et al., 2017).

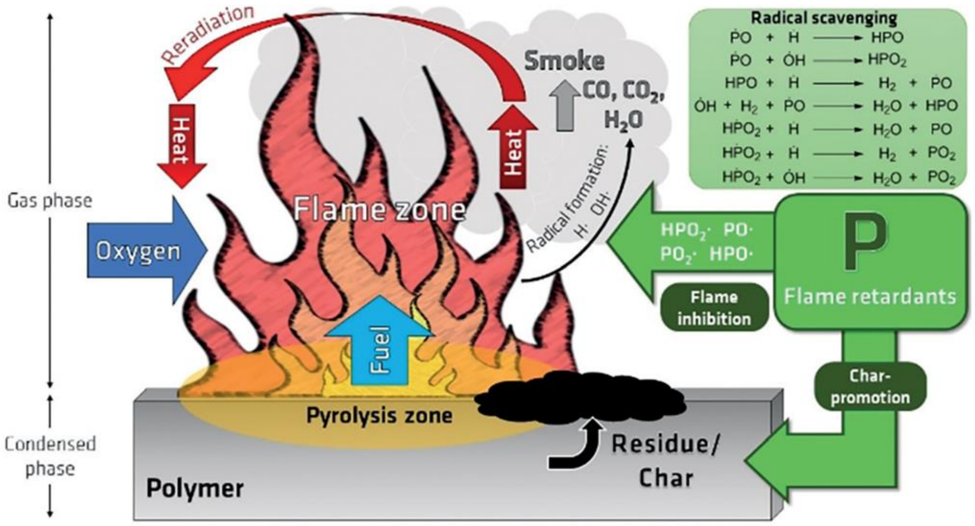


Figure 2.1. Flame-retarding Mechanism of phosphorus-based fire retardants (Velencoso et al., 2018).

To date, various P-based FRs from inorganic phosphorus (e.g., red phosphorus) to organic phosphorus including phosphates (Jing et al., 2017) and phosphonates (Zhang et al., 2021, Mauldin et al., 2014) were applied in PLA materials to reach improved fire safety. Furthermore, the P element is able to exhibit synergistic effect when combining with other heteroatoms, for instance, nitrogen (N), silicon (Si) and sulfur (S). Among them, P/N synergistic flame-retarding systems have attracted more attention. Different with the radicals-quenching action, N-containing chemicals principally play a key role in diluting oxygen/fuels via releasing nonflammable gases (e.g., NH_3, NO, or NO_2). Another contribution of N is in some cases it can promote the crosslinking of polymer chain and encourage the retention of phosphorus in the condensed phase, leading to thermally stable char layers (Morgan, 2018). As a result, P/N FRs are expected to show better fire-resistant properties due to their multiply actions.

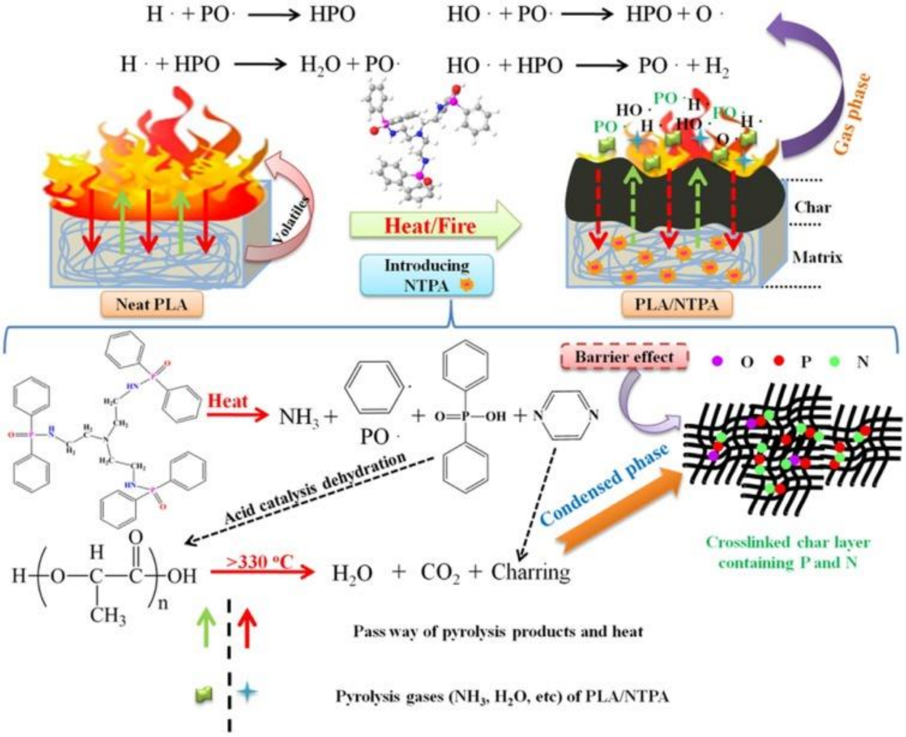


Figure 2.2. A typical flame-retarding mechanism of P/N synergistic (Liu et al., 2021).

A wide variety of P/N-containing organophosphorus FRs have been developed up to now, and many of them help polymers (including PLA) to achieve a desirable fire retardancy. For example, an ammonium polyphosphate (APP)-based intumescent flame retardant (named as A-A), endows PLA with a (limiting oxygen index) LOI of 30.5% and a UL-94 vertical burning V-0 rating when its loading reaches 15 wt%. Another case of APP is the design of core-shell structures, and they (a 10 wt% loading) bring PLA a V-0 rating in UL-94 testing and an LOI value of ~30% (Jin et al., 2019, Zhang et al., 2020). In addition, phosphazene-based branched FRs were used in PLA, with good fire-retarding performance shown in results (Chen et al., 2017a, Chen et al., 2017b). Despite the encouraging flame retardancy achieved by these foregoing P/N FRs, their fire-retarding efficiency is not high enough, and a high loading level tends to cause acute deterioration in physical properties of PLA bulk. Therefore, it still remains a challenge for PLA to achieve a balance between fire safety and mechanical performance.

2.1 PROERTIES CHARACTERIZATIONS

This review mainly focuses on the fire-retardant properties of phosphoramides-containing polymers but with other physical properties including thermal stability and mechanical performance taken into account. For this reason, it is necessary to introduce relevant properties characterizations.

2.11 FIRE-RETARDANT PROPERTIES CHARACTERIZATIONS

Many national and international regulatory bodies have established polymeric materials flammability testing method standards to assess the major fire properties: limiting oxygen index (LOI), Underwriters Laboratories (UL)-94 rating and heat release performance.

The LOI tester measures the minimum oxygen concentration required to support candle-like downward flame combustion. Usually, an LOI > 26% is viewed as the qualification of self-extinguishing. For the LOI test, samples with a dimension of 100×65×3 mm^3 are commonly used. Then, a flame is applied to the specimen top. If the specimen does not ignite, rise the concentration of oxygen and test again until the sample is ignited. The LOI value is the limiting concentration of oxygen when the specimen self-extinguishes in less than 3 min with less than 5 cm of the consumed sample. Details regarding the LOI test is advised to refer to International Organization for Standardization (ISO) 4589 or American Society for Testing and Materials (ASTM) D2863. This testing is suitable as a semi-qualitative indicator of the effectiveness of fire retardants during development stage.

UL-94 testing examines the tendency of a polymer or composite to either self-extinguish or spread the flame upon the sample is ignited. Usually, a sample size of 125×13×3.2 (or 1.6) mm^3 is preferred. A vertical or horizontal burn test is performed by a UL-94 test chamber and the flammability is rated from V-2 to V-0, or HBF to HF-1. For example, to achieve the best fire-retarding rating (V-0), the burning of a specimen must stop within 10 s after two applications of a 10 s flame, with no flaming dripping. Details testing methods and rating classification are suggested to refer to ASTM D3801.

Cone calorimetry is carried out by a cone calorimeter according to the standard ISO 5660 at a varied heat flux (35 or 50 kW/m2 is more preferred). The sample dimension applied usually is 100×100×3 mm^3. Many heat release parameters including peak heat release rate (pHRR) and total heat release (THR) and smoke production index such as total smoke production (TSP) and total smoke release (TSR) can be obtained via this testing.

2.12 THERMAL PROPERTIES CHARACTERIZATIONS

Thermal stability of polymers can be measured by thermogravimetric analysis (TGA) in which the mass of a sample is measured over time as the temperature rises. For evaluating the thermal properties of a fire retardant or its polymeric composites, generally, an approximate 5~10 mg sample is heated from 40 to 1000 °C with a heating rate of 10 or 20 °C/min. In addition, it is widely accepted that regarding the temperature at 5% weight loss (T_5) as the initial temperature to decompose. Also, the temperature at maximum decomposition rate (T_{max}) is a key parameter. Moreover, char yield (the weight percentage of residue relative to initial sample weight) at a particular temperature is often presented. Detailed testing methods can be obtained via ISO 11358.

2.13 MECHANICAL PROPERTIES CHARACTERIZATIONS

Mechanical performance (e.g., tensile strength, Young's modulus, flexural strength and impact strength) is necessary to be characterized given the practical use of a fire-retarding polymer. For tensile testing, an electronic universal testing machine is applied and a varied of crosshead speed are chosen (e.g., 5, 10, 20, or 50 mm/min). The tests results include tensile (or break) strength, elongation at break, Young's modulus etc. Detailed testing methods are advised to refer to ISO 527 or ASTM D638. The flexural and impact properties are also key index when assessing the mechanical performance of a material, and their detailed testing methods can refer to ISO 178 and ISO 179.

2.2 PHOSPGORAMIDES FIRE RETARDANTS

Phosphoramides, a variety of P(O)−N compounds that combine P and N covalently. This species has higher thermal stability, lower volatility and higher viscosity (Bauer et al., 2017). These merits make phosphoramides easier to remain in polymers during combustion, thus leading to more char residues. More importantly, phosphoramides chemicals were found highly efficient when used in PLA, which directs a promising way to enhance the fire safety of PLA but largely avoid the degradation of mechanical strength.

In general, phosphoramides are synthesized through nucleophilic substitution reactions between phosphonyl chlorides (or phosphite ester) and amino compounds. A wide variety of phosphoramides can be designed by tailoring their structures and tuning the molar ratios of starting materials. Generally, they can be categorized into three major types: small-molecular, oligomeric, and branched according to the magnitude of their molecular weight and their structures. This chapter will mainly focus on their chemical structures and discuss their flame-retardant effectiveness on typical polymers, including PLA, epoxy (EP), polyurethane (PU), etc.

2.2.1 SMALL-MOLECULAR PHOSPHORAMIDES

Figure 2.3 displays various small-molecular phosphoramides used in EP resin, and solvents and catalysts involved in their synthesis are given in **Table 2.1**. Two phosphoramides, DPPIO (S1) and DPIPP (S2), were synthesized and then their flame retardancy in EP were compared (Xu et al., 2018). The results show 15 wt% DPPIO enables EP resin to pass a UL-94 V-0 rating (at 1.6 mm thickness) and a high LOI of 38.0%, whereas EP containing 15 wt% DPIPP only achieves a V-1 rating and an LOI of 31.5%. In addition, both the flame-retardant EP samples exhibit reduced pHRR values (~430 kW/m^2), but DPIPP shows better smoke suppression properties in EP, as reflected by the lower TSP value (13.3 m^2·m^{-2}). Also, in TGA testing, both DPPIO/EP and DPIPP/EP show higher thermal stability and char yields, as well as lower a degradation rate, than the EP control sample. The authors ascribed the difference to their different dominant flame-retardant actions. For DPPIO, it acts more in the gas phase, and the action leads to a faster fire-extinguishing, but its counterpart shows a main effect in the condensed phase via promoting charring ability of EP.

Another two similar phosphoramides D-AZ (S3) (Jian et al., 2017) and DOP-ABZ (S4) (Jian et al., 2019) were synthesized by Jian et al. The results show with 5 wt% D-AZ, EP resin achieves a UL-94 V-0 rating and a high LOI of 34.7%. More excitingly, the mechanical performance of EP improves when D-AZ loading increases to 7.5 wt%. For example, the tensile and flexural strength of this EP sample reach 107 MPa and 112 MPa, respectively (compared with 90 MPa and 85 MPa of the EP control sample). In contrast, for DOP-ABZ, its efficiency is lower than D-AZ, and it needs a 17.5 wt% loading level to make EP pass a V-0 rating in UL-94 testing. Also, the LOI value only rises to 27.5% from 25.2%. Moreover, the mechanical strength of EP fire-retarding composites significantly improves. For example, the EP2 sample presents increased tensile strength and flexural strength of 81 and of 119 MPa respectively, relative to 71 and 98 MPa of pure EP. However, the authors did not summary the two investigation and give an underlying reason for the large difference in their efficiency, but it might be associated with their different dominant actions.

