UNIVERSIDAD POLITÉCNICA DE MADRID

ESCUELA TÉCNICA SUPERIOR DE

INGENIEROS INDUSTRIALES

**Halogen-free phosphorus-containing flame-
retardant epoxy composites**

TESIS DOCTORAL

XIAOMIN ZHAO

Chemical Engineering

2017

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ABSTRACT

Epoxy resins are widely applied in transportation, aerospace, electrical and electronic (EE) industrial sectors due to their excellent properties, such as mechanical strength, chemical and heat resistance, adhesiveness and electrical insulation. Nevertheless, flammability is one paramount disadvantage of epoxy-based materials in most applications.

As a result of the current concern for the environment and the human health, halogen-free phosphorous-containing flame retardants (P-FRs) are considered to be the most promising additives to enhance the fire resistance of epoxy materials for industrial applications. Within this context, the main objectives of this doctoral thesis were four. The first one was to synthesize and characterize P-FRs with varied phosphorous' (P') chemical environments in the molecular structures. The second one was that investigate the impact of P' chemical environment in P-FRs on flame retardancy of epoxy and epoxy/carbon fiber composites with P-FRs. The third one was that understand the impact of P' chemical environment on the flame-retardant mechanism of P-FRs in the gas and the condensed phases of the epoxy, respectively. Finally, the thermal stability and mechanical properties of flame-retardant epoxy and epoxy/carbon fiber composites were studied.

Following these objectives, the synthesis and characterization of two series of P-FRs with varied P' chemical environments based on phenylphosphonate (PO-Ph) and phenylphosphoric (PO-OPh) structures are presented in Chapter 3. A comprehensive comparison of both series of P-FRs on flame retardancy of epoxy was carried out via different tests (limiting oxygen index, UL 94 and cone calorimeter) and presented in

Chapter 4. The thermal stability and mechanical properties of epoxy containing P-FRs were studied as well.

Chapter 5 summarizes the flame-retardant mechanisms of the two series of P-FRs in epoxy that were assessed from both gas and condensed phases via investigating the thermal decomposition behaviors of P-FRs and epoxy with P-FRs, respectively. The thermal phenomena in epoxy with P-FRs during the combustion were investigated via recording surface and near-to-surface temperatures in the UL 94 test. Flame-retardant mechanisms were proposed for the two series P-FRs in epoxy based on the results.

Finally, flame-retardant RTM 6/carbon fiber reinforced composites (CFR) were developed based on the results in the previous chapters and the overall results are presented in Chapter 6. Flame-retardant CFR were prepared by resin transfer moulding. The rheological, mechanical properties and flame retardancy of flame-retardant CFR were studied with different tests. In particular, the combustion of the CFR and of the RTM6 epoxy matrix were compared and analyzed as well as the interlaminar shear strength and in-plane shear strength of CFR with and without flame retardants.

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Abbreviations

EP	Epoxy resin with brand name EPC
DGEBA	Diglycidyl ester of bisphenol A type epoxy
CFR	Carbon fiber reinforced RTM 6 epoxy composite
FR	Flame retardant
P-FR	Phosphorous-containing FR
P	Phosphorous
NMR	Nuclear magnetic resonance
FTIR	Fourier transform infrared spectroscopy
DSC	Differential scanning analysis
TGA	Thermal gravimetric analysis
MS	Mass spectroscopy
LOI	Limiting oxygen index
DMA	Dynamic mechanical analysis
SEM-EDS	Scanning electron microscopy with X-ray microanalysis
VT-FTIR	Variable temperatures FTIR
RTM	Resin Transfer Moulding
ILSS	Interlaminar shear strength
IPSS	In-plan shear strength

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CHAPTER 1

INTRODUCTION

"If you can't explain it simply, you don't understand it well enough."

- Albert Einstein

1.1 Epoxy resins

Epoxy resins are one of most important synthetic thermoset polymers in modern society. The world market for epoxy resins has grown rapidly since the 1940s (Pascualt and Williams *et al.* 2009). The global epoxy resin market was worth up to USD 7.99 billion in 2015 (Grand View Research Inc.). Epoxy resins are widely applied as durable paints, coatings, adhesives, composites and laminate materials in transportation, aerospace and electrical and electronic (EE) engineering applications due to their excellent properties, such as their high mechanical strength, outstanding chemical and heat resistance, excellent adhesiveness and electrical insulation (Hartshorn *et al.* 2012).

Generally, epoxy resins are a broad class of synthetic polymers in which a cross-linking structure is formed via a reaction between epoxy groups (shown in Scheme 1-1) and other functional groups such as amines and anhydrides (May *et al.* 1987). Epoxy resins contain at least two components: the epoxy monomer and the curative. The main commercial structures of epoxy monomers are described in Scheme 1-2: diglycidyl ester of bisphenol A (DGEBA), phenol novolac, tetraglycidyl methylene dianiline (TGMDA) and cycloaliphatic types. DGEBA and phenol novolac epoxy resins are a classic type of phenol glycidyl ether formed via a condensation reaction between epichlorohydrin and a phenol group. TGMDA is a typical class of glycidyl amine formed via a reaction between epichlorohydrin and an amine. Cycloaliphatics are a class of epoxy resin containing an aliphatic ring, which mainly have low viscosity.

Scheme 1-1 Epoxy group

As is well known, the epoxy monomer cannot be used as a product until it forms cross-linking structures by reacting with the curative. The most commonly applied curatives are amine, thiol, anhydride and phenol compounds, as shown in Scheme 1-3 (a-d respectively). The curing reactions are also described in Scheme 1-3. Amine, thiol and phenol compounds lead to a nucleophilic addition reaction with the epoxy groups. Anhydride initially reacts with hydroxyl groups on the epoxy chain to form carboxylic acids (Scheme 1-3 c'). The epoxy groups then react with the carboxylic acid in a ring-opening addition reaction (Scheme 1-3 c). The multi-functionality of the epoxy monomer and curative induces the cross-linking structures in an epoxy resin.

Scheme 1-2 The common commercialized epoxy resin structures

Depending on the curing temperature (T), the curatives are classified as room T, latent and high T types. The typical compounds within this classification are shown in Scheme 1-4.

-Room T curatives: diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylenepentamine (TEPA), meta-xylenediamine (MXDA), tertiary amine and polyamides are commonly used room T curatives of epoxy monomers. The epoxy resins cured using room T curatives have low-thermal resistance. The products are generally applied as a coating, adhesive or sealant to materials such as metal and wood.

Scheme 1-3 The curing reactions with different functional groups: amine (a), thiol (b), anhydride (c' and c) and phenol (d)

-Latent curatives: this type of curative is curable not only at room T but also at high T. Isophoronediamine (IPDA), methylene-di(cyclohexylamine) (PACM), BF_3 complex, substituted imidazoles and dicyandiamide (DICY) are well-known commercialized latent curatives. They are often used as accelerators in conjunction with other curatives.

Scheme 1-4 Curative classification from low T to high T

-High T curatives: the curing reaction commonly occurs at $> 150^{\circ}\text{C}$ for this type of curative. 4, 4'-diaminodiphenyl methane (DDM), metaphenylene diamine (MPD), 4, 4'-

diaminodiphenylsulfone (DDS) and their derivatives are the main aromatic amine curatives. Phthalic anhydride (PDA), trimellitic anhydride (TMA), pyromellitic anhydride (PMDA) and their derivatives are commonly used anhydride curatives added to epoxy monomers. Epoxy resins cured with high T curatives have a high glass transition temperature (T_g), excellent mechanical strength and outstanding chemical resistance and electronic properties. The products are often used in the electrical and electronics (EE) industries, aerospace and transportation.

Epoxy resins in EE applications

In its 2016 annual report, Grand View Research Inc. listed EE applications as the second largest segment for epoxy resins in the globe market. Epoxy resins are widely used as an adhesive in composites, sealants, coatings, impregnation compounds, moldings and encapsulating materials in most electronic devices such as computers and complex telecommunications equipments. Printing wiring boards (PWB) are one of the most commonly used EE components those use epoxy resin as the matrix material. In numerous structures, DGEBA and phenol novolac epoxy resins are the two primary epoxy resins used in semiconductor encapsulation and PWB. The corresponding curatives are DDS, DICY and phenol novolac as shown in Scheme 1-5.

Scheme 1-5 The common curatives in EE application

Epoxy-DICY systems show relatively low thermal performance ($T_g < 140\text{ }^{\circ}\text{C}$) and are commonly used in applications without a high temperature requirement. Epoxy phenol novolac systems have a higher T_g than epoxy-DDS and epoxy-DICY systems. However, their brittleness is one significant disadvantage of this system. Currently, epoxy-DDS systems are the main choice for a high temperature epoxy matrix due to its high T_g and also its high mechanical strength in EE applications.

Nevertheless, high flammability is an unavoidable disadvantage of epoxy resins in EE applications (Rakotomalala, Wagner et al. *et al.* 2010). In PWBs, 80% of epoxy composite materials are graded as FR-4 by the National Electrical Manufacturers Association (NEMA). The epoxy resins in this grade are generally of the DGEBA type. Providing flame retardancy in epoxy resin is achieved by mixing with tetrabromobisphenol A (TBBA) as shown in Scheme 1-6. The bromine content is up to 20 wt% in the FR-4 epoxy resins current used by the PWB industry.