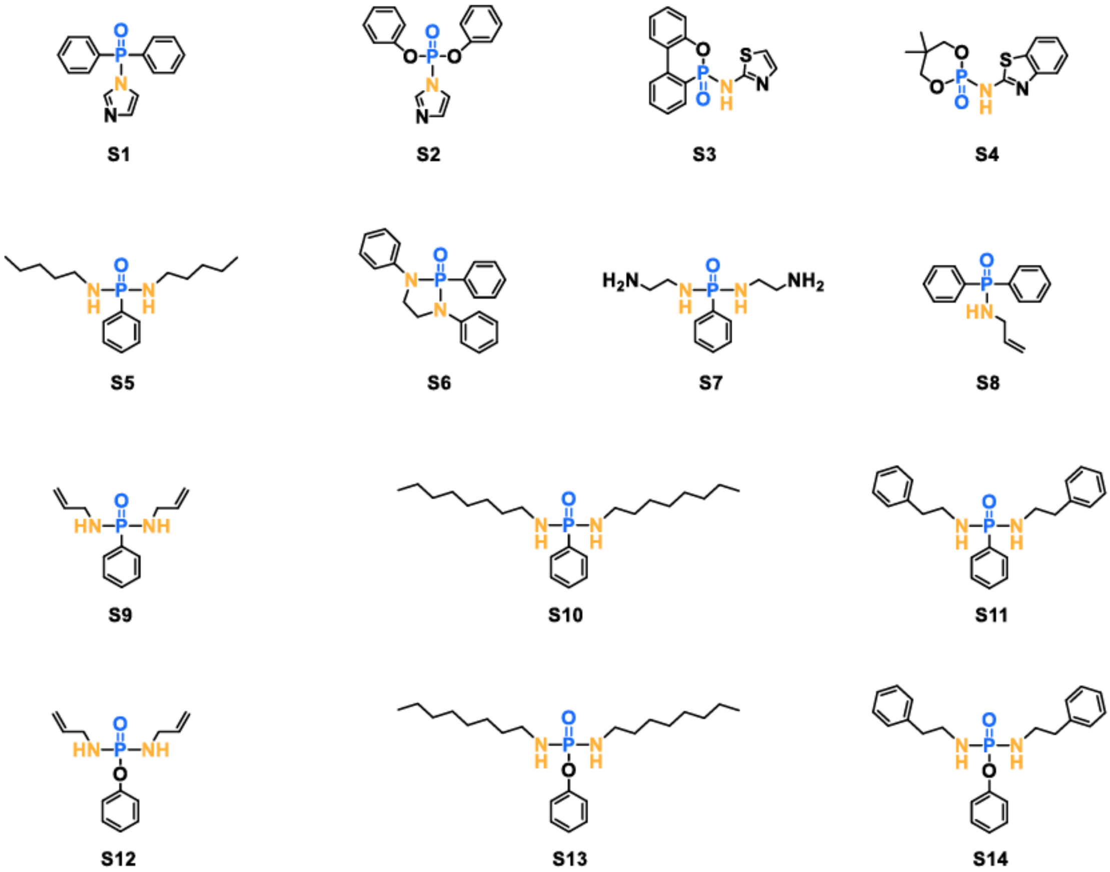


Figure 2.3. Chemical structures of small-molecular phosphoramides used in Epoxy resin.

P-MA (S5) was reported (Zhao et al., 2017d), and the addition of this FR (12 wt%) endows EP with a UL-94 V-0 rating and a high LOI of 36%. Meanwhile, the pHRR value decreases by 66% compared to that of pure EP, which can be ascribed to the barrier effect of its char layers. Li and co-workers prepared a phosphoramide named TPDPO (S6), and this FR shows good fire retardancy in epoxy resin. For instance, addition of 8 wt% TPDPO helps EP to achieve a UL-94 V-0 rating and an LOI of 33%. The TGA results show the addition of TPDPO notably decreases the initial temperature to decompose ($T_{5\%}$) but increase the char yields. Moreover, the researchers believed that the enhanced dehydration process supported by the appearance of C=C groups in char should be responsible for the improved fire retardancy (Li et al., 2018).

Phosphoramides have been explored as crosslinking agents for epoxy coatings. For instance, PPEDD (S7) (Jirasutsakul et al., 2013) gives EP an LOI value of 27% with a high char yield in N_2 atmosphere when the phosphorus content in EP is 2 wt%. Another example is APA (S8) (Çakmakçı, 2017) that combines with POSS in an epoxy acrylate coating. The results show the coating with 20 wt% APA has an LOI of 27 % but fails to pass the UL-94 testing.

A series of phosphoramides (S9~14) were designed by Zhao et al. and their flame-retardant mechanisms were also investigated. The FP species (S9~11) show better fire retardancy than the FPO compounds (S12~14) in EP. Addition of only 5 wt% FP1 (S9) enables EP to achieve a UL-94 V-0 rating and an LOI of 31%. For the EP sample with 7.5 wt% FP2 (S12), its LOI reaches 37%. By contrast, the FPO agents fails to make EP pass a V-0 rating even the loading level reaches 30 wt%. By TG-IR detection and char analysis, the authors believed that both FP1 and FPO1 (S12) act in the same way in the condensed phase, and the foam-like char residues block the heat and gaseous products transfer between inner and outer parts of the EP matrix. However, the charring rate of FP1 is faster than FPO1, and in the gas phase, the former shows efficient flame inhibition effect whereas FPO1 does not. These reasons lead to the better flame retardancy of FP than FPO. More excitingly, the addition of the two FRs does not largely compromise the mechanical strength of EP, and its rigidity even can be enhanced, as evidenced by increased Young’s modulus (Zhao et al., 2016).

In addition to EP, phosphoramides can be used to treat cotton fabrics, to improve their fire-resistant properties. Some important compounds are displayed in **Figure 2.4**. Gaan et al. developed a variety of phosphoramides including S15~17, and when P content (add-on value) reaches 4 wt%, the LOI value rises to ~30% for cotton treated by S15, to ~27% for S16 and 17 (Gaan et al., 2009).

A similar phosphoramide, MHP (S18), was synthesized (Nguyen et al., 2013). The treated fabric with 19 wt% (add-on value) MHP shows an LOI of 37.2% and a rate of flame spread of 0.8 mm/s, as well as a reduced pHRR value of 128.3 w/g (decreased by 40% compared to the control sample). The authors also designed two compounds TEPP (S19) and DEPP (S20), using piperazine and its derivatives, respectively. (Nguyen et al., 2014). TGA results in nitrogen atmosphere indicate that the FR-treated fabrics generate a higher carbonaceous residue but lower onset temperature to degrade compared to the control sample. In addition to the increased LOI (31.0% for DEPP-18 and 33.1% for TEPP-19, and the value of control sample is 18.4%), their pHRR values drop by 35% and 45%, respectively. The authors concluded that both phosphoramides are promising FRs for cotton textiles, but TEPP is superior to DEPP given its lower burning rate and combustion heat.

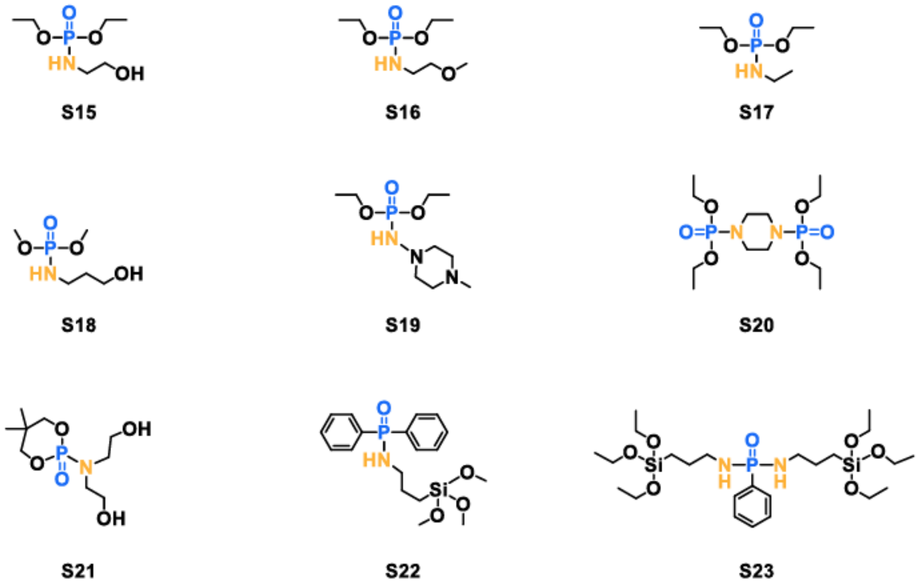


Figure 2.4. Chemical structures of small-molecular phosphoramides for treating cotton fabrics.

Zhao et al. reported a compound (S21) that presents good flame retardancy in cotton. The cotton-5 sample (add-on value is 25.2%) has an LOI of 29.3% and a flame spread rate of 10 mm/s, in addition to a pHRR value of 93 kW/m^2 (decreases by 40% relative to neat cotton). By analysis of gaseous products and char residues, the authors believe this phosphoramide can promote cotton to form phosphorus-rich char in the condensed phase. TGA results also support this view as reflected by the high residue yield (can achieve ~35% at 700 °C) of FR-treated cotton. In the gas phase, the compound has good inhibition of fire and leads to less flammable gases (Zhao et al., 2017b).

Silane coupling agents were also used to prepare phosphoramides. Yang and co-workers synthesized a phosphoramide (S22, marked as FR-0). After treated by FR-0, the LOI of fabric rises to 33.2% from 18.3% (untreated). But this flame-retardant coating is semi-durable for cotton given its LOI value reduces after home laundering (Yang et al., 2012). Another example is PPD-PTES (S23). The treated cotton (treat time of 5, 10 and 20 min) fails to stop fire but leaves a lot of char residues after combustion. In the case of the cotton-30 min, the flame extinguishes quickly after a removal of the ignitor. More excitingly, this FR not only make cotton obtain more residue, but also improves its thermal stability. For example, T_5 of the sample cotton-30min considerably increases to 270 from 241 °C of the control sample. Furthermore, this sample shows a low pHRR value of 129 W/g, a 42% reduction compared to pure cotton. The improved fire retardancy can be ascribed to the formation of thermally stable char preventing the underlying fabrics from heat and flame and blocking the release of flammable gases from the cotton (Liu et al., 2016).

Phosphoramides are widely investigated in PU materials (see **Figure 2.5**). Gaan and co-workers developed flame-retardant PU foams by means of phosphoramides (S24~26) based on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). According the UL-94 HBF testing, EDAB-DOPO (S26) achieves the best result (an HBF-1 rating) with a loading of 10 wt% (relative to polyol). Also, this sample shows the lowest pHRR value of 275 kW/m^2. The authors pointed out these DOPO-based phosphoramides primarily act in the gas phase but exhibit limited condensed-phase action. For EDAB-DOPO, its better thermal stability leads to longer gas-phase activity during the entire burning process (Gaan et al., 2015).

PNMPD (S27) was incorporated into waterborne PU (WPU) preparation. The results show the sample PNWPU-12 (with 12 wt% PNMPD) achieves a V-0 rating in UL-94 testing and an LOI of 27.2%. This is an obvious improvement compared to the control WPU (no rating and an LOI of 18.5%). Additionally, the cone calorimetry presents exciting results. For example, with increasing PNMPD content (3~12 wt%), the pHRR tends to continuously decrease (from 1059 kW/m^2 of WPU, to 854 kW/m^2 of PNWPU-6, then to 586 kW/m^2 of PNWPU-12). For PNWPU-12, its THR value reduces to 43.6 MJ/m^2 that is only 61% relative to the WPU sample. Its TSR value also shows a visible reduction from 482 m^2/m^2 to 308 m^2/m^2. A mechanism for the improved fire retardancy was proposed: the conjugation of PNMPD accelerates its degradation at a lower temperature, which promotes the formation of phosphorus-rich chars. Then the carbonaceous char layers acts as a barrier for PU bulk to block the heat conduction, and oxygen/fuel mixtures transfer (Zhang et al., 2016).