Scheme 1-6 TBBA structure

Owing to increasing concerns regarding environmental protection and human health, novel flame-retardant epoxy resins are being demanded for EE applications. On the basis of this background, a DGEBA-DDS epoxy system was selected as the study matrix in this PhD research as shown in Scheme 1-7.

Scheme 1-7 The epoxy-curative system studied in this research

1.2 Literature review

Flame retardants (FRs) for polymer materials are additives to reduce the ease of ignition or slow down the spread of the flame after the ignition of these materials. The aim of an FR is to reduce the risks associated with polymer ignition rather than to form a noncombustible material. Nowadays, FRs are mainly classified as: halogenated and halogen-free types.

1.2.1 Halogenated FR for epoxy resins

In current EE applications, halogenated FRs are the most commonly used FRs to provide the required flame retardancy to the epoxy matrix. 2,2',6,6'-tetrabromo-3,3',5,5'-tetramethyl-4,4'-biphenol (TBTMBA)(Levchik and Weil *et al.* 2004), bis(hexachlorocyclopentadieno) cyclooctane (Dechlorane Plus)(Xian, Siddique *et al.* *et al.* 2011), polybrominated diphenylether (BDE), hexabromocyclododecane (HBCD) and tris(dibromopropyl) phosphate (TDBPP) are the most common commercial halogenated FRs for epoxy resin, as well as TBBA. (Rakotomalala, Wagner *et al.* *et al.* 2010)

Halogenated FRs are well-known for their flame inhibition effect in the gas phase during the burning of epoxy resins. They are effective at improving the flame retardancy of epoxy resins. (Rakotomalala, Wagner *et al.* *et al.* 2010) To achieve a UL 94 V-0 rating,

a loading of between 20 wt% and 37 wt% TBBA is needed in the epoxy matrix of a PWB. However, they induce another hazard when they burn: toxic smoke is released when the flame retardant action occurs. Highly toxic halogenated dibenzofurans and dibenzodioxins are formed during the thermal decomposition of halogenated FRs such as BDE. This toxic smoke is the primary cause of the death during the “escape time” in a fire. The environmental hazard of halogenated FRs is severe as well: acid rain is formed when halogen hydride (HX) is released to the atmosphere; in addition, halogenated compounds are able to bio-accumulate in soil and animals.

Scheme 1-8 Halogenated FRs used in epoxy resins

In the past two decades, growing concerns regarding human health and environmental safety have resulted in calls for a reduction in halogenated FRs. A lot of legislation has been enacted and implemented in the Europe Union (EU) and North American. The Waste Electrical and Electronic Equipment (WEEE) Directive and the Restriction on the Use of Certain Hazardous Substances (RoHS) Directive were successively enacted by the EU in 2003. A large number of halogenated FRs have been phased out of use in the EU market in compliance with these two directives. For instance, polybrominated biphenyl and BDE have been completely banned as flame retardants in EE applications since

2004. In addition, RoHS was combined with the European Union Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) in 2008. According to REACH, only registered flame retardant chemicals with hazard data that pass various tests relating to emissions and possible end-of-life issues can be used. Overall, halogenated FRs are associated with a high risk during their usage. The development of halogen-free flame retardants is a promising trend for the future.

1.2.2 Halogen-free FRs for epoxy resins

1.2.2.1 Inorganic and nano FRs

Inorganic FRs are mainly metal hydroxides, natural minerals, borates and layered double hydroxides. Hybrid FRs are mainly hybrid polyhedral oligomeric silsesquioxane (POSS) structures. Inorganic FRs represent a large portion of the global FR market (>50%) as they are low cost, halogen-free and corrosion resistant in comparison to other flame retardants. However, a non-negligible disadvantage of the FRs in this category is their high loading in the polymer matrix. In EE applications, this high FR loading not only significantly influences the processability and melt viscosity of the epoxy matrix but it also reduces the mechanical strength and toughness of the final component. Therefore, these FRs are generally used in combination with phosphorous-containing FRs (P-FRs) in EE applications. A brief description of the principle FRs in this category is provided below.

-Metal hydroxides

Aluminum hydroxide (ATH) and magnesium hydroxide (MDH) are two examples of metal hydroxides that are used as flame retardants. (*et al.*!!! INVALID CITATION !!!) The flame-retardant mechanism is well known as the material acts as a heat sink due to the strong

endothermic reaction that occurs when they decompose. (Camino, Maffezzoli et al. *et al.* 2001) The reaction is shown in Equation 1-1. The consequences of this reaction are that: the high endothermic enthalpy decreases the energy from the ignition source on the matrix surface; the released water is able to dilute the flammable gases arising from the thermal decomposition of matrix; and the aluminum oxide acts as a surface protective barrier on the matrix underneath.

B. Schartel et al. (Schartel, Knoll et al. *et al.* 2006) carried out a comparison between adding phosphonium-modified montmorillonite and ATH, and adding both additives to DGEBA-MHHPA. Antagonistic behavior was found only for some characteristics.

A wide range of ATH particle sizes and shapes are commercially available. For instance, Ground Bayer hydrate ATH, which is the most common ATH used as a FR, has a particle size ranging from 1.5 μm to 35 μm . A tailored dimensioning and sometimes a surface treatment are considered to be the best methods to improve dispersion and reduce ATH loading of the polymer matrix.

-Clay

Clay is a general term referring to natural compounds with a layered aluminum silicate structure. Between the layers, cations such as Na^+ and Ca^{2+} are exchangeable with other organic cations. Montmorillonite (MMT) is typical clay used as reinforcing filler in a polymer. Over the past two decades, modified MMT has been widely used to prepare polymer-clay composites aiming to improve the mechanical stiffness, barrier properties and thermal stability of polymer matrixes. (Wang, Du et al. *et al.* 2002, Kashiwagi, Harris

et al. *et al.* 2004, Li, Schulz et al. *et al.* 2010) Polymer-clay composites show high flame retardancy due to their synergistic effect with P-FRs. For instance, reactive phosphorous-containing organoclay (RPC) was derived from MMT after intercalation with hexyltriphenylphosphonium bromide and grafting with glycidyloxypropyltrimethoxy silane. (Wang, Chen et al. *et al.* 2008) A 5 wt% RPC loading increased LOI value of DGEBA-DDS from 23% to 34%. B. Schartel reported a synergistic interaction between phosphonium-modified MMT and ATH. (Braun, Balabanovich et al. *et al.* 2006) R. Yang et al. studied the synergistic effect between ammonium polyphosphate (APP) and MMT that had been combined in DGEBA-DDS using two methods: physical mixing (APP+MMT) and APP self-assembly growth on the surface of MMT (APP-MMT). An intumescent flame-retardant effect was showed in both two systems. At a 10 wt% loading, DGEBA-DDS with APP-MMT showed higher flame retardancy than that with APP+MMT. The pHRR of an epoxy with APP-MMT decreased from $862 \pm 22 \text{ kW/m}^2$ to $393 \pm 11 \text{ kW/m}^2$; the LOI increased from 23% to 30% in comparison with DGEBA-DDS and a V-0 level was achieved in the UL 94 test. (Zhang, He et al. *et al.* 2015, He, Zhang et al. *et al.* 2016)

Scheme 1-9 RPC structure

-Boron-based compounds

Numerous kinds of boron-based compounds are used as flame retardant in polymer materials, these include boric acid (BA) (Wang, Li et al. *et al.* 2004), boric oxide (B_2O_3) (Dogan and Unlu *et al.* 2014), zinc borates (ZnB) (Bourbigot and Duquesne *et al.* 2007), melamine borate (Schartel, Weiß et al. *et al.* 2010)(Schartel, Weiß et al. *et al.* 2010)(Schartel, Weiß et al. *et al.* 2010)(Schartel, Weiß et al. *et al.* 2010), Schartel, Weiß et al. *et al.* (2010), Schartel, Weiß et al. (2010)(Schartel, Weiß et al. 2010)(Schartel, Weiß et al. 2010)Schartel, Weiß et al. (2010)(Schartel, Weiß et al. 2010)[21][21][21][21], boron phosphate (Zhao, Xu et al. *et al.* 2012)and borosiloxane(Marosi, Márton et al. *et al.* 2003). ZnB, BA and melamine diborate have been reported to show a synergistic effect with other FRs and to act as a char promoter in epoxy resin. (Formicola, De Fenzo et al. *et al.* 2009, Yang, Wang et al. *et al.* 2012, Unlu, Dogan et al. *et al.* 2014) M. Dogan et al. (Dogan and Murat Unlu *et al.* 2014) studied the effect of ZnB, BA and B_2O_3 on the flammability of an epoxy resin containing red phosphorus. A good synergistic effect was found between B_2O_3 and red phosphorous in a DGEBA-polyamine system. Y. Hu et al. (Yu, Xing et al. *et al.* 2016) prepared hexagonal boron nitride (BNO)/modified DGEBA-DDM nanocomposites via a sol-gel process (Scheme 1-10). BNO was uniformly dispersed in the epoxy matrix and had strong interfacial adhesion. The pHRR of modified DGEBA-DDM showed a reduction by 43% at a 3 wt% loading with BNO. P. Liu et al. (Zhang, Liu et al. *et al.* 2016) reported a synergistic effect between an aromatic boronic acid derivative and MH in DGEBA-ethylenediamine.

Scheme 1-10 Illustration of the synthetic process for BNO/MEP nanocomposites

-Layered double hydroxides (LDHs)

LDHs are a host–guest material consisting of positively charged metal hydroxide sheets with intercalated anions and water molecules. (Xu, Zhang *et al.* 2011, Wang and O'Hare *et al.* 2012) The structure of LDH is similar to that of MH, in which some M^{2+} cations are replaced by M^{3+} cations and the excess positive charge is balanced by anionic species as shown in Scheme 1-11. (Coluccini, Sporer *et al.* 2014)

Scheme 1-11 LDH structure (Coluccini, Sporer et al. *et al.* 2014)

LDH materials have been used as flame retardants by Jeffrey W. Gilman in polymer materials since 2000. (Gilman, Jackson et al. *et al.* 2000) The flame retardancy of a wide range of polymers such as polyolefin (Wang, Chen et al. *et al.* 2008, Wang, Das et al. *et al.* 2010, Wang, Das et al. *et al.* 2011, Wang, Leuteritz et al. *et al.* 2011, Kang, Wang et al. *et al.* 2013), poly (methyl methacrylate) (Nyambo, Songtipya et al. *et al.* 2008, Wang, Das et al. *et al.* 2010, Huang, Zhuo et al. *et al.* 2011, Huang, Chen et al. *et al.* 2014), polyester (Wang, Leuteritz et al. *et al.* 2010, Shan, Song et al. *et al.* 2012, Cai, Heng et al. *et al.* 2016) and epoxy resin (Zammarano, Franceschi et al. *et al.* 2005, Wang, Zhou et al. *et al.* 2013, Liu, Yan et al. *et al.* 2014, Kalali, Wang et al. *et al.* 2015, Wang, Kalali et al. *et al.* 2015, Kalali, Wang et al. *et al.* 2016) was improved by the addition of LDHs and modified LDHs. Z. Fang et al. reported a synergistic effect between graphene nanosheets (GNS) and LDH in improving the LOI of a DGEBA-polyamine system. (Liu, Yan et al. *et al.* 2014) D.-Y. Wang et al. did excellent work in developing novel LDHs to improve the flame retardancy of epoxy resins. (Kalali, Wang et al. *et al.* 2015, Wang, Kalali et al. *et al.* 2015, Kalali, Wang et al. *et al.* 2016) A novel bio-based eugenol

derivative, SIEPDP, was synthesized to modify MgAl-LDH. The new SIEPDP-LDH endowed DGEBA-DDS with a strong self-extinguishing ability (V-0 rating) at only 8 wt% loading. (Wang, Kalali et al. *et al.* 2015) In this work, the LDHs indicated or intercalated with multimodifiers showed a strong condensed phase flame-retardant mechanism in epoxy resins. As shown in Scheme 1-12, novel LDHs (sCD-DBS-T-LDH) with multimodifiers (hydroxypropylsulfobutyl-beta-cyclodextrin (sCD) sodium, DBS and taurine (T)) were developed via one-step coprecipitation. (Kalali, Wang et al. *et al.* 2015) Compared to a reference epoxy resin, an epoxy resin with 6 wt% sCD-DBS-T-LDH achieved a V-0 rating in the UL 94 test and showed a significant pHRR reduction (66%) in cone calorimetry testing. The increased amount of residue and enhanced char layer structure significantly improved the shielding effect relating to the transfer of heat and mass during the burning. Furthermore, they reported on other LDH multimodifiers including sCD, functionalized sCD (fCD), phytic acid (Ph), SDBS and chalcone. (Kalali, Wang et al. *et al.* 2016) The novel fCD-DBS-Ph-LDHs not only endowed epoxy resins with a strong self-extinguishing ability but also gave them excellent anti-UV properties at a loading of only 7 wt%.

Scheme 1-12 Synthesis of sCD-DBS-T-LDH (Kalali, Wang et al. *et al.* 2015)

-Silicon-based compounds

Silicon-based compounds such as silica, silicates, organosilanes and silsesquioxane are considered to have low toxicity, high thermal stability and be a compatible halogen-free FR for polymer materials. (Hsiue, Liu et al. *et al.* 2000, Hsiue, Liu et al. *et al.* 2001, Mercado, Galia et al. *et al.* 2006, Gao, Li et al. *et al.* 2011, Qian, Wei et al. *et al.* 2013, Chruściel and Leśniak *et al.* 2015) (Jung, Lim et al. *et al.* 2007) They are well known for their excellent thermal stability in all kinds of FR. No corrosive or toxic compounds are released from an unmodified silicon-based FR with organic compounds during a fire.

Scheme 1-13 Structures of PDMS and POSS

In the literature, polydimethylsiloxane (PDMS) (Li, Jiang et al. *et al.* 2005, Belva, Bourbigot et al. *et al.* 2006, Zhong, Wei et al. *et al.* 2007) (Cardelli, Ruggeri et al. *et al.* 2012) and polyhedral oligomeric silsesquioxane (POSS) (Hsiue, Liu et al. *et al.* 2001, Pellice, Fasce et al. *et al.* 2003, Wu, Song et al. *et al.* 2009, Wang, Hu et al. *et al.* 2010, Zhang, Li et al. *et al.* 2011, Zhang, Li et al. *et al.* 2012) (as shown in Scheme 1-13) are the silicon compounds most commonly used to improve the flame retardancy of polymers via their synergistic effects with phosphorous-containing FRs. Y.-L. Liu et al. (Liu and Chou *et al.* 2005) compared the synergistic effects of various types of silicon additives including nanoscale colloidal silica (CS), tetraethoxysilane (TEOS), and diglycidylether terminated polydimethylsiloxane (PDMS-DG) in a phosphorus-containing epoxy resin. CS failed to show synergism with phosphorus, whereas PDMS-DG and TEOS showed significant synergistic mechanisms between the phosphorous and silicone in the epoxy resin owing to the formation of a protective silicon-based compound layer on the surface of the epoxy resin. W. Zhang et al. (Qi, Zhang et al. *et al.* 2016) reported several effective synergistic systems for POSSs with different P-FRs (Scheme 1-14) in an epoxy resin. At a 5 wt% loading, the epoxy resin/DPP-POSS achieved a V-0 rating in the UL 94 test; the LOI increased from 23% to 33.2% and pHRR reduced by 45% compared to a reference epoxy resin. The main flame retardant activity of DPP-POSS, DPOP-POSS and DOPO-

POSS was an especially strong condensed phase activity through charring and intumescence due to the synergism between phosphorus and silicon in these three POSSs. DOPO-POSS showed a blowing-out extinguishing effect in DGEBA-PDA/DOPO-POSS at 2.5 wt%. (Zhang, Li et al. *et al.* 2011) The LOI of this system increased from 25% to 32% compared with the DGEBA-PDA system and a V-1 rating was achieved in the UL 94 test. The blowing-out effect was also found in the TGDDM-DDS /DOPO-POSS system. (Zhang, Li et al. *et al.* 2014)

Scheme 1-14 P-FRs modified POSS structures(Qi, Zhang et al. *et al.* 2016)

Another application for silicon-based FRs in epoxy resins is to incorporate silicon-based structures into the epoxy resin chain. (Chen, Zhou et al. *et al.* 2014, Chao, Li et al. *et al.* 2015) For instance, epoxy-block-silicone copolymers were synthesized by J. Hao et al. (Chen, Zhou et al. *et al.* 2014) as shown in Scheme 1-15. This method was useful as it improved thermal and mechanical properties.

Scheme 1-15 Epoxy-block-silicone copolymer

1.2.2.2 Nitrogen-containing FRs

With respect to the flame-retardant mechanism, nitrogen-containing FRs (N-FR) are mainly divided into two families. (Morgan and Wilkie *et al.* 2014) One is the ammonia-based FRs which primarily acted via energy consumption (endothermic decomposition) and via a dilution effect on the flammable gases in the gas phase (releasing non-flammable gases) within polymers. The other family is the melamine-based FRs which acted primarily by enhancing the charring process in the condensed phase.

- Ammonium polyphosphate (APP) and its derivatives

The representatives of ammonia-based FRs (Grishchuk, Sorochnytska *et al.* *et al.* 2013) are the ammonia-compounds guanidine (Jin, Xia *et al.* *et al.* 2014), urea, APP (Nie, Hu *et al.* *et al.* 2008, Wu, Wang *et al.* *et al.* 2008, Wang, Liu *et al.* *et al.* 2009, Scharrel, Weiß *et al.* *et al.* 2010, Liu, Zhang *et al.* *et al.* 2011, Lim, Mariatti *et al.* *et al.* 2012, Tang, Wang *et al.* *et al.* 2013, Wu, Zhang *et al.* *et al.* 2013, Zhang, Wu *et al.* *et al.* 2013, Qu, Wu *et al.* *et al.* 2014, Wang, Zhang *et al.* *et al.* 2014, Qin, Li *et al.* *et al.* 2015, Wang, Qian *et al.* *et al.* 2015, He, Zhang *et al.* *et al.* 2016, Tan, Shao *et al.* *et al.* 2016, Matykiewicz, Przybyszewski *et al.* *et al.* 2017), ammonium pentaborate (Alongi and Malucelli *et al.* 2012, Shen *et al.* 2014) and ammonium sulfamate (Dahiya, Kandola *et al.* *et al.* 2013, Coquelle, Duquesne *et al.* *et al.* 2014, Tang, Zhang *et al.* *et al.* 2016). In particular, APP is the most common N-FR used as a single composition FR or as part of intumescent FRs in thermoplastics, thermosets, foams and coatings. As shown in Scheme 1-15, its linear structure is classified as APP I, which has a low degree of polymerization ($n < 100$); or a branched or cross-linked structure, classified as APP II, which has a high degree of polymerization ($n > 1000$).