Zhao et al. synthesized DEPA (S28) and then combined it with expanded graphite (EG) to enhance fire safety of rigid PU foam. For the sample RPUF/EG8/DEPA16, its LOI rises to 30.4%, and there is a 56% reduction in its pHRR value compared to pure PU foam. Although there is a reduction in thermal stability of PU foams, their char yield increases. The authors believed that DEPA primally act in the gas phase via releasing radical scavenger (PO·), and in the condensed phase, protective char layers are formed due to the expandable effect of EG and phosphorus-rich residues (Zhao et al., 2017a).

Another study investigated the effect of DTP (S29) and EG on the fire-retarding properties of rigid PU foam. The PU sample containing 8% EG and 16% DTP, firstly shows an increased LOI value (30.2%), and then presents a drop in its pHRR value (reduces by 40%). TGA results support an increase in char residue from 11.4 to 23.1 wt%. The authors claimed the good flame retardancy is a result of a barrier effect formed by EG and phosphorus-rich chars (Liu et al., 2018).

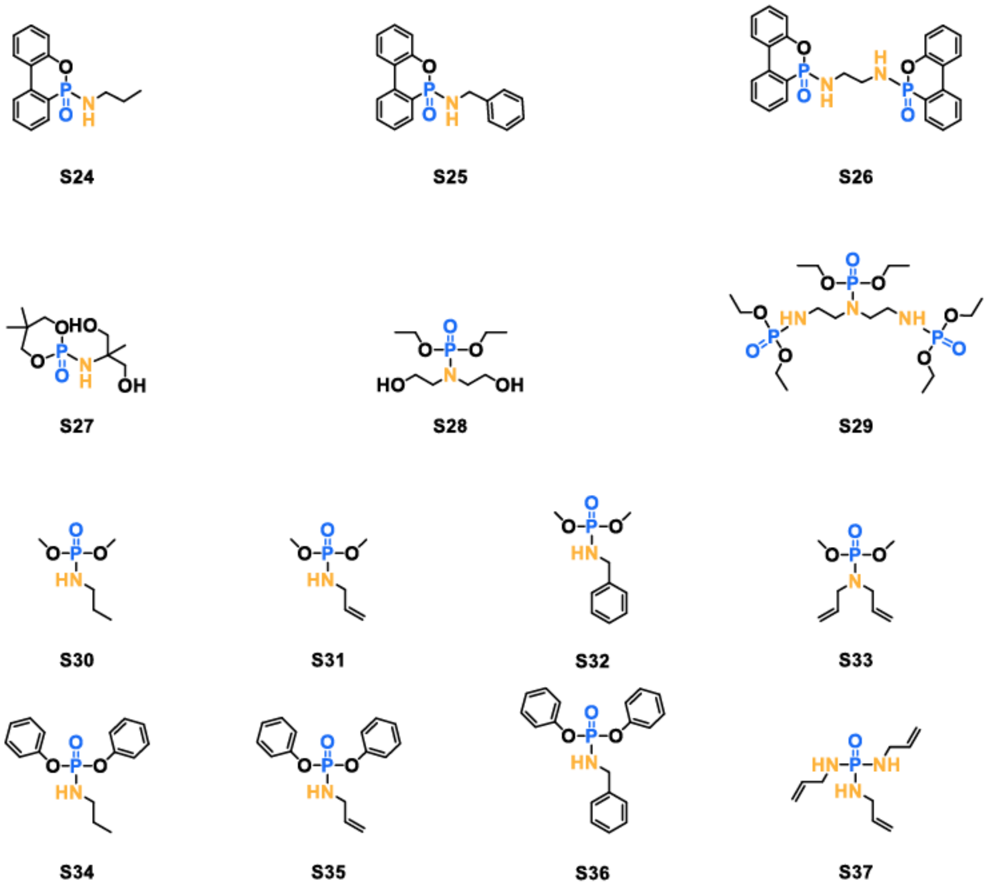


Figure 2.5. Chemical structures of small-molecular phosphoramides used in polyurethane.

In 2013, Gaan' group designed a series of phosphoramides (see S30~37 in **Figure 2.5**) by tunning the phosphite and amino-containing compounds (Neisius et al., 2013). Among them, only DMAPR (S31) makes PU foam achieve an HF1 rating in UL-94 HB testing at a 10 wt% loading level, with a slightly increased LOI value (23.9%). Other phosphoramides such as DMPPR (S34), DMBPR (S32), DPAPR (S35) and DMDAPR (S33) bring PU foam only an HF2 rating. The higher phosphorus content is believed to account for the better fire-retarding performance of methyl ester FRs than analogous phenyl ester derivatives in PU foam at an equal loading level.

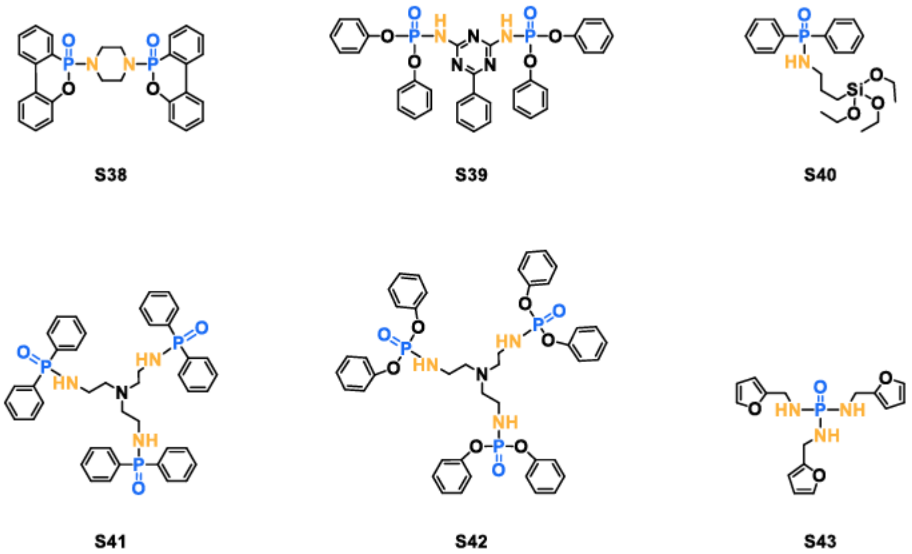


Figure 2.6. Chemical structures of small-molecular phosphoramides used in PC (S38), ABS (S39), PBT (S40). PLA (S41~43).

A phosphoramide named DPZ (see S38 in **Figure 2.6**) was prepared, and it (10 wt% loading) enables polycarbonate (PC) resin to achieve a UL-94 V-0 rating (Liu and Yao, 2017). Also, phosphoramides shows improved but limited flame retardancy in acrylonitrile-butadiene-styrene (ABS) resin. For example, DPCPB (S39) was developed, and the ABS with 25 wt% DPCPB exhibits an LOI of 24.7% compared to 18.1% for pure ABS, but it only pass a UL-94 V-2 rating, and also its initial temperature of thermal decomposition clearly decreases from 330 to 250 °C (Mo et al., 2018). For polybutylene terephthalate/glass fiber (PBT/GF) composites, after the GF was treated by P-APTES (S40), the LOI of the composite shows a rise to 25.5%. When combined with 15 wt% aluminum phosphinate (AIP), the resulting PBT composite owns not only a high LOI of 33%, but also a UL-94 V-0 rating (Yang et al., 2017).

Phosphoramides have a high fire-retarding efficiency in PLA. Only 0.3 wt% P-AA (same structure with S9 in **Figure 2.3**) enables PLA to achieve a UL-94 V-0 rating (3.2 mm thickness) and an LOI of 25.5%. For a 1.6 mm thickness level, it needs 1 wt% to help PLA to pass the V-0 rating, along with a high LOI of 29.6%. The extremely addition level makes the mechanical properties well preserved. (Zhao et al., 2015). In comparison, it requires 1 wt% PO-AA (same structure with S12) for PLA to reach a V-0 rating (3.2 mm thickness), and 2 wt% for a 1.6 thickness level. Meanwhile, Young's modulus slightly rises upon addition of 2 wt% PO-AA. (Zhao et al., 2015). Although the authors ascribed the improved fire retardancy to the actions in the gas phase, they did not analyze the reason for the different efficiency between the two similar phosphoramides. Given that there is a same trend when they used in EP, thus, it can be assumed that P-AA shows more actions than PO-AA in the gas phase, leading to a better flame inhibition effect.

Lu and co-workers synthesized a FR named as NTPA (S41), and the results show the PLA with 2.5 wt% NTPA is able to achieve a UL-94 V-0 rating and an LOI of 28.5% (Liu et al., 2021).Excitingly, this fire-retarding PLA sample also presents a well-preserved tensile strength of 58.3 MPa relative to 60.3 MPa of pure PLA. The authors proposed a flame-retardant mechanism mainly concerning radicals trapping and inert gases releasing. Although they mentioned the improved charring ability for flame-retardant PLA, the actions in the condensed phase should not be obvious given the very limited char residues.

Table 2.1. Synthesis information for small-molecular phosphoramides

FRs	Solvent/Catalyst	Ref.
S1-3	DCM/TEA	Xu et al., 2018; Jian et al., 2017
S4, S27	ACN/TEA	Jian et al., 2019; Zhang et al., 2016
S5	TL/TEA	Li et al., 2018
S6, S9-14	DEE/TEA	Zhao et al., 2017d; Zhao et al., 2016
S7, S22	THF [a]	Jirasutsakul et al., 2013; Yang et al., 2012
S8, S15-19, S28-37, S39-40, S42	THF/TEA	Çakmakçı, 2017; Gaan et al., 2009; Nguyen et al., 2013; Nguyen et al., 2014; Zhao et al., 2017a; Liu et al., 2018; Neisius et al., 2013; Mo et al., 2018; Yang et al., 2017; Tawiah et al., 2019
S20	ACN/ K_2CO_3	Nguyen et al., 2014
S21	AC/TEA	Zhao et al., 2017b
S23	DEE [a]	Liu et al., 2016
S24-26, S38	DCM/TEA	Gaan et al., 2015; Liu and Yao, 2017
S41, S43	TCM/TEA	Liu et al., 2021; Sun et al., 2019

[a] Only THF or DEE used as a solvent, no catalysts involve.

By comparison, HNETP (S42) exhibits better fire-resistant performance than NTPA. Firstly, it only needs 1% to make PLA achieve a UL-94 V-0 rating. Furthermore, this FR (a 3 wt% loading) enables PLA to reduce its pHRR and THR value by ~50% and~ 43%, which is caused by its high char yield (as high as 15.2 wt%). The TGA results exhibit that the char yields obviously increase upon the addition of HNETP, although the all T_5 values of flame-retardant PLA samples reduce. The authors concluded that the non-flammable P/N network generates into a dense char layer in the condensed phase, resulting in a char layer network that shields the spread of flammable volatiles (Tawiah et al., 2019).

Another phosphoramide for PLA is POCFA (S43). Only 2 wt % POCFA brings PLA a UL-94 V-0 rating and an LOI of 29.6%. It did not show much effect on heat release in cone calorimetry, and by analysis of gaseous pyrolysis products, the authors believed the radicals quenching effect in the gas phase should be responsible for the improved anti-ignition ability and extinguishing performance. The T_5 decreases upon the addition of POCFA, indicating a lower thermal stability of fire-retarding PLA composites, but their char yields increase (up to 3.8 wt%). But the tensile modulus is well preserved and even the tensile strength shows an increase by 7 MPa for the PLA sample with 2 wt%. (Sun et al., 2019).

In summary, small-molecular phosphoramides exhibit the versatility in various polymer matrixes including EP, cotton, PU and PLA. Particularly for PLA, these agents are extremely highly efficient to help PLA to achieve excellent fire retardancy even at a 1 wt% loading level. Thus, this makes them as suitable FRs for PLA materials. But most FRs tend to decrease the onset temperature or thermal decomposition, this will impair the thermal stability of polymer matrices. Also, the deterioration of mechanical performance should be noticed.

2.2.2 MACROMOLECULAR PHOSPHORAMIDES

It is well known that small molecules can be released from a polymer matrix over time (Morgan, 2018). This leach-out problem will lead to degradation in physical properties of the polymers. For this issue, many researchers focus on developing macromolecular phosphoramides to avoid the migration of flame-retardant additives.