Scheme 1-16 Structures of APP I and APP II

APP was used as an effective N-FR which could decrease heat release and endow a self-extinguishing ability to epoxy resins by promoting char formation. This effect was influenced by the structures of an epoxy resin. For instance, the pHRR and THR of DGEBA- diethylenetriamine (Gérard, Fontaine et al. *et al.* 2012) were decreased by 31% and 21% respectively, while they were decreased by 70% and 38% respectively in a DGEBA-polyamide (Wang, Liu et al. *et al.* 2009) with a 5 wt% APP loading. DGEBA-polyamide/APP (5 wt%) (Wang, Liu et al. *et al.* 2009) achieved a V-0 rating, whereas DGEBA- triethylenetetramine/APP (5 wt%) (Liu, Zhang et al. *et al.* 2011) achieved a V-1 rating in UL 94 tests. In addition, an epoxy resin containing 5 wt% APP only showed a HB rating in the work of B. Schartel et al. (Schartel, Weiß et al. *et al.* 2010) A remarkable disadvantage of APP is its incompatibility with polymers, which leads to phase separation and spill problems. In current research, APP is usually modified using different compounds by means of an encapsulation method to solve this problem, such as glycidyl methacrylate (Tang, Wang et al. *et al.* 2013), a urea–melamine–formaldehyde shell (Wu, Wang et al. *et al.* 2008, Wang, Zhang et al. *et al.* 2014), melamine–formaldehyde resin (Nie, Hu et al. *et al.* 2008), cyclodextrin (Wang, Qian et al. *et al.* 2015) and vinyltrimethoxysilane (Qin, Li et al. *et al.* 2015). L. Chen et al. (Tan, Shao et

al. *et al.* 2016) modified APP directly using curative polyethyleneimines (PEI) via a cation exchange reaction. The novel curative (PEI-APP, shown in Scheme 1-16) achieved the uniform dispersion of APP in epoxy resin.

Scheme 1-17 PEI-APP structure

Epoxy resin/APP can be considered as an intumescent flame-retardant epoxy resin system mainly owing to the charring property of the epoxy resin. (Schartel, Weiß *et al.* *et al.* 2010, Liu, Zhang *et al.* *et al.* 2011, Tang, Wang *et al.* *et al.* 2013, Qu, Wu *et al.* *et al.* 2014, Tan, Shao *et al.* *et al.* 2016) J.-S. Wang *et al.* (Wang, Liu *et al.* *et al.* 2009) reported that a better intumescent effect was shown in a synergistic system of APP and metal compounds such as CoSA than with epoxy resin alone. The char residue was increased 11% and the total heat release and smoke release were significantly decreased as well.

- Melamine-based FRs

Melamine, its condensation products and salts are the main components of N-FRs. (Morgan and Wilkie *et al.* 2014) Melamine-based FR has an amino group which is able to react with epoxy group under certain condition. (Chen, Wang *et al.* *et al.* 2004) The influence of melamine cyanurate (MC) (Lim, Mariatti *et al.* *et al.* 2012, Wu, Zhang *et al.* *et al.* 2013, Cheng, Li *et al.* *et al.* 2015) and melamine polyphosphate (MPP) (Schartel, Weiß *et al.* *et al.* 2010, Müller and Schartel *et al.* 2016, Matykiewicz, Przybyszewski *et al.* *et al.* 2017) on the flame retardancy of epoxy resin has been widely investigated. Their

structures are shown in Scheme 1-17. The LOI of DGEBA-melamine phosphate was up to 34 %. Used on its own as a FR, MC showed low efficiency in flame retardancy in epoxy and epoxy/glass fiber composites. Y. Liu et al. (Cheng, Li et al. *et al.* 2015) reported that a DGEBA- phenol novolac system showed no rating in the UL 94 test even at 30 wt% MC loading. However, in combination with cyclotriphosphazene, the synergistic system achieved a V-0 rating and the pHRR was significantly decreased. An acidic buffer synergistic mechanism was proposed as the reason for the above results. A V-0 rating was achieved at a high MC loading of 20 wt% in an epoxy/glass fiber composite. (Lim, Mariatti et al. *et al.* 2012) However, MC showed a good synergistic effect with APP in the same epoxy/glass fiber composite as well. When the MC:APP ratio was 1:4, a V-0 rating was achieved easily and the thermal stability and mechanical properties were improved as well compared with a composite containing single compound of them.

Scheme 1-18 Structures of melamine, MC and MPP

D. Matykiewicz et al. (Matykiewicz, Przybyszewski et al. *et al.* 2017) reported that MPP could significantly increase the LOI of epoxy resins. At a 5 wt% loading, the LOI of epoxy resin was increased from 26% to 32%. B. Schartel et al. (Müller and Schartel *et al.* 2016) investigated the influence of MPP in a DGEBA-isophoronediamine system. A significant intumescent flame-retardant effect was observed in the condensed phase. At a 20 wt% loading, the epoxy resin showed a strong self-extinguishing ability

and the heat release was greatly depressed in the burning behavior. A V-0 rating was achieved and the pHRR was reduced by 77%. Moreover, smoke release and CO production were suppressed significantly. In addition, MPP showed excellent synergistic effects with melamine poly (zinc phosphates) (shown in Scheme 1-19).

Scheme 1-19 Melamine poly (zinc phosphates) (Müller and ScharTEL *et al.* 2016)

In the literature, N-FRs are used as a synergistic composition to improve the flame retardancy of polymers. Most of them show endothermic decomposition and release inert volatiles into the gas phase during the burning. In the presence of phosphorous element, an excellent intumescent flame-retardant synergistic effect was shown by promoting char formation in the epoxy resin. Nevertheless, the incompatibility problem still limits the application of N-FRs in epoxy resin in current research.

1.2.2.3 Phosphorous-containing FRs (P-FR)

-Non-reactive P-FRs

Nowadays, it is commonly acknowledged that P-FRs are the most promising choices to replace the halogenated FRs in epoxy resins, especially those used in EE applications. (Rakotomalala, Wagner *et al.* *et al.* 2010, ScharTEL *et al.* 2010, Morgan and Wilkie *et al.* 2014) The advantages of P-FRs are that they are eco-friendly during the burning compared to halogenated FRs. Generally, P-FRs are classified into two types: non-

reactive P-FRs and reactive P-FRs. This relates to whether the incorporation method is either by chemical bonding or by physical mixing with the epoxy resin.

Inorganic, inorganic-organic hybrid and non-reactive organic P-FRs are the main family members of non-reactive P-FRs used in the epoxy resins. (Morgan and Wilkie *et al.* 2014) Red phosphorus, ammonium phosphates and metal phosphate/hypophosphite are the main inorganic P-FRs. Amine and melamine salts of phosphoric acids, metal salts of organophosphinic acids and phosphonium salts are the commonly used inorganic-organic P-FRs. Phosphate and phosphonate esters are the main non-reactive organic P-FRs. A large proportion of the P-FRs are of the non-reactive type as they are easy to produce, store and physically mix with the polymer matrix due to their low cost and chemically inert properties. However, there are many disadvantages of non-reactive P-FRs that need to be overcome as well. Red phosphorous and metal phosphate/hypophosphite are poorly compatible with epoxy resin, which lead to a degradation of the mechanical and electrical properties of epoxy resins. Phase dispersion and separation is the main problem with this type of P-FR in epoxy resins. In addition to the above problem, inorganic-organic P-FRs have low thermal stability during the processing, usage and thermal decomposition of epoxy resins. Non-reactive organic P-FRs show good compatibilities with epoxy resins, whereas they are easy to hydrolyze and spill out of epoxy resins. The high moisture uptake ability limits the high loading of non-reactive P-FRs in some performances, for instance, electric conductivity.

Currently, three approaches are under investigation to obtain flame retardant additives with a high hydrolytic stability and good compatibility with the epoxy matrix, and they have already led to novel commercial FRs: dialkylphosphinate-based salts;

oligomeric rod-shaped FRs and oligomeric star-shaped FRs. (Ciesielski, Burk et al. *et al.* 2017)

Scheme 1-20 Structures of dialkylphosphinate-based salts

X.Q. Liu et al. (Liu, Liu et al. *et al.* 2012, Liu, Liu et al. *et al.* 2014) reported a comparative study of aluminum diethylphosphinate (Al(DEP), Scheme 1-20), aluminum methylethylphosphinate (Al (MEP), Scheme 1-20) and zinc methylethylphosphinate (Zn(MEP), Scheme 1-20) on the flame retardancy of DGEBA-DDM composites. The char residue yield of DGEBA-DDM was significantly increased to 11.5% and 14.3% at a 15 wt% loading of Al(DEP) and Al(MEP) respectively. DGEBA-DDM containing Al(MEP) or Al(DEP) at such a loading achieved a V-0 rating in the UL 94 test. A 20 wt% Zn (MEP) loading was necessary to endow DGEBA-DDM with a V-0 rating. The Tg of DGEBA-DDM/Zn(MEP) was 179 °C which was 20 °C higher than that of DGEBA-DDM/Al(DEP) at a 20 wt% loading. Recently, they (Liu, Liu et al. *et al.* 2015) synthesized aluminum b-carboxylethylmethylphosphinate (Al(CEP), Scheme 1-20) and added it in the same epoxy system. But the flame retardant efficiency was not as good as Al(MEP), Al(DEP) or Zn(MEP). L. Qian et al. (Wang, Qian et al. *et al.* 2015) reported a polymeric aluminum poly-hexamethylenephosphinate additive (APHP, Scheme 1-21) for a DGEBA-DDM system. At a 4 wt% APHP loading, DGEBA-DDM showed a LOI value of 32.7% which was an increase of 6.5% compared with the reference system and it achieved a V-1 rating in the UL 94 test.