In 2011, Tai et al. synthesized three polyphosphoramides (see M1~3 in **Figure 2.7**) containing similar aromatic structures. The TGA results present that all of them are thermally stable both in nitrogen or air atmosphere. Take PDSPD (M2) in N_2 as an example, its $T_{0.1}$ (the temperature at 0.1 wt% weight loss) reaches as high as 366 °C, and also it shows a 47 wt% char yield. However, PDSPD shows a sharp peak in its HRR curve, making its pHRR value (814 W/g) much higher than PDMPD (M1, 114 W/g) and PDEPD (M3,92 W/g). The researchers ascribed the high combustion intensity of PDSPD to its flaky char with small pores caused by larger amounts of volatiles in a short time during combustion. As for PDEPD, a honeycomb-like char can be seen and also it exhibits a more compact and smooth morphology when compared to the other samples. As a result, the authors demonstrated the low flammability of polyphosphoramides, and claimed that, PDMPD and PDEPD potentially can be used as FRs for polymeric materials (Tai et al., 2011).

Then, Zhao and co-workers designed another three polyphosphoramides (M4~6) that are very similar with M1~3 but replace P−O with P−C (Zhao et al., 2017c). The researchers applied them (at a 15 wt% loading) in epoxy, and then compared their performance on EP resin. The combustion testing shows the EP samples containing POS (M5) and POA (M6) achieve a UL-94 V-0 rating, whereas the sample with POM (M4) only passes a V-1 rating. All three EP samples have improvement in LOI values (~29%), but this is not significant given the original value of ~25%. In cone calorimetry results, EP/15%POS presents the lowest pHRR of 462 kW/m^2 that is only half of the value (944 kW/m^2) of pure EP. Other two EP samples show slightly higher pHRR values (~500 kW/m^2) than EP/POS. Element analysis of the char proves the polyphosphoramides promote the char-forming of EP in the condensed phase. Also, the phosphorus-containing fragment can be detected in the gas phase, indicating a flame inhibition effect. Due to the synergistic effect between the heteroatom and P, POS and POA show better fire retardancy than POM. At last, the authors mentioned that the polyphosphoramides might promote a design of new EP composites with high flame retardancy for future application. However, all fire-retarding EP samples show distinct reduction in thermal stability, as evidenced by the decrease in T_5. Thus, the thermal stability of EP resin should be balanced when improving its fire retardancy.

A Boron-containing polyphosphoramide (M7, named as PPSPSDB) was prepared by Ba et al. Despite the molecular weight information was not given, it shows synergistic effect with APP, and endow linear low density polyethylene (LLDPE) with enhanced fire resistance. For instance, the LLDPE sample with 20 wt% APP and 10 wt% PPSPSDB is able to pass a UL-94 V-0 rating and show an LOI of ~30%. For this good flame retardancy, the authors attributed it to the combination of P, N and B, but without further evidence both in the gas and condensed phases (Ba et al., 2017).

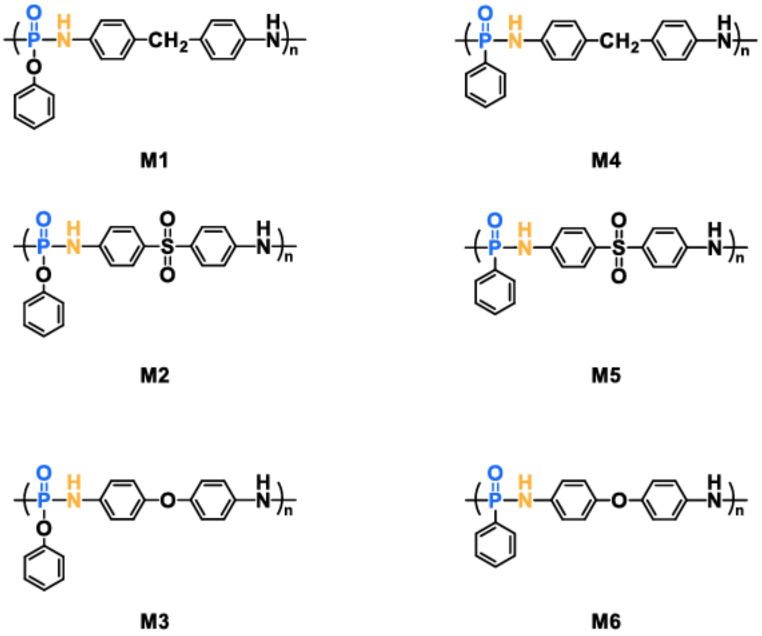
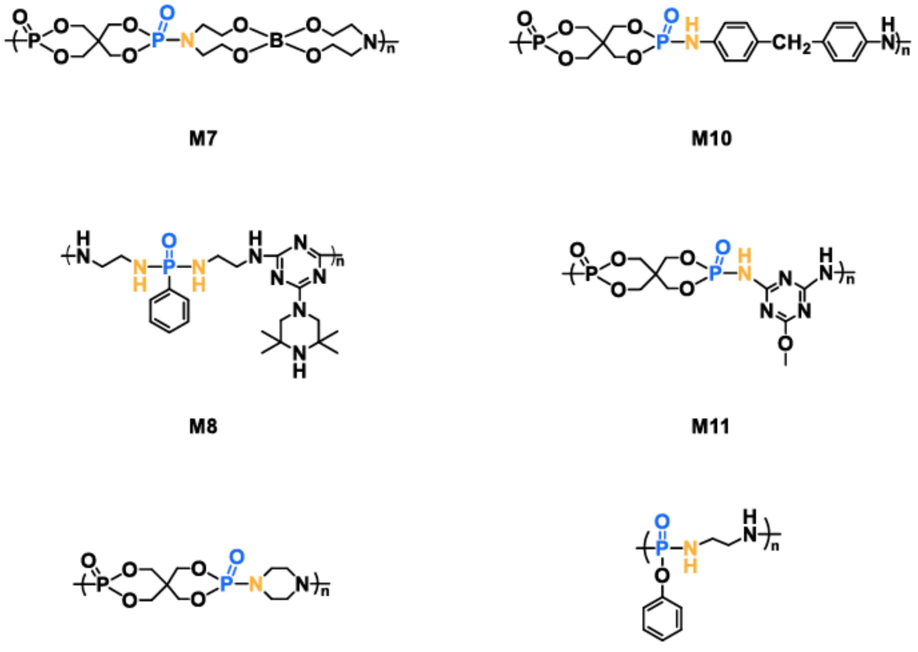

M1 M4 M2 M5 M3 M6

Figure 2.7. Chemical structures of macromolecular phosphoramides that are intrinsic (M1~3) and used in EP (M4~6).

HAPN (M8) was designed and it shows good fire resistance in polypropylene (PP) when combined with APP (Xie et al., 2016). For example, the PP sample with 12.5 wt% HAPN and 12.5 wt% APP shows a UL-94 V-0 rating and an LOI of 29.5%. But 25 wt% HAPN or APP fails to bring PP any UL-94 rating, which indicates there is a synergistic effect between HAPN and APP. Also, this sample shows a very low pHRR value (255.6 kW/m^2) that is only 28% of the original value. Based on the analysis of pyrolysis products and char residues, the authors believed that HAPN can generate nitroxyl radicals, triazine and amine compounds via thermal degradation and oxidizing reaction. The nitroxyl radicals is capable of quenching active radicals in the gas phase. The triazine and amine compounds can react with the phosphate produced from APP, then to form cross-linking structures.

Chen et al. developed a polyphosphoramide, PPSPB (M9), and studied its heat release performance during combustion on low density polyethylene/ethylene-vinyl acetate (LDPE/EVA) blends. The sample LDPE/EVA/PPSPB20 shows a reduced pHRR value of 365 kW/m^2, compared to 578 kW/m^2 of LDPE/EVA. When combined with OMMT, the pHRR value reaches as low as 289 kW/m^2 that decreases by 50% relative to the control sample. The researchers believed that a combined effect from PPSPB and montmorillonite (MMT) promotes fire safety of the LDPE/EVA blend. Unfortunately, the small-fire testing such as LOI and UL-94 was not performed, but these properties might be more necessary to evaluate the flame inhibition effect of flame-retardant agents (Chen et al., 2013).

Polyphosphoramides also can be used in ABS resin, but it is not easy to obtain a satisfactory result. For instance, 30 wt% PDSPB (M10) bring ABS only a very low pHRR (388 kW/m^2) compared to 930 kW/m^2 of pure ABS (Ma et al., 2007). But there is an obvious increase in LOI (28.6%) given the original value is only 19.1%. But the problem is that the high loading will decrease the physical properties of ABS bulk, which influents its practical use. Another example is PSPTR (M11) (Hu et al., 2012). It needs a 30 wt% loading level to make ABS pass a UL-94 V-2 rating, and even combined with phenol formaldehyde resin, the best results are a V-1 rating and an LOI of 28.2%. Although the mechanical performance was not discussed, the high loading level will certainly damage the mechanical strength of the polymer bulk.



M7

M10

M8

M11

M9

M12

Figure 2.8. Chemical structures of macromolecular phosphoramides used in PE (M7), PP (M8), PE/EVE (M9), ABS (M10~11) and cotton (M12).

A polyphosphoramide, PPAP (M12), was reported by Dong et al. and then they studied its flame-retardant effect on cotton fabrics (Dong et al., 2012). The results show the char length after combustion becomes shorter as PPAP concentration for fabrics increases. The treated cotton exhibits self-extinguishment, and when the PPAP concentration reaches 400 g/L, the char length reduces to 9.7 cm (all burn for the untreated cotton). Under the optimum process, the treated fabric shows an LOI of 27.2%, but this research did not give other flame-retarding properties such as UL-94 rating and heat release data, which makes it difficult to evaluate the overall performance of this flame-retarding additive.

Wang's group designed a few polyphosphoramides for PLA. PNFR (see M13 in **Figure 2.9**) shows a M_n of 5,500 g/mol with a PDI of 1.3.

Only 3 wt% PNFR makes PLA achieve a UL-94 V-0 rating and an LOI of 31.5%. In addition, the PLA with 5 wt% PNFR reduces its pHRR value to 258.4 kW/m^2 (310.3 kW/m^2 for pure PLA), as well as a reduction of 44% in THR. TGA results both in nitrogen and air conditions were investigated. The T_5 values of fire-retarding PLA composites are preserved in nitrogen to some extent, whereas they obviously decrease in air condition. Also, a lower char yield can be obtained in air because oxygen accelerates the degradation of both PNFR and PLA. (Liao et al., 2015). Another example is PCNFR (M14) that needs a 30 wt% loading to impart PLA a V-0 rating (Shi et al., 2017), indicative of a low efficiency. For PNSFR (M15, M_n=4,800 g/mol, a PDI of 1.04), addition of 20 wt% can brings PLA a UL-94 V-0 rating and an LOI of 25% (Liao et al., 2014). The authors ascribed the enhanced fire resistance to the action in the condensed phase as reflected by the compact char layers. However, they did not disclose the underlying reasons for the flame-retardant efficiency difference among the three similar oligomeric phosphoramides. Also, the mechanical performance is not investigated, this would make the practical use of modified PLA ambiguous.

Wu and co-workers reported a polyphosphoramide (M16, named as PPDA) and with only 3 wt% PPDA, the PLA is able to achieve an LOI of 25.5% and a UL-94 V-0 rating. In addition, the residue weight at 700 °C has a distinct rise upon the addition of PPDA. For example, the char yield of pure PLA is 1.5 wt% whereas it increases to 6.0 wt% for PLA/5 wt% PPDA. But their tensile strength experiences a reduction, from 68.1 to 53.9 MPa. The researchers proved that PPDA acts in the gas phase by a combination of radicals trapping and inert gases releasing. In the condensed phase, the aromatic groups in PPDA promote a condensed coating that suppresses combustion (Wu et al., 2019).

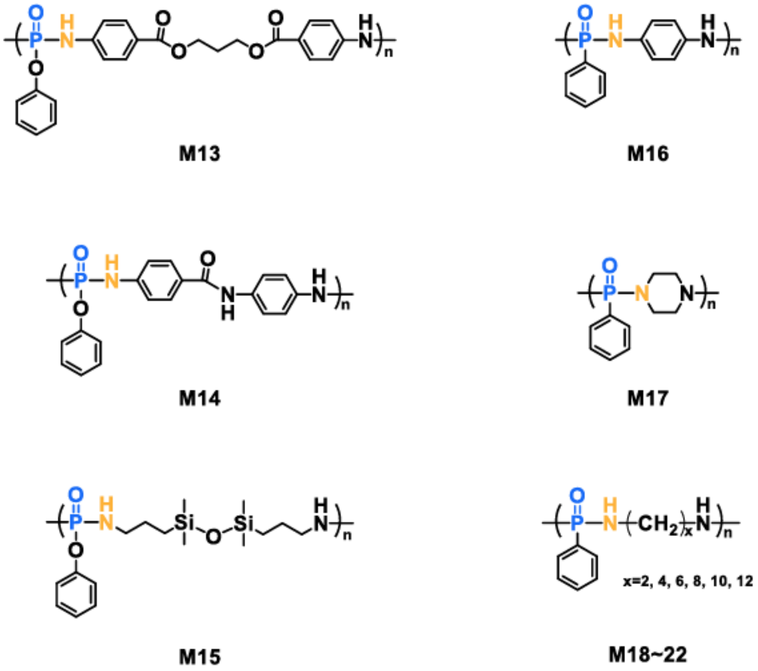


Figure 2.9. Macromolecular phosphoramides used in PLA.

Xue et al. synthesized a piperazine-containing polyphosphoramide (M17) that owns a M_n of 4,300 g/mol and a PDI of 2. When this FR (PPP) used in PLA, only 3 wt% loading endows PLA with a UL-94 V-0 rating and a high LOI of 32.5%. Although the nitrogen element participates in the char-forming, the undesirable pHRR results indicates a very limited action in the condensed phase. Thus, it can be concluded the improved fire retardancy in LOI and UL-94 testing results from the flame inhibition effect in the gas phase. Finally, the tensile strength tends to decrease upon the addition of PPP. For example, 3 wt% PPP reduces the value to 55.4 MPa (compared to 60.6 MPa of the PLA control), and when content rises to 7 wt%, the tensile strength drops to only 44.7 MPa. (Xue et al., 2020). This impairment of mechanical strength would limit the application of PLA.

In 2021 , Xue and co-workers designed a series of polyphosphoramides (M18~22) with tunable aliphatic diamines. PPDA-x (x represents the number of methylene in the diamines) presents an oligomeric characteristic with tunable M_n ranging from 2,800 to 4,100 g/mol. More importantly, these oligomers exhibit high fire-retarding efficiency in PLA. For example, only 1 wt% PPDA-4, or PPDA-6, or PPDA-8 enables PLA to achieve a UL-94 V-0 rating. For PPDA-10 and -12, they need 3 wt% to reach this rating. High LOI values are shown at a loading level of 5 wt%, as reflected by the order of PPDA-12 (40.5%) > PPDA-4 (36%) > PPDA-6 (33%) > PPDA-10 (32%) > PPDA-8 (31%), compared to a low value (20.5%) of pure PLA. In spite of the excellent outcomes in LOI and UL-94 tests, the results in cone calorimetry are not satisfactory due to the little loading level. For instance, PLA/1.0PPDA-8 only shows a pHRR of 383 kW/m^2 which is close to the original value (428 kW/m^2). Moreover, the tensile strength of modified PLA is largely preserved when the FR loading level < 3 wt% (apart from PPDA-12 system).Briefly, this flame-retarding system is highly efficient on enhancing fire safety of PLA, primally owing to the radicals quenching and inert gases releasing in the gas phase (Xue et al., 2021). This work well balances the fire retardancy and mechanical properties of PLA by a detailed investigation, achieving high-performance PLA materials with excellent flame retardancy and well-preserved mechanical strength.

Table 2.2. Synthesis information for macromolecular phosphoramides

FRs	Solvent/Catalyst	Ref.
M1-3, M9, M14, M17-22	ACN/TEA	Tai et al., 2011; Chen et al., 2013; Shi et al., 2017; Xue et al., 2020; Xue et al., 2021
M4-6, M10	ACN [a]	Zhao et al., 2017c; Ma et al., 2007
M7	DMF [a]	Ba et al., 2017
M8	DOX/NaOH	Xie et al., 2016
M11	PX/TEA	Hu et al., 2012
M12-13	TCM/TEA	Dong et al., 2012; Liao et al., 2015
M16	TCM [a]	Wu et al., 2019

[a] Only THF or DEE used as a solvent, no catalysts involve.

In summary, the improvement of fire safety is shown in many polymeric materials because of the incorporation of polyphosphoramides. Especially for PLA, macromolecular phosphoramides exhibit a talent for the small-fire testing such as LOI and UL-94. Normally, only a 3 wt% loading level is able to achieve a V-0 rating and an LOI > 30% in PLA. The very low addition level makes PLA well preserve its physical properties including thermal stability and mechanical strength. Therefore, polyphosphoramides show great potential in developing fire-retardant PLA materials and are capable of leading PLA to new applications where fire safety is required.

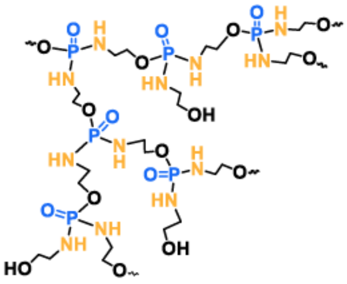
2.2.3 BRANCHED PHOSPHORAMIDES

By tuning the number of reactive groups (NH_2 and P−Cl, usually A_3+B_2 type), branched phosphoramides can be developed (displayed in **Figure 2.10**). HBPE (B1) was reported by Li and co-workers. They founded this branched additive is effective for PLA, as reflected by an LOI of 33% and a UL-94 V-0 rating by a 2 wt% loading. But the pHRR only shows a limited reduction from 604 to 554 kW/m^2 even though the loading reaches 6 wt% (Li et al., 2014).

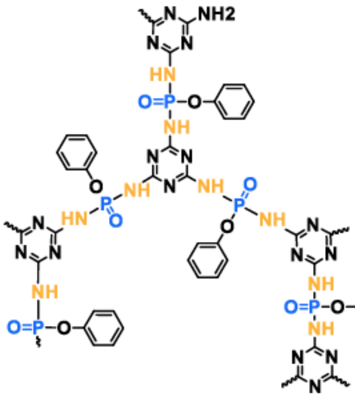
Another branched example is HBPPDA (B2) (Ye et al., 2017), but a single usage of it (25 wt%) only contributes the reduction in heat release during PP combustion, but cannot bring an achievement in LOI and UL-94 rating. When combined with APP (12.5 wt%/12.5 wt%), PP is able to have a V-0 rating and an LOI of 29.2%. The authors claimed HBPPDA enhances the char-formation via generating P-containing compounds. Although they believe the synergistic effect from HBPPDA and APP contributes to a strong and thick char layer, the actions in the gas phase due to APP should be discussed. In addition, the authors found that HBPPDA has less negative effect on the mechanical properties of PP, which might result from its good compatibility with the PP matrix.

A similar case in HPCFA is that a combination of HPCFA (B3) and APP (6.67 wt%/13.33 wt%) makes PP pass a UL-94 V-0 rating and an LOI of 31%. In addition to the increased char residue, the thermal stability of PP is well preserved. Particularly for Tmax, it increases by up to 13 °C. The fire-retardant PP sample also exhibits a low pHRR value of 107.4 kW/m^2 and a THR of 44.2 MJ/m^2, relative to the 780.4

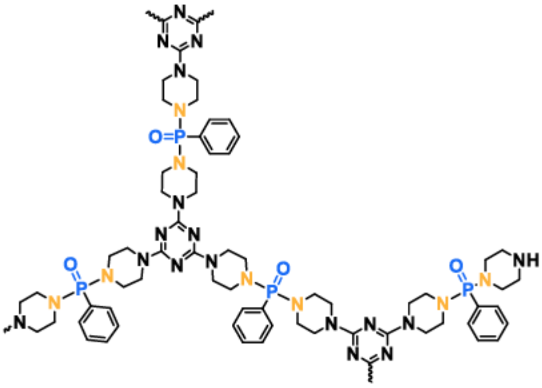
kW/m² and 85.6 MJ/m² of pure PP. The compact char residues in the condensed phase are responsible for such a good flame retardancy, but the fire retardant should play a partial role in the gas phase as evidenced by the high LOI value and the V-0 rating (Zhu et al., 2018).



B1



B2



B3

Figure 2.10. Branched phosphoramides used in PLA (B1), PP (B2~3).

In belief, although it is difficult for branched phosphoramide to achieve good flame-retarding results in PP at a low loading level, they are highly efficient for PLA materials, which makes them promising additives for the design of fire-retardant PLA.

2.3 RESEARCH GAPS

The foregoing phosphoramides have clearly demonstrated high fire-retardant efficiencies in PLA. However, there are some knowledge gaps to be bridged, which include their chemical synthesis methodologies, a limited understanding of their modes of actions in PLA and how they affect the microstructure and comprehensive property (e.g., fire-resistant, thermal, mechanical, and transparent properties) of the final fire-retardant PLA, specifically:

(a) The existing synthesis of (poly)phosphoramides often involves a large amount of organic and even toxic solvents. For example, toxic solvents/catalysts, such as DCM, ACN, THF, and TEA are often used (see their toxicity in **Table 2.3**) and the synthesis of 1 g of (poly)phosphoramide normally consumes about 10~50 mL solvent. In addition, the side products, such as TEA-HCl, also involves complicated post-treatments. This can not only increase the production cost but also cause environmental issues. Therefore, it is highly desirable to develop inexpensive and sustainable solvent-free synthesis methods for (poly)phosphoramides.

Table 2.3. Toxicity of the solvents and catalysts involved in the synthesis of (poly)phosphoramides

Toxic solvents/catalyst	Oral LD50 *a*	Inhalation LC50 *b*	Skin contact LD50 *a*
ACN	469 mg/kg (Mouse)	3,587 ppm (Mouse)	>2,000 mg/kg (Rabbit)
DCM	>2,000 mg/kg (Rat)	86 mg/L (Mouse)	>2,000 mg/kg (Rat)
DEE	1,600 mg/kg	397 mg/L	>20,000

	(Rat)	(Mouse)	mg/kg (Rabbit)
THF	1,650 mg/kg (Rat)	16.9 mg/L (Rat)	>2,000 mg/kg (Rat)
TEA	730 mg/kg (Rat)	3.63 mg/L (Rat)	580 mg/kg (Rabbit)

[a] LD50 means lethal dose that cause 50% subjects to die. [b] LC50 refers lethal concentration cause 50% subjects to die. These data are provided by Sigma-Aldrich.

(b) The understanding of fire-retarding mechanisms of (poly)phosphoramides still remains insufficient. Particularly for the actions in the gas phase, most studies only discuss the inhibition effects regarding radicals quenching and inert gases releasing, but lack enough evident to support their conclusions. Usually, a TG-IR testing or reduced EHC values are used to prove the gas-phase actions, which is not enough for demonstrating the mechanisms. Hence, it is necessary to develop detailed gas-phase actions via multiple characterizations.

(c) The previous research lacks in-depth understanding of how the concentration of (poly)phosphoramides affect comprehensive properties of PLA. Few literatures focus on the relationship between the loading level of polyphosphoramides and the comprehensive properties of PLA. In addition, almost all studies fail to achieve enhanced thermal stability of fire-retardant PLA, and also there are no reports investigating the transparency of PLA. Consequently, it is imperative to study the concentration-properties relationship of PLA/polyphosphoramide fire-retardant composites.

2.4 RESEARCH OBJECTIVES

To fill the above research gaps, the three main aims of this thesis are:

(a) To develop solvent/catalyst-free approaches to synthesize polyphosphoramides with tunable chemical structure. This green synthesis method will make a contribution to the sustainability of PLA/polyphosphoramide fire-retardant materials;

(b) To unveil modes of actions of polyphosphoramides in PLA. More mechanism characterizations in the gas are expected to be applied in this thesis to demonstrate the modes of actions proposed; and

(c) To gain an in-depth understanding of how the comprehensive properties (e.g., thermal stability, mechanical performances, and transparency) are affected by polyphosphoramides loading levels.

CHAPTER 3: PAPER 1 - ONE-POT, SOLVENT- AND CATALYST-FREE SYNTHESIS OF POLYPHOSPHORAMIDE AS AN ECO-BENIGN AND EFFECTIVE FLAME RETARDANT FOR POLY(LACTIC ACID)

The study in this chapter innovatively developed a solvent-free synthesis approach for a polyphosphoramide (DM-H). The as-synthesized DM-H exhibits excellent fire retardancy in PLA (a UL-94 V-0 rating and a LOI of 29.7%) but without compromising its mechanical strength. This study is shown as a published article.