Scheme 1-21 Structure of APHP

Bridged aromatic diphenyl phosphates have been reported as acting as non-reactive P-FRs in epoxy resins as well. Polymeric bisphenol A bis (diphenyl phosphate) (PBDP, Scheme 1-22) showed a flame-retardant mechanism in both the gas and condensed phases in a DGEBA-(m-PDA) system. (Zhao, Liu et al. *et al.* 2015) A 20 wt% loading of PBDP was needed to achieve a UL 94 V-0 rating for this system. In a DEN 438-DICY/fenurone system, an 11.5 wt% PBDP loading (2 wt% P loading in epoxy) was needed to achieve a V-0 rating. (Ciesielski, Schäfer et al. *et al.* 2008) DOPO-based rod-shaped P-FRs (as shown in Scheme 1-23) were synthesized and studied in a DEN 438-DICY/fenurone system. (Ciesielski, Schäfer et al. *et al.* 2008) BA-(DOP)₂ and DDM-(DOP)₂ endowed the epoxy with a V-0 rating with a P loading of less than 1.0 wt%, while BA-(DOP)₂-O, BA-(DOP)₂-S and DDM-(DOP)₂-S achieved the same rating with a P loading above 1.2 wt%. In the literature, the flame-retardant efficiency increased when the oxygen atom connected with P was replaced by sulfur. DOPO based bismaleimide (PBMI, in Scheme 1-23) was reported and used in the DGEBA-DDS. (Kumar and Denchev *et al.* 2009) The LOI value for DGEBA-DDS increased from 19% to 26% at 10

wt% PBMI. An enhanced char residue formation was showed in DGEBA-DDS with PBMI.

Scheme 1-22 Structure of PBDP

Scheme 1-23 Structures of DOPO-based rod-shape P-FRs

M. Döring et al. (Zang, Wagner et al. *et al.* 2011) studied star-shaped DOPO and DDPO (5, 5-dimethyl-1, 3, 2-dioxaphosphorinan-2-one) based derivatives (S1, S2 and S3 in Scheme 1-24) as flame retardants in DGEBA-DICY/fenurone and DEN 438-DICY/fenurone systems. With 2.5 wt% P content, the addition of S3 allowed a DGEBA-DICY/fenurone system to achieve a UL 94 V-0 rating, whereas with the addition of S1 or S2 it passed the V-2 rating. Regarding the DEN 438-DGEBA-DICY/fenurone system, a V-0 rating was achieved after the addition of S1, S2 or S3 with a 1.5 wt%, 1.0 wt% or 2.5 wt% P content, respectively. S1 and S2 showed higher flame retardant efficiency in the

DEN 438-DICY/fenurone system than they did in the DGEBA-DICY/fenurone system. Oligomer P-FRs (OS1, OS2 and OS3) were synthesized based on the structures of S1, S2 and S3, as shown in Scheme 1-25. OS1, OS2 and OS3 showed different flame-retardant efficiencies compared with S1, S2 and S3 in a DGEBA-DICY/fenurone system. With 2.5 wt% P content, a UL 94 V-0 rating was achieved after the addition of OS1 or OS2, whereas no rating was attributable after the addition of OS3. The results were explained by the different flame-retardant mechanism for DOPO-based and DDPO-based derivatives. S1, S2, OS1 and OS2 showed mainly gas phase action, whereas S3 and OS3 mainly acted in the condensed phase.

Scheme 1-24 Structures of S1, S2 and S3

B. Schartel et al. studied star-shaped P-FRs DOPP and DOPI, based on DOPO for RTM6 and RTM6/carbon fiber composites (CFR). (Perret, Schartel et al. *et al.* 2011) Both DOPI and DOPP showed effective gas and condensed phase actions by promoting char formation in RTM6 and CFR. A synergism for CFR/DOPI was found in LOI results. With 2 wt% P content, RTM6/DOPI achieved a UL 94 V-0 rating. In these papers, the glass transition temperatures (T_gs) of the epoxy systems were maintained at a consistent level after the addition of the star-shaped P-FRs compared with reference levels. Flame retardants with multi aromatic rings are beneficial to maintain the T_g of epoxy resin.

Scheme 1-25 The structures of OS1, OS2 and OS3

- Reactive P-FRs

Currently, reactive P-FRs have been attracting the attention of many researchers. The development of reactive P-FRs is motivated by the leaching of non-reactive P-FRs from the polymer matrix during processing or usage. Two different approaches have been used to achieve the following aims in epoxy resin: to synthesize reactive phosphorous-containing curatives and co-curatives; to synthesize phosphorous containing epoxy compounds.

Scheme 1-26 Structures of DOPO-based reactive P-FRs used as curatives in epoxy resin

Phosphorous containing anhydride, amide and phenol compounds are the most common reactive P-FR curatives and co-curatives in epoxy resins. (Cho, Fu et al. *et al.* 1998, Wang and Lin *et al.* 1999, Kuo, Wang et al. *et al.* 2001, Nakamura, Asano et al. *et al.* 2003, Artner, Ciesielski et al. *et al.* 2008, Ciesielski, Schäfer et al. *et al.* 2008, Kumar

and Denchev *et al.* 2009, Perret, Schartel *et al.* *et al.* 2011, Zang, Wagner *et al.* *et al.* 2011, Liang, Cao *et al.* *et al.* 2013, Ménard, Negrell *et al.* *et al.* 2015, Xu, Zhao *et al.* *et al.* 2015, Zhao, Liu *et al.* *et al.* 2015) DOPO-based curatives, as shown in Scheme 1-26, were reported to cure o-cresol formaldehyde novolac epoxy and DGEBA.(Cho, Fu *et al.* *et al.* 1998, Wang and Lin *et al.* 1999, Nakamura, Asano *et al.* *et al.* 2003) DGEBA cured with the DOPO-based amide compound shown in Scheme 1-26 had a 32% char residue at 700 °C under N₂ and the LOI value was 30 %(Wang and Lin *et al.* 1999). Two novel phosphorus-containing Mannich-type bases, PTTA and PEDA (as shown in Scheme 1-27), were used as curatives in DGEBA (Liu, Xu *et al.* *et al.* 2009). A DOPO-based diamine compound, DBDH (as shown in Scheme 1-27), was synthesized and used as a co-curative in a DGEBA-DDS system(Artner, Ciesielski *et al.* *et al.* 2008). DGEBA-DDS-DBDH/carbon fiber composites showed a LOI value of 48% and achieved a V-1 rating in the UL 94 test with 2.5 wt% P content in the epoxy matrix. DOPO-based aryl phosphinate dianhydride (BPAODOPE) was reported to be a co-curative with methylhexahydrophthalic anhydride (MeHHPA) in DGEBA. (Liang, Cao *et al.* *et al.* 2013) With a 1.75 wt% P content, DGEBA-MeHHPA/BPAODOPE achieved a V-0 rating in the UL 94 test and the LOI was increased from 19.8% to 29.3%. P.-L. Kuo *et al.* synthesized four phosphonic amide curatives in DGEBA. (Kuo, Wang *et al.* *et al.* 2001) Compared with a DGEBA-DDM system, the DGEBA- phosphonic amide systems showed higher LOI values. A phenophosphazine-containing compound, HD-DPPA (as shown in Scheme 1-27), was studied by S. Liu *et al.* and used as a co-curative for a DGEBA-DDM system(Luo, Yuan *et al.* *et al.* 2016). With 0.19 wt% P content, DGEBA-DDM/HD-DPPA achieved a V-0 rating in the UL 94 test and a LOI value of 31.3%.

Scheme 1-27 Structures of PEDA, DBDH, BPAODOPE and HD-DPPA

Z. Cai et al. (Luo, Yuan et al. *et al.* 2016, Wang, Yang et al. *et al.* 2016) synthesized a DOPO-based oligomer containing amine group, PDAP (Scheme 1-28). As a co-curable to DGEBA-DDM, this novel epoxy system achieved a V-0 rating in the UL 94 test and the LOI value was 35.3% with a 0.64 wt% P content. The T_g of the flame retardant epoxy was 163 °C, which was 8 °C lower than that of DGEBA-DDM. W. Hu et al. studied a branched poly (phosphonamidate-phosphonate) (BPPAPO) oligomer in DGEBA-DDM. (Ma, Yu et al. *et al.* 2016) With a 7.5 wt% BPPAPO loading, the peak heat release rate and total heat release were decreased by 66.2% and 37.3%, respectively compared with DGEBA-DDM. A flame inhibition effect was shown in the gas phase. Recently, R. Jian et al. (Luo, Yuan et al. *et al.* 2016) studied a DOPO-based P-FR (DOPO-ABZ, in Scheme 1-28) containing phosphorous/nitrogen/sulfur elements for DGEBA-DDM. A flame retardant mechanism was proposed suggesting that DOPO-ABZ exerted a predominantly gaseous phase activity in flame-retardant epoxy resin through producing nitrogen/sulfur containing volatiles which can then produce nitrogen/sulfur-containing gases (such as NH_3 , HCN , NO , NO_2 , H_2S , SO_2 and SO_3) with oxygen and

phosphorus-containing free radicals that play an important role in interrupting free radical reactions.