CHAPTER 4: PAPER 2 – A Si-CONTAINING POLYPHOSPHORAMIDE VIA GREEN CHEMISTRY FOR FIRE-RETARDANT POLYLACTIDE WITH WELL-PRESERVED MECHANICAL AND TRANSPARENT PROPERTIES

The study in this chapter synthesized a Si-containing polyphosphoramide via green chemistry. The as-synthesized polyphosphoramide (DM-Si) shows high fire-retarding efficiency in PLA. Only addition of 1 wt% DM-Si makes PLA achieve a UL-94 V-0 rating and a LOI of 27.9, but the mechanical strength and transparency are well preserved. This study is displayed as a published article.

CHAPTER 5: PAPER 3 - SOLVENT-FREE SYNTHESIS OF ORGANIC-INORGANIC POLYPHOSPHORAMIDE-HALLOYSITE NANOHYBRIDS FOR THERMAL STABLE AND FIRE-RESISTANT POLYLACTIDE

The study in this chapter developed a series of organic-inorganic hybridized polyphosphoramides (DM-OHn). The as-synthesized DM-OH16 is effective on improving fire retardancy of PLA. Addition of 1.5 wt% DM-OH16 enables PLA to reach a UL-94 V-0 rating and a LOI of 32.6%. There is also a 5 °C increase in T_5, and the tensile strength is not sacrificed. This study is shown as a submitted article.

CHAPTER 6: DISCUSSION AND CONCLUSION

6.1 MAIN FINDINGS

This thesis developed solvent/catalyst- free approaches for the syntheses of three polyphosphoramides used as highly efficient FRs for PLA. In addition to excellent flame retardancy and detailed modes of actions, physical properties (thermal stability, mechanical performance and transparency) of fire-retarding PLA were discussed deeply. Specifically,

(a) A polyphosphoramide (DM-H) was successfully synthesized via a solvent-free polycondensation. Addition of 2 wt% DM-H makes PLA reach a desirable UL-94 V-0 rating and a high LOI (29.7%). The exceptional fire-retarding properties mainly result from the actions in the gas phase concerning radicals trapping and inert gases releasing, as well as the secondary condensed phase actions via promoting dense and intact char layers. Furthermore, the resulting PLA (with 2 wt%) preserves a comparable tensile strength of 59.7 MPa relative to pure PLA.

(b) A Si-containing polyphosphoramide (DM-Si) was developed via a green strategy without using any solvents and catalysts. Only 1.0 wt% DM-Si enables PLA to achieve an LOI of 27.9% and a V-0 rating in UL-94 testing, as well as a 16% reduction in its pHRR value compared to unmodified PLA. In addition to a barrier effect from P/Si collaboration in char residues, the extraordinary fire-retarding efficiency of DM-Si is ascribed to the flame inhibition effect in the gas phase. Moreover, the PLA/1.0DM-Si fire-retardant composite exhibits an increase (by 68%) in tensile toughness, and a competitive tensile strength of 59.2 MPa, as well as satisfactory transparency (80.3%).

(c) A variety of organic-inorganic polyphosphoramide-halloysite nanohybrids (DM-OHn) were successfully synthesized through a one-pot co-polycondensation without any solvents and catalysts. With only 1.5 wt% DM-OH16, the resulting PLA shows a UL-94 V-0 rating and a high LOI of 32.6%. This exceptional fire retardancy is mainly attributed to the gas-phase actions regarding free radicals quenching and fuel mixture dilution. Moreover, this fire-retarding PLA exhibits enhanced thermal stability (a 5 °C increase in T_5 relative to pure PLA), and preserves a tensile strength of 55.8 MPa.

6.2 CONTRIBUTION OF THE THESIS

Primally, this thesis offers an innovative, sustainable and feasible strategy for synthesis of polyphosphoramides and organic-inorganic polyphosphoramide nanohybrids that can be used as highly efficient FRs for PLA. The solvent-free synthetic method opens a new avenue for green production of FRs and it is promising to mitigate the health and environmental hazards from toxic solvents. This work fills a knowledge gap in this research area and would encourage more efforts to develop green FRs, finally furthering the sustainable development of FRs, as well as fire-retarding bioplastics.

Then, we proposed detailed fire-retardant mechanisms of polyphosphoramides both in the gas and condensed phase. The in-depth analysis and discussion on the modes of actions of polyphosphoramides contributes to a better understanding of how phosphoramides affect the combustion. More importantly, this knowledge will guide polyphosphoramides to be effectively applied in more polymeric materials.

Lastly, we investigated the physical properties of fire-retarding PLA, with the thermal, mechanical and transparent properties deeply discussed. A concentration-properties relationship in fire-retarding PLA was well developed. This relationship provides guiding significance for creating fire-retarding PLA with balanced comprehensive properties to meet the requirements in real-world applications.

6.3 FUTURE PERSPECTIVES

Although we developed the green chemistry methods for synthesis of polyphosphoramides for creating fire-retardant PLA, there still remains some questions to be answered in the future.

(a) The first question is whether other phosphonate or phosphite compounds (e.g., dimethyl phenylphosphonate, dimethyl phosphite) can be used in this green chemistry approach? Polycondensation reactions between dimethyl phosphite and diols was reported to synthesize polyphosphonates (Busch et al., 2017). Also, diphenyl phosphite was viewed as more suitable starting materials to achieve high molecular wight polyphosphonates (Pretula et al., 1997). Thus, it is reasonable to assume that other phosphonates or phosphites are capable of reacting with diamine to form polyphosphoramides via solvent-free amine ester exchange reaction. By tuning the P-containing starting materials, a family of polyphosphoramides with different structures via green synthesis are expected to be obtained.

(b) Then, do the new polyphosphoramides share the same modes of actions with the ones developed in this thesis? Studies have demonstrated that phosphoramides with different side groups (bonded to the P atom) exhibit different fire retardancy in PLA (Zhao et al., 2016). Additionally, some diamine structures will affect the char-formation behavior of the matrix (Xue et al., 2020). Another current gap is lack of direct detection of free radicals. A breakthrough in radicals detection via novel equipment or methods could be considered to solidify the radicals quenching action. For these reasons, in-depth flame-retardant mechanisms of new polyphosphoramides are still deserving to be investigated

(c) Finally, do the polyphosphoramides have any advantages if used in other polymers such as polyvinyl alcohol (PVA)? A recent study shows a P/N fire retardant that also can serves as reinforcing/toughing agent for PVA due to its rich amines (Liu et al., 2022). Thus, polyphosphoramides are expected to have H-bond cross-linking effect in PVA given the existence of abundant amine groups in their molecular chain. By blending polyphosphoramides with PVA, it is promising to create high performance PLA materials with excellent fire retardancy and mechanical properties. Meanwhile, a deep structure-properties relationship will be required to fill the gap in this research area.

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APPENDIX A: SUPPORTING INFORMATION FOR PAPER 1

This appendix 1 is attached as the Supporting Information (published) for the paper in chapter 3: One-pot, solvent- and catalyst-free synthesis of polyphosphoramide as an eco-benign and effective flame retardant for poly(lactic acid).

Supporting Information

One-Pot, Solvent- and Catalyst-Free Synthesis of Polyphosphoramide as An Eco-Benign and Effective Flame Retardant for Poly(lactic acid)

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This Supporting Information contains:

Number of pages: 4

Number of figures: 4

Number of tables: 1

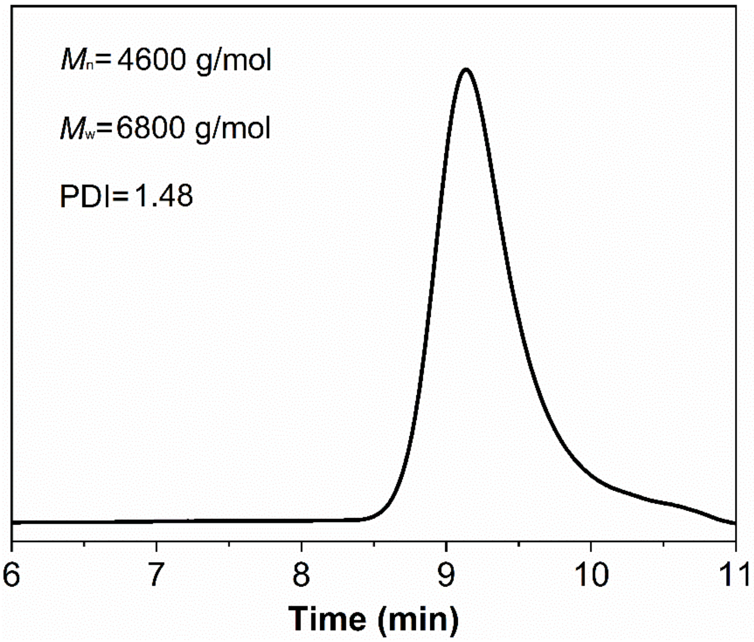

Figure S1. The GPC curve of as-synthesized DM-H.

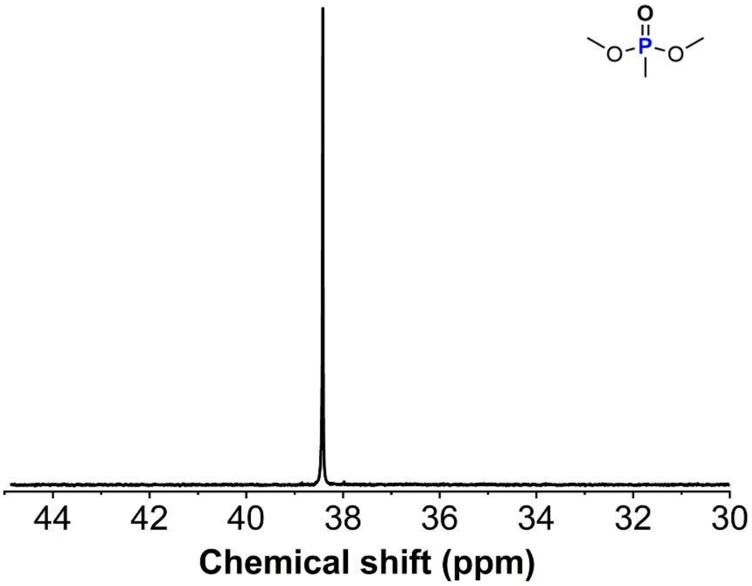

Figure S2. The ^{31}P NMR spectrum of DMMP.

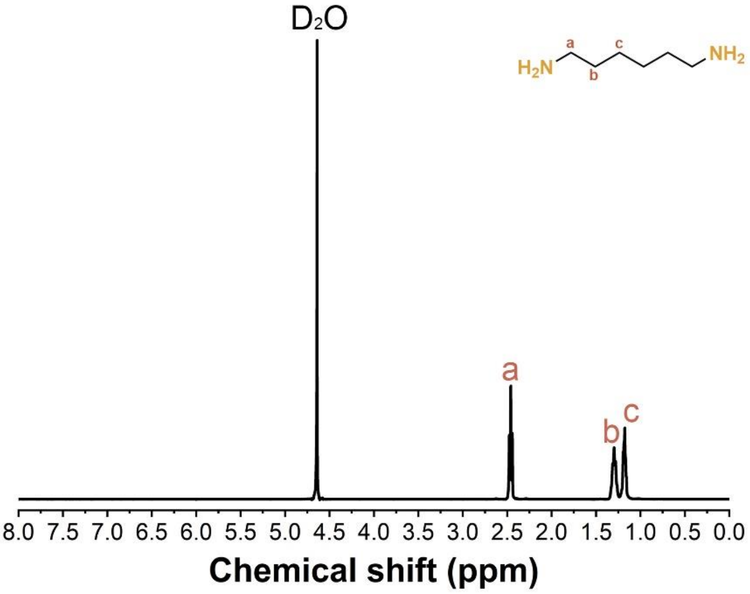

Figure S3. The ^{1}H NMR spectrum of HDA.

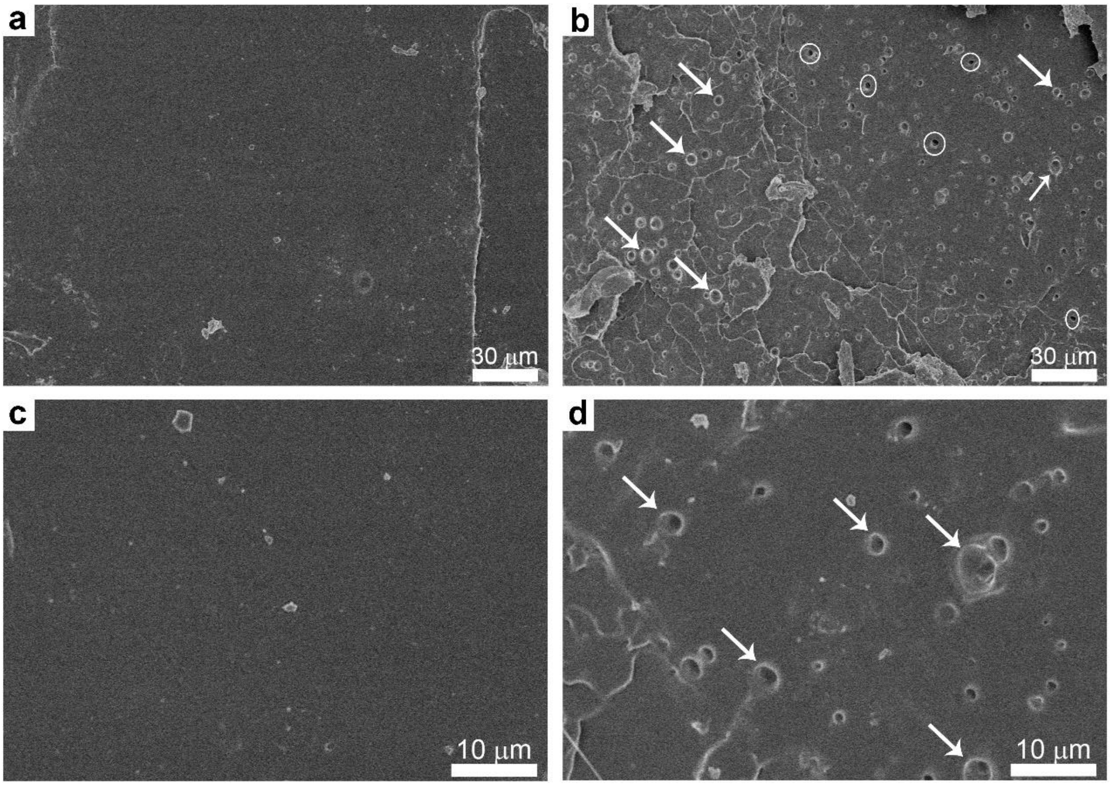

Figure S4. **SEM images of cross-section after tensile failure.** a, c) PLA, and b, d) PLA/2.0DM-H.

Table S1. Theoretical and Experimental Values of Chemical Composition of DM-H

Elements	C (wt%)	H (wt%)	O (wt%)	N (wt%)	P (wt%)
Theoretic values	47.7	9.7	9.1	15.9	17.6
EA	35.8	9.4	32.1	7.1	15.6 [a]
XPS	45.1	-	32.5	10.5	11.9

[a] calculated based on EA results.

APPENDIX B: SUPPORTING INFORMATION FOR PAPER 2

This appendix 2 is attached as the Supporting Information (published) for the paper in chapter 4: A Si-containing polyphosphoramide via green chemistry for fire-retardant polylactide with well-preserved mechanical and transparent properties.

Supporting Information

A Si-containing polyphosphoramide via green chemistry for fire-retardant polylactide with well-preserved mechanical and transparent properties

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[1] Dr Feng and Mr Ma equally contributed to this work and were listed as co-authors of this work.

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Figure S1- S8

Table S1-S2

EquationS1-S2

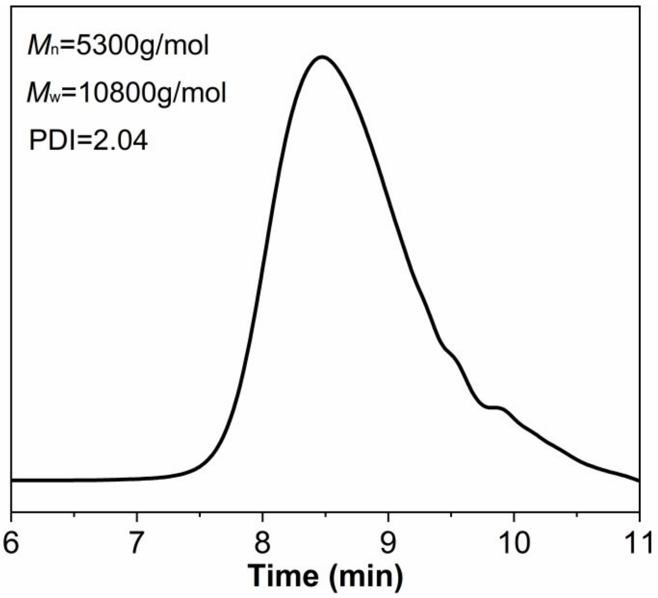

Fig. S1. The GPC curve of DM-Si.

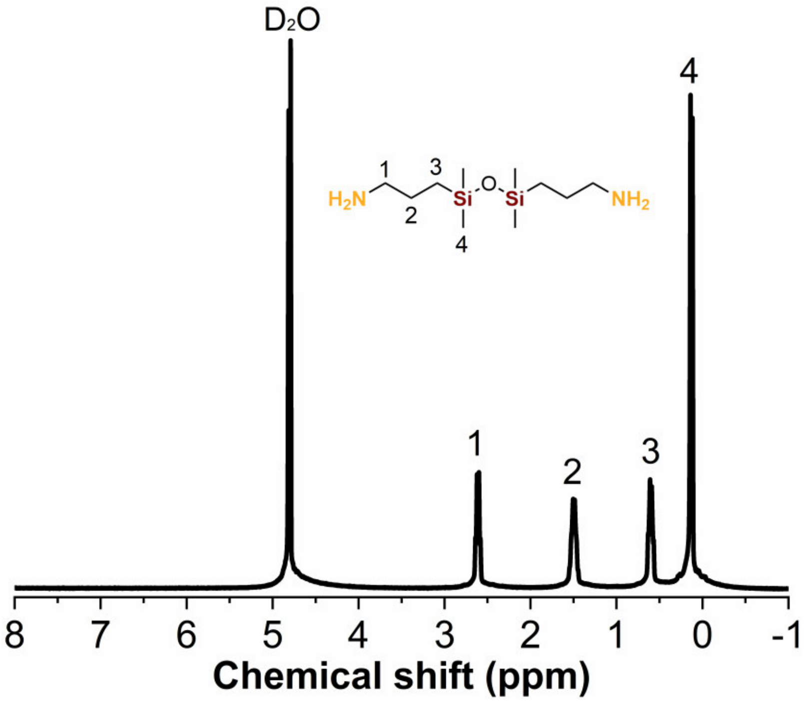

Fig. S2. ^{1}H NMR spectrum of BATMDS

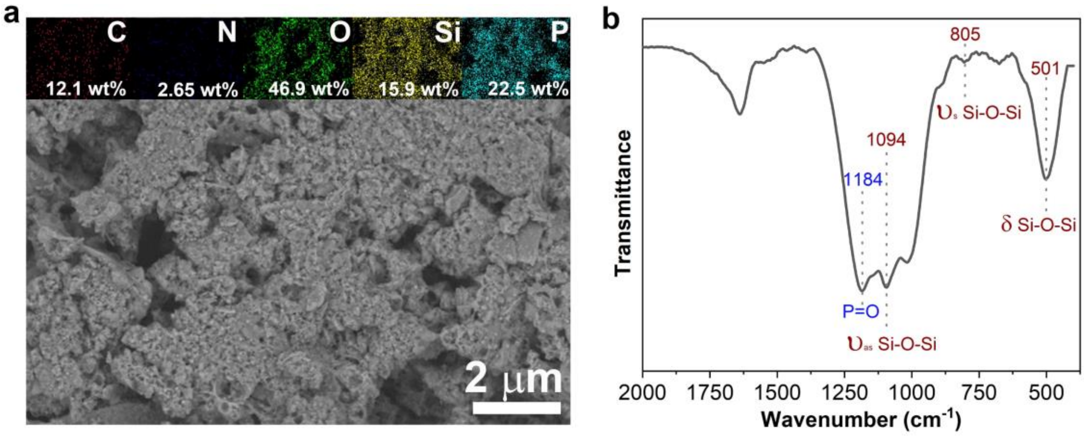

Fig. S3. Analysis of the DM-Si residue obtained in air atmosphere. (a) the SEM image with embedded element mapping images, (b) the FTIR spectrum.

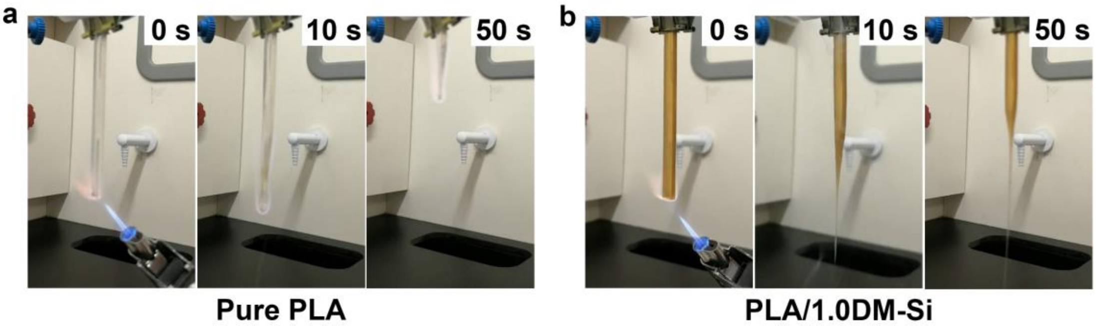

Fig. S4. Burning rate testing of (a) PLA and (b) PLA/1.0DM-Si.

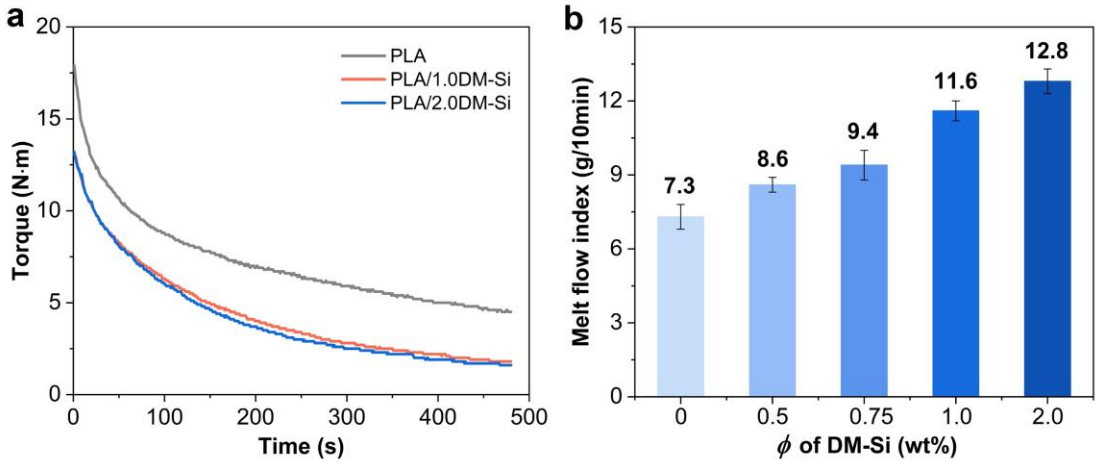

Fig. S5. The melt viscosity of PLA and PLA/DM-Si composites. (a) torque curves during melt blending at 180 ºC, (b) melt flow index values tested under 2.16 kg loading at 180 ºC.