Scheme 1-28 Structure of PDAP

B. Schartel et al. (Braun, Balabanovich et al. *et al.* 2006) investigated the oxidation state of phosphorous on the fire behavior of flame retardant epoxy/carbon fiber composites. Ar_3PO , Ar_2PO_2 , ArPO_3 and PO_4 (as shown in Scheme 1-29) are four phosphorous containing curatives for DGEBA. The results showed that the curative Ar_3PO showed the strongest gas phase flame inhibition effect, whereas PO_4 and Ar_2PO_2 showed the best effect on increasing the amount of char residue in the condensed phase.

Scheme 1-29 Structures of Ar_3PO , Ar_2PO_2 , ArPO_3 and PO_4

An increasing number of reactive phosphorous-containing acid and phenol compounds have been commercialized by several companies such as Clariant SE and Sanko. (Ciesielski, Burk et al. *et al.* 2017) As shown in Scheme 1-30, Exolit EP 150 and Exolit EP 200 are the brand names of two phosphinic acid compounds from Clariant SE. The company claims that they are high-efficiency halogen-free P-FRs for epoxy resins.

HCA-HQ is one of the DOPO-based phenol compounds from Sanko that was introduced onto the flame retardant market as a bifunctional reactive P-FR. A “chain enlogator” concept is claimed for the product.

Scheme 1-30 Structures of Exolit EP 150, Exolit EP 200 and HCA-HQ

The second approach to preparing reactive P-FRs is to chemically bond structures containing epoxy groups with flame retardant groups. (Liu *et al.* 2001, Alcón, Ribera *et al.* 2005, Hergenrother, Thompson *et al.* 2005, Ho, Leu *et al.* 2006, Perez, Sandler *et al.* 2006, Liu, Wang *et al.* 2010, Meenakshi, Sudhan *et al.* 2011) Y.L. Liu (Liu *et al.* 2001) synthesized DOPO-based novolac DOPO-PN via an addition reaction between DOPO and 4-hydroxyl benzoaldehyde. The epoxy systems showed high thermal stability when DOPO-PN was used as curative. K. S. Meenakshi *et al.* (Meenakshi, Sudhan *et al.* 2011) synthesized a DOPO-based tetraglycidyl epoxy (TG-DOPO, in Scheme 1-31). With DDM as a curative, the cured epoxy showed an LOI value of 43% and a char yield of 58%. A UL 94 V-0 rating was achieved as well. Nevertheless, the initial decomposition temperature of the cured epoxy was 215 °C, which was lower than that of a DGEBA-DDM system. The phosphorus-containing epoxy resin DODPP-EP was synthesized from 5, 5-dimethyl-2-oxide-1,3,2-dioxaphosphorinane (DODP) and *p*-benzoquinone (BQ)(Gao, Wang *et al.* 2008). With a 2.0 wt% P

content, the cured DODPP-EP showed an LOI value of 28% and it achieved a V-1 rating in the UL 94 test.

Scheme 1-31 Structure of TG-DOPO

1.3 State-Of-The-Art

A brief overview of flame retardant epoxy resins has been given in Sections 1.1 and 1.2. Numerous articles and patents on halogen-free FRs for epoxy resins have been published by many scientists since the halogenated FRs were found to be non-eco friendly. In current research, several kinds of inorganic FRs such as clays, boron-based compounds, LDH and silicon-based compounds have been found to induce or promote the charring process especially in combination with P-FRs. The research groups of R. Yang, M. Dogan, Y. Hu, D.Y. Wang, B. Scharrel and Y.L. Liu did representative work on inorganic FRs. The action mode of metal hydroxides (ATH and MDH) in polymers was considered to be a cooling effect on the matrix surface due to endothermic decomposition and a diluting effect on flames due to the release of inert gaseous compounds such as water vapor in addition to increasing the char residue. Boron compounds such as BNO showed an effect on promoting highly thermally stable char residues which can protect the polymer matrix. A small loading of intercalated LDH endowed an epoxy with a strong self-extinguishing ability and suppressed the release of heat and smoke. A blowing

effect from DOPO modified POSS compounds was reported to be efficient at improving the flame retardancy of epoxy resin. N-FRs were generally used as a synergistic part, acting as a gas donor in intumescent flame retardant systems. P-FRs were considered to be the most likely candidates to fulfill the requirements for flame retardancy in industry. An increasing number of papers on P-FRs, especially DOPO-based ones, have been published over the past twenty years. A view now accepted by most researchers is that P-FRs act in both the gas and condensed phases during the burning of epoxy resins. Flame inhibition effects in the gas phase are reported in some papers. The phosphorous acidic compounds are able to promote the charring process of epoxy resins in the condensed phase. Due to the efforts in developing halogen-free FRs, novel commercial FRs have been introduced to the market, such as Fyrol PMP, phosphinic acid, APP, ATH, MPP and boron-containing salts.

There are still several challenges that remain unsolved in relation to flame retardant epoxy resins. Firstly, the influence of the chemical structures of P-FRs on the efficiency of flame retardants in epoxy resins was evident in the results of a literature review; however, this relationship has still not been clearly explained. Customizing P-FRs for particular epoxy resins requires a deeper insight into these structure-property relationships. The flame retardant mechanism of P-FRs in epoxy is still too little understood to be able to explain the relationship between molecular structure and flame-retardant efficiency. Currently, the influence of FRs on the mechanical properties and T_g of epoxy resins is being investigated by some research groups. In general, improving flame retardancy (UL 94 V-0 rating) and mechanical properties (such as tensile strength) are mutually exclusive in epoxy resins. Reducing the P-FR loading in epoxies is one

approach to solving this phenomenon. In addition, few research groups studied the flame retardancy of epoxy/fiber composites although this is receiving increasing attention from industry. The difference between the burning of epoxy and epoxy/fiber composites needs to be clarified in the future.

1.4 Objectives

The objectives of this study were to:

- 1) design and synthesis a series of P-FRs with different P' chemical environments in their molecular structures;
- 2) investigate the impact of P' chemical environments on the flame-retardant efficiency of P-FRs in epoxy and epoxy/carbon fiber composites;
- 3) understand the impact P' chemical environments have on the flame-retardant mechanism of P-FRs in the gas and condensed phases of epoxy resin;
- 4) study the thermal stability and mechanical properties of flame-retardant epoxy and epoxy composites.

CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

“Anyone who has never made a mistake has never tried anything new.”

-Albert Einstein

2.1 Materials

Phenylphosphonic dichloride (PPDCI, 90%), phenyl dichlorophosphate (PDCIP, 95%), allylamine (AA, 98%), n-octylamine (OA), 2-phenylethylamine (PA), diethyl ether, tetrahydrofuran (THF), potassium bromide (KBr), triethylamine (TEA) and the curing agent 4,4-diaminodiphenylsulfone (DDS) were purchased from the Sigma Aldrich Corporation. DGEBA type of epoxy resin (EPC) was purchased from Faserverbundwerkstoffe® Composite Technology. RTM6 and carbon fiber fabric were supplied by the composites research, development and application center (FIDAMC) in Spain.

2.2 Nuclear magnetic resonance (NMR)

The chemical shifts of elements in the chemical structures of FPx and FPOx (x=1, 2 and 3) which were synthesized as flame retardants were studied via NMR spectroscopy, as reported in Chapter 3. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on an NMR spectrometer (Oxford AS400, UK) at room temperature using DMSO- d_6 as a solvent. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS) as a reference for ^1H (400 Hz) and ^{13}C NMR (100 MHz). The ^{31}P NMR (162 MHz) spectra were referenced to 85% H_3PO_4 .

2.3 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra for FPx and FPOx (x=1, 2 and 3) were recorded on an FTIR Spectrometer (iS50, USA). The scanning range was from 4000 cm^{-1} to 500 cm^{-1} and the resolution was set as 4 cm^{-1} . Sample preparation was using the KBr pellets method. Samples were dried at $80\text{ }^\circ\text{C}$ in an oven before the FTIR scan.

Variable temperature FTIR (VT-FTIR)

The reactions between the epoxy groups in epoxy resin and the amide groups in FPx and FPOx (x=1, 2 and 3) were studied via variable temperature FTIR (VT-FTIR), as reported in Chapter 4. The VT-FTIR spectra were obtained using a FTIR Spectrometer (iS50, USA) connected with a temperature-controlled heating device. Serial FTIR spectra for EP, EPC/FP1 and EPC/FPO1 were collected regularly from $25\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Fig. 2-1 illustrates the schematic working principle of the VT-FTIR test. The liquid sample was dropped fully into the space between two pressed KBr disks. Then the two disks were put inside the heating sample holder. The scanning range for the FTIR

spectra was $4000\text{--}500\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . The sample was scanned 16 times and the sampling interval was 15.58 s.

Fig. 2-1 Schematic illustration of the VT-FTIR system

2.4 Differential scanning calorimetry (DSC)

The heat history of the EPC, FP1, FPO1, EPC/DDS, EPC/FP1 and EPC/FPO1 mixtures was tested by DSC to show the reactivity between EPC and FP x and FPO x ($x=1, 2$ and 3), as reported in Chapter 4. DSC experiments were carried out on a DSC instrument (Q200, USA) under a nitrogen (N_2) atmosphere. Samples weighing $7 \pm 0.5\text{ mg}$ were tested from $25\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

2.5 Thermal gravimetric analysis (TGA)

The thermal decomposition of EP and flame retardant EP was studied via TGA, as reported in Chapter 4. The testing was performed on a Thermogravimetric Analyzer (Q50, USA) under N_2 . The sample gas purge flow rate was set as $90\text{ mL}/\text{min}$. Samples weighing $7 \pm 0.5\text{ mg}$ were tested over a temperature range from room temperature to $700\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

2.5.1 TGA-FTIR

TGA-FTIR (TGA (Q50, USA) interfaced with a FTIR Spectrometer (iS50, USA)) was used to study the evolved gas products from the thermal decomposition of FP1, FPO1, EP, EFP1-5 and EFPO1-5 at different temperatures, as reported in Chapter 5. Fig. 2-2 describes the scheme of the TGA-FTIR system. The decomposition products in the TGA furnace were transferred through a stainless steel line into the gas cell under a nitrogen carrier gas for FTIR detection. The transfer line and the gas cell were maintained at 300 °C and 250 °C respectively to prevent the condensation of gaseous products. FTIR spectra were recorded regularly over a range of 4000–500 cm^{-1} with a 4 cm^{-1} resolution and averaging 16 scans. The sampling interval was 15.58 s. Samples weighing 15 ± 1 mg were examined by TGA at a heating rate of 10 °C/ min under N_2 flow (90 mL/min) from room temperature to 800 °C.

Fig. 2-2 Schematic illustration of the TGA-FTIR system

2.5.2 TGA-MS

The gaseous compounds evolved from the thermal decomposition of FP1, FPO1, EP, EFP1-5 and EFPO1-5 were studied via TGA-MS (thermal gravimetric analysis-mass spectroscopy) as reported in Chapter 5. The Mass Spectrometer (MSC200, UK) was connected with the TGA (Q50, USA) as shown in Fig. 2-2. Samples weighing 10 ± 0.2 mg were tested under helium with a flow rate of 100 mL/min. The transfer lines between the TG and MS were maintained at 250 °C in order to prevent the condensation of evolved gaseous compounds.

Fig. 2-3 Schematic illustration of the TGA-MS system

2.6 Limiting oxygen index (LOI)

A LOI test was used to evaluate the minimum concentration of oxygen that supports the flaming combustion of a specimen in a flow-controlled mixture of oxygen and nitrogen.

LOI values for EP, EFPx and EFPOx (x=1, 2 and 3) were measured on an Oxygen Index Meter (Fire Testing Technology (FTT), UK) with a precision of $\pm 0.2\%$, as reported in Chapter 4, in accordance with ASTM D2863-97. The sheet dimensions of the samples were $130 \times 6.5 \times 3.2$ mm. The typical LOI test equipment is illustrated in Fig. 2-4, which is taken from ASTM D 2863-97.

Fig. 2-4 Typical equipment layout of LOI test

2.7 UL 94 test

A UL 94 test measures the ability of a sample to self-sustain ignition and propagation in an upward flame spread configuration. The vertical burning tests were carried in a UL 94 Horizontal/Vertical Flame Chamber (FTT, UK) in accordance with ASTM D3801. The sheet dimensions of the samples were $130 \times 13 \times 3.2$ mm.

Fig. 2-5 Illustration of UL 94 test equipment

Tab. 2-1 Rating classification of UL 94 test

Criteria conditions	V-0	V-1	V-2
Afterflame time for each individual specimen t_1 or t_2	≤ 10 s	≤ 30 s	≤ 30 s
Total afterflame time for any condition set (t_1+t_2 for 5 specimens)	≤ 50 s	≤ 250 s	≤ 250 s
Afterflame plus afterglow time for each individual specimen after the second flame application (t_2+t_3)	≤ 30 s	≤ 60 s	≤ 60 s
Afterflame or afterglow of any specimen up to the holding clamp	No	No	No
Cotton indicator ignited by flaming particles or drops	No	No	Yes

Fig. 2-5 shows the UL 94 test layout. The specimen was placed vertically in the clamp. The flame was applied centrally to the bottom of the specimen for 10 s. The

afterflame time (t_1 or t_2) was recorded twice, when the flame was removed and after 10 s each time. The afterglow time was recorded if the specimen shows afterglow phenomenon after the second flame application. A piece of cotton (approximately 50x50x6 mm) was positioned 300 ± 10 mm below the end of the specimen in order to record whether any dripping induced ignition of the cotton. The classification is listed in Tab. 2-1 in accordance with ASTM D3801.

2.8 Cone calorimetry test

A Cone Calorimeter is a bench scale fire testing instrument and it provides a wealth of information on the combustion of polymer materials. It provides comprehensive insight into fire risk via parameters such as time to ignition (TTI), heat release rate (HRR), mass loss, smoke release and carbon monoxide (CO)/carbon dioxide (CO₂) release. Cone calorimetry tests were carried out using a Cone Calorimeter (FTT, UK) in accordance with the ISO 5660-1 standard. Specimens with sheet dimensions of $100 \times 100 \times 3.2$ mm were irradiated at a heat flux of 50 kW/m^2 . Fig. 2-6 shows the scheme for the cone calorimetry test. A specimen was placed under a cone shaped radiant heater. The specimen was ignited once the pyrolysis products were ignited in the atmosphere. The combustion products went through an instrument exhausted pipe and were filtered prior to detection.

Fig. 2-6 Scheme illustrating the cone calorimeter test

2.9 Dynamic mechanical analysis (DMA)

Thermo mechanical properties were examined on a dynamic mechanical analyzer (DMA) (Q800, USA), as reported in Chapter 4. The dimensions of the samples were $35 \times 10 \times 2$ mm. The samples were tested in a single cantilever clamp with a frequency of 1 Hz at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ from room temperature to $240\text{ }^{\circ}\text{C}$.

2.10 Tensile test

Tensile test, as reported in Chapter 4, was measured on an universal Electromechanical Testing Machine (INSTRON 3384, USA) at a rate of $0.5\text{ mm}/\text{min}$. The cross-section dimension of dumbbell-shaped specimens was 4 mm in width $\times$ 4 mm in thickness. The testing length was 25 mm . At least 5 specimens were tested for each sample in this study.

2.11 Scanning electron microscopy with X-ray microanalysis (SEM-EDS)

The morphology of char residues after the cone calorimeter test was studied by SEM-EDS (EVO MA15, Germany), as reported in Chapter 4. The samples were coated with a fine gold layer under 20 kV condition.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF HALOGEN-FREE P-FRS WITH VARIED P' CHEMICAL ENVIRONMENTS

"Sharp tools make good work."

-Confucius

3.1 Synthesis of P-FRs with varied P' chemical environments

Phenylphosphonic dichloride (PPDCl) and phenyl dichlorophosphate (PDCIP) were chosen as one pair acyl chlorides to synthesize P-FRs. The synthetic routes are illustrated in Scheme 3-1. Three amines with different substitutes (allyl group (AA), alkyl chain (OA) and benzene structure (PA)) were used to react with the dichloride group of PPDCl and PDCIP. In the reference study (Hetherington, Greedy et al. *et al.* 2000), the nucleophilic addition reaction between PPDCl and amines showed a low yield of 41%. In this study, the synthetic procedure was modified aiming to increase the yield of this reaction. In the following description, P-FRs synthesized from the reaction between three amines and PPDCl were named FPx (x=1, 2 and 3), while those synthesized from the reaction between the amines and PDCIP were named FPOx (x=1, 2 and 3), as shown in Scheme 3-1.

The general synthesis procedure for P-FRs developed from Reference (Hetherington, Greedy et al. *et al.* 2000) was the following. In a 500 mL three-neck flask, an appropriate amine compound (AA, OA or PA) (0.21 mol) and triethylamine (TEA, 0.2 mol) were dissolved in solvent at 0~5 °C. Then a mixture of an appropriate chloride compound (PPDCl or PDCIP, 0.1 mol) and solvent was added dropwise into the flask at 0~5 °C. The mixture was stirred at 0~5 °C for 2 h. Then the stirring was continued at room temperature (RT) for 2~5 h. After the stirring, the solid-liquid mixture was filtered off to remove the triethylamine hydrochloride salt and the filtrate was evaporated under vacuum to obtain the crude P-FR product. The product was purified by washing with de-ionized water three times.

Scheme 3-1 The synthetic routes for P-FRs with varied P' chemical environments

3.1.1 Synthesis of N, N'-diallyl-p-phenylphosphonicdiamide (FP1)

Synthesis of FP1 followed the general procedure by using an amine compound of AA (0.21 mol) and a chloride compound of PPDCl (0.1 mol). The solvent chosen was either diethyl ether or THF. Firstly, 0.21 mol AA and 0.2 mol TEA were dissolved in 100~200 mL diethyl ether at 0~5 °C. Then the mixture of 0.1 mol PPDCl and 50~100 mL diethyl ether was added dropwise into the previous mixture at 0~5 °C. The reaction was allowed to continue at an even temperature for 2 h. Then the mixture was stirred for 2~5 h at RT. After that, the triethylamine hydrochloride salt was filtrated off. Crude FP1 was obtained after evaporation of the filtrate. De-ionized water was used to wash the crude FP1 three times. FP1 (melting point (m.p.) 67 °C; yield, 80%) was obtained as a white solid at room temperature.