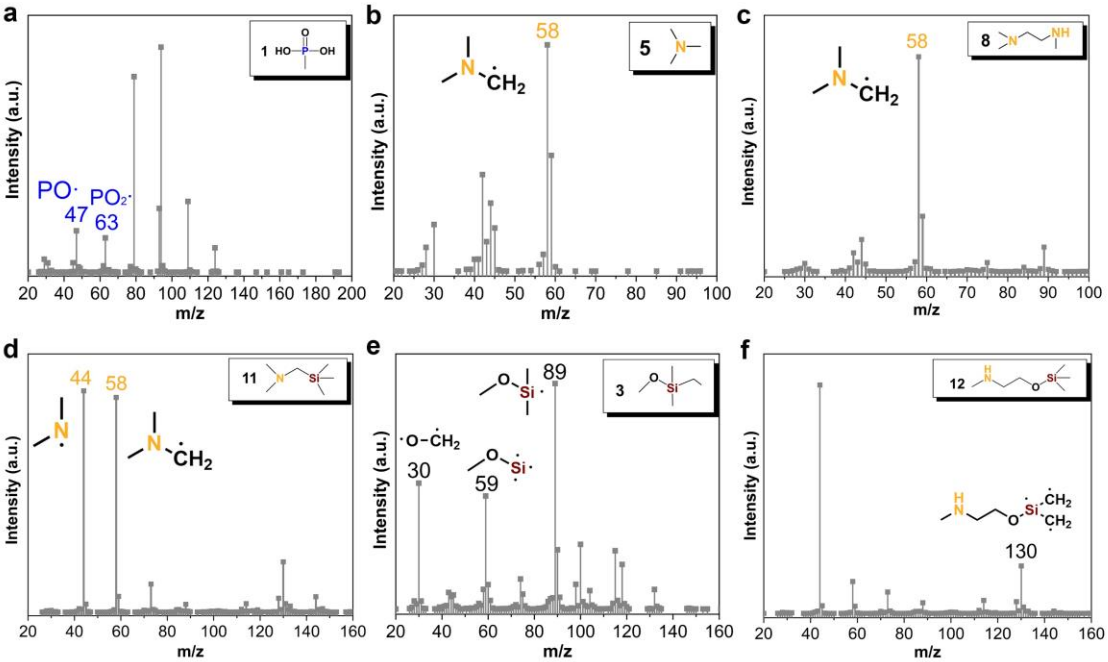

Fig. S6. Mass spectra of gaseous pyrolysis products of DM-Si at 600 ºC. The products' sequence numbers correspond to the structure in Gas chromatogram. (a) compound 1, (b) compound 5, (c) compound 8, (d) compound 11, (f) compound 3 and (e) compound 12.

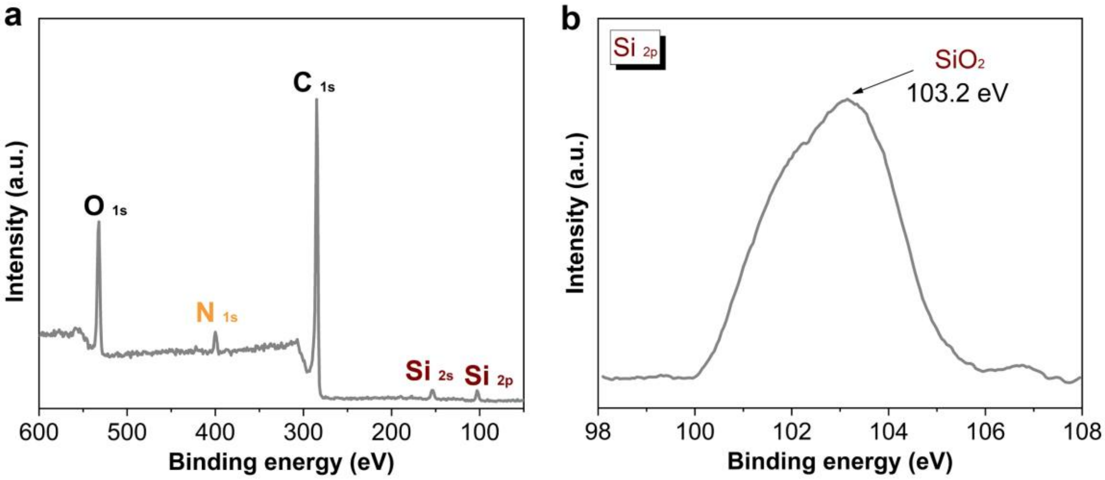

Fig. S7. XPS spectra of the char residue from PLA/2.0DM-Si. (a) full XPS spectrum, (b) high-resolution XPS spectra of Si 2p.

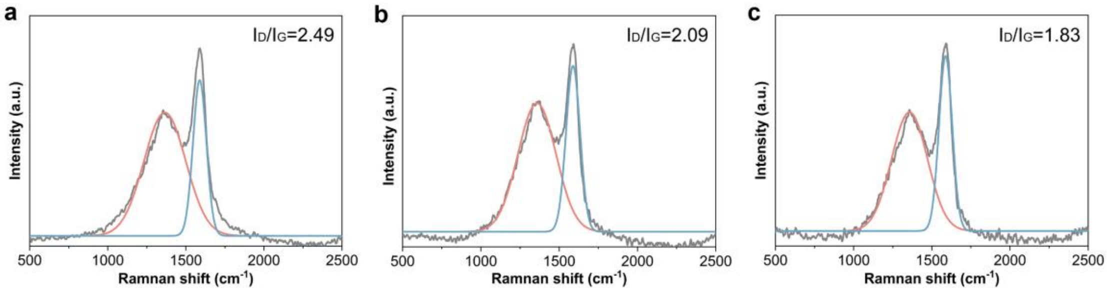

Fig. S8. Raman spectra of (a) PLA, (b) PLA/1.0DM-Si and (c) PLA/2.0DM-Si

Table S1
Theoretical and experimental values of chemical composition of DM-H

Elements	C (wt%)	H (wt%)	O (wt%)	N (wt%)	P (wt%)	Si (wt%)
Theoretic values	42.8	9.5	10.4	9.1	10.0	18.2
EA	35.6	9.6	13.2	7.4	22.6 [a]	11.6
XPS	36.9	-	24.1	8.0	14.4	16.60

[a] calculated based on EA results.

Table S2
Theoretical and experimental char yield values of PLA and PLA/DM-Si composites

Samples	Residue in N_2 (wt%)		Residue in Air (wt%)	
	Theoretical values [a]	TGA values	Theoretical values [a]	TGA values
DM-Si	/	6.5	/	17.9
PLA	/	0.4	/	0
PLA/0.5DM-Si	0.43	0.7	0.09	0.2
PLA/0.75DM-Si	0.44	0.9	0.13	0.2
PLA/1.0DM-Si	0.46	1.0	0.18	0.3
PLA/2.0DM-Si	0.52	1.5	0.36	0.4

[a] Theoretical values were calculated based on the char of PLA and DM-Si at 600 ℃.

Equation S1

$t_{ig} = b/(q_{ex}-q_{crit})$, b is a fitted constant, t_{ig} is the ignition time, q_{ex} is the external heat flux and q_{crit} is the critical heat flux.

Equation S2

$t_{ig} = (\mathrm{TRP}/\ q_{ex})^2$, t_{ig} is the ignition time, q_{ex} is the external heat flux and TRP means thermal response parameter.

APPENDIX C: SUPPORTING INFORMATION FOR PAPER 3

This appendix 3 is attached as the Supporting Information (submitted) for the paper in chapter 5: Solvent-free synthesis of organic-inorganic polyphosphoramide-halloysite nanohybrids for thermally stable and fire-resistant polylactide.

Supporting Information

Solvent-free synthesis of organic-inorganic polyphosphoramide-halloysite nanohybrids for thermally stable and fire-resistant polylactide

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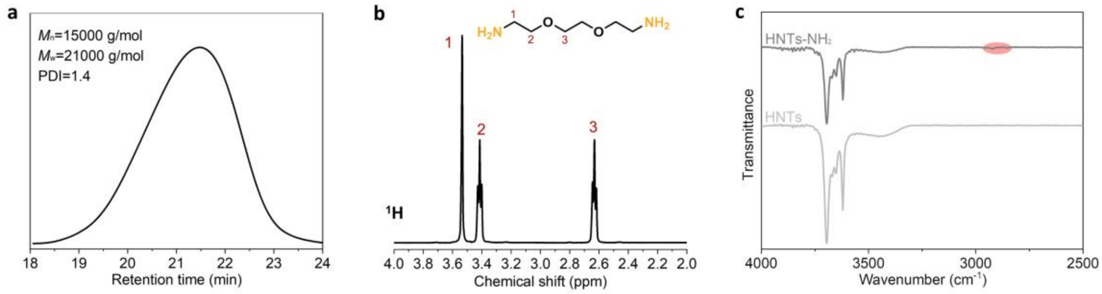

Figure S1. Chemical characterization. (a) GPC curve of DM-O, (b) ^{1}H NMR spectrum of DADO, (c) FTIR spectra of HNTs and HNTs-NH_2.

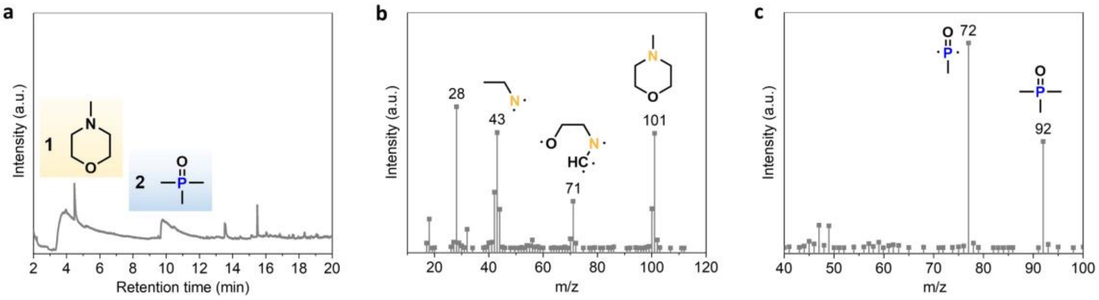

Figure S2. Gaseous pyrolysis products of DM-O at 550 °C. (a) Gas chromatogram, mass spectra of (b) compound 1 and (c) compound 2.

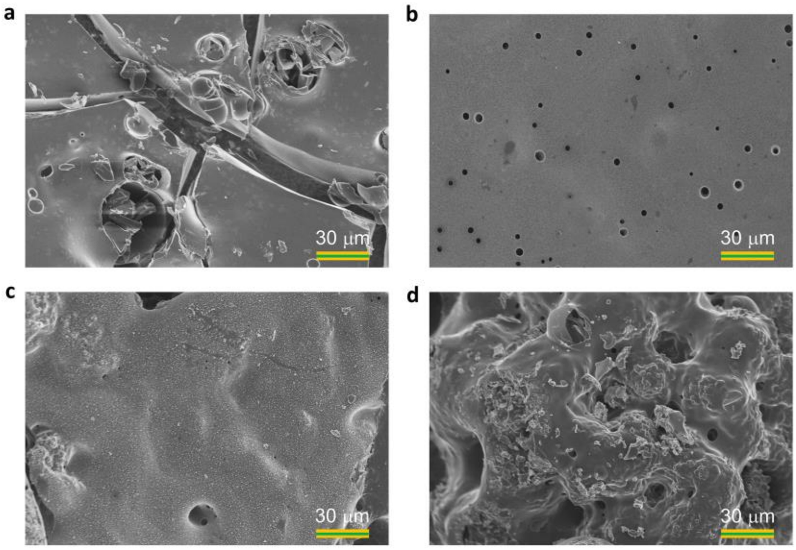

Figure S3. SEM images of char residue of PLA and its composites after cone calorimetry. (a) PLA, (b) PLA/DM-O, (c) PLA/DM-OH8, (d) PLA/DM-OH16.

Table S1. Synthesis yields of DM-O and DM-OHn

DM-O	DM-OH4	DM-0H8	DM-OH12	DM-OH16
82.5%	81.7%	81.5%	82.6%	82.0%

Table S2. Cone calorimetry testing results of PLA and its fire-retardant composites.

Samples	t_{ig} [a] (s)	pHRR [b] (kW/m^2)	THR (MJ/m^2)	pCOP [b] (g/s)	av-EHC [c] (MJ/kg)	Residue (wt%)
PLA	62±2	401±11	68±2	0.0013	18.9	0.4±0.1
PLA/1.5DM-O	73±2	375±12	65±1	0.0041	15.6	1.8±0.2
PLA/1.5DM-OH4	68±1	385±10	66±1	0.0022	17.5	1.2±0.2
PLA/1.5DM-OH8	68±2	383±12	66±2	0.0037	16.5	2.1±0.1
PLA/1.5DM-OH12	66±1	417±10	65±1	0.0023	17.2	1.8±0.1
PLA/1.5DM-OH16	62±1	415±11	66±1	0.0017	16.4	2.1±0.2

[a] t_{ig} refers to the time to ignition. [b] pHRR and pCOP represent peak values of HRR, CO Production. [c] av-EHC denotes average value of effective heat of combustion.