3.1.2 Synthesis of N, N'-dioctyl-p-phenylphosphonicdiamide (FP2)

Synthesis of FP2 followed the procedure described above; using an amine compound of OA and a chloride compound of PPDCl. 0.21 mol OA and 0.2 mol TEA were dissolved in 100~200 mL diethyl ether or THF at 0~5 °C. Then the mixture of 0.1 mol PPDCl and 50~100 mL diethyl ether or THF was added dropwise into the previous mixture at 0~5 °C. The reaction was allowed to continue at 0~5 °C for 2 h. Then the mixture was stirred for 2~5 h at RT. After the reaction, the triethylamine hydrochloride salt was filtrated off. Crude FP2 was obtained after evaporation of the filtrate. De-ionized water was used to wash the crude FP2 three times. FP2 was obtained as a white solid. (m.p. 75 °C; yield, 80%);

3.1.3 Synthesis of N, N'-di-phenylethyl-p-phenylphosphonicdiamide (FP3)

Synthesis of FP3 followed the above procedure by using an amine compound of PA (0.21 mol) and a chloride compound of PPDCl (0.1 mol). 0.21 mol PA and 0.2 mol TEA were dissolved in 100~250 mL diethyl ether or THF at 0~5 °C. Then the mixture of 0.1 mol PPDCl and 50~100 mL diethyl ether or THF was added dropwise into the previous mixture at 0~5 °C. The reaction was allowed to continue at 0~5 °C for 2 h. Then it was allowed to continue for 2-5 h at room temperature. After the reaction, the triethylamine hydrochloride salt was filtrated off. Crude FP3 was obtained after evaporation of the filtrate. De-ionized water was used to wash the crude FP3 three times. FP3 was obtained as a light yellow solid (m.p. 85 °C; yield, 85%);

3.1.4 Synthesis of N,N'-Diallyl-phenylphosphoricdiamide (FPO1)

The detail procedure to synthesize FPO1 was as follows: 0.20 mol AA and 0.2 mol TEA were dissolved in 100~200 mL diethyl ether or THF at 0~5 °C. Then the mixture of 0.1 mol PDCIP and 50~100 mL diethyl ether was added dropwise into the previous mixture at 0~5 °C. The reaction was allowed to continue at 0~5 °C for 2 h. Then it was allowed to continue for 2~5 h at room temperature. After the reaction, the triethylamine hydrochloride salt was filtrated off. Crude FPO1 was obtained after evaporation of the filtrate. De-ionized water was used to wash the crude FPO1 three times. FPO1 was obtained as a white solid at room temperature (m.p.:64 °C; yield, 95%);

3.1.5 Synthesis of N, N'-diamyl-p-phenylphosphoricdiamide (FPO2)

Synthesis of FPO2 followed the procedure described in 3.1.4 by using an amine compound of OA (0.21 mol). 0.20 mol OA and 0.2 mol TEA were dissolved in 100~200 mL diethyl ether or THF at 0~5 °C. Then the mixture of 0.1 mol PDCIP and 50~100 mL diethyl ether or THF was added dropwise into the previous mixture at 0~5 °C. The reaction was allowed to continue at 0~5 °C for 2 h. Then it continued for 2~5 h at room temperature. After the reaction, the triethylamine hydrochloride salt was filtrated off. Crude FPO2 was obtained after the evaporation of the filtrate. De-ionized water was used to wash the crude FPO2 for three times. FPO2 was obtained as a white solid (m.p. 73 °C; yield, 95%);

3.1.6 Synthesis of N, N'-di-phenylethyl-p-phenylphosphonicdiamide (FPO3)

Preparation of FPO3 followed the procedure described in 3.1.4 by using an amine compound of PA (0.21 mol). 0.20 mol PA and 0.2 mol TEA were dissolved in 100~200 mL diethyl ether or THF at 0~5 °C. Then the mixture of 0.1 mol PDCIP and 50~100 mL diethyl ether or THF was added dropwise into the previous mixture at 0~5 °C. The reaction was allowed to continue at 0~5 °C for 2 h. Then it was allowed to continue for 2~5 h at room temperature. After the reaction, the triethylamine hydrochloride salt was filtrated off. Crude FPO3 was obtained after evaporation of the filtrate. De-ionized water was used to wash the crude FPO3 three times. FPO3 was obtained as a yellow solid (m.p. 82 °C; yield, 95%);

3.2 Characterizations

3.2.1 NMR

NMR spectroscopy is the most common spectral method used in modern research. It is used to characterize the structures of organic compounds by detecting the magnetic properties of certain atomic nuclei. In this section, NMR analysis was used to characterize the synthesized P-FRs. Fig. 3-1 to 3-7 show the ^1H , ^{13}C and ^{31}P NMR spectra of FPx and FPOx (x=1, 2 and 3).

In the ^1H spectra it is possible to distinguish the chemical environments of each hydrogen atom in the structure of the compound by means of a chemical shift (δ), coupling constant and integrated intensity area. Fig. 3-1 shows the ^1H NMR spectra and chemical structures for FPx (x=1, 2 and 3) in which the hydrogen atoms were classified by different chemical environments. The assignments of the peaks are marked in the figure. In detail,

FP1: (ppm) 7.8, 7.4 (H-benzene ring, 5 H); 5.8 (HC=, 2 H); 5.1, 4.9 (H₂C=, 4 H); 3.4 (-H₂C-, 4 H);

FP2: (ppm) 7.7-7.4 (H-benzene ring, 5H); 2.7 (-H₂C-(NH), 4 H); 1.3, 1.5 (-H₂C-, 24 H); 0.8 (H₃C-, 6 H);

FP3: (ppm) 7.7-7.2 (H-benzene ring, 15 H); 2.7, 3.1 (H₂C-, 8 H).

In the ^{13}C spectra, each carbon nucleus has a characteristic δ owing to its own electronic environment. Fig. 3-2 shows the ^{13}C spectra and chemical structures for FPx (x=1, 2 and 3) in which the carbon atoms are numbered according to the different chemical environments. The peaks in each spectrum are assigned in the figure as well.

In detail:

FP1: (ppm) 137.8, 135.5(134.3), 131.2, 127.8, 114.2, 42.4;

FP2: (ppm) 136.8(135.2), 131.8, 131.1, 128.4, 44.4, 31.0, 28.2, 23.3, 22.0, 13.8;

FP3: (ppm) 140.4, 136.5(135.0), 131.8, 128.9, 126.6, 42.5, 38.7.

Fig.3-1 ^1H NMR spectra for FP1, FP2 and FP3

Fig.3-2 ^{13}C NMR spectra for FP1, FP2 and FP3

The ^{31}P spectra clearly show the chemical environment of the phosphorous nucleus. Fig. 3-3 shows the ^{31}P spectra for FPx (x=1, 2 and 3). One dominant peak was shown on each spectrum, indicating that the chemical environment of the phosphorous nucleus was single in each structure for FPx (x=1, 2 and 3). The chemical shifts of FPx (x=1, 2 and 3) show at 19.8, 20.4 and 20.0 ppm respectively. Overall, the assignments of the ^1H , ^{13}C and ^{31}P NMR spectra were consistent with the structural analysis of FPx (x=1, 2 and 3).

Fig.3-3 ^{31}P spectra for FP1, FP2 and FP3

Fig. 3-4 shows the spectra for the ^1H spectra chemical structures of FPOx (x=1, 2 and 3) in which the hydrogen atom was grouped in different chemical environments. The assignments for the ^1H spectra are as follows:

FPO1: (ppm) 7.4-7.0 (Ar-H, 5H); 5.9-5.7 (=CH, 2H); 5.2- 5.0 (=CH₂, 4H);
3.5-3.4 (-CH₂-, 4H);

FPO2: (ppm) 7.7-7.4 (H-Ar, 5H); 2.6 (-H₂C (NH), 4H); 1.3-1.5 (-H₂C-,
12H); 0.9 (-H₃C, 6H);

FPO3: (ppm): 7.4-7.1 (H-Ar, 15H); 2.7-3.1 (-H₂C-, 8H).

Fig.3-4 ¹H NMR spectra for FPO1, FPO2 and FPO3

Fig. 3-5 shows the ¹³C spectra and chemical structures for FPO_x (x=1, 2 and 3) in which the carbon atoms were numbered according to the different chemical environments. The peaks in ¹³C spectra are assigned as:

FPO1: (ppm) 151.6, 137.4, 129.2, 123.6, 120.5, 114.5, 43.1;

FPO2: (ppm) 152.5, 129.9, 124.1, 121.1, 41.3, 31.9, 29.5, 26.9, 22.7, 14.6;

FPO3: (ppm) 152.3, 140.2, 129.9, 129.3, 128.9, 124.3, 121.1, 43.1, 38.3.

Fig.3-5 ^{13}C NMR spectra for FP1, FP2 and FP3

Fig. 3-6 shows the ^{31}P spectra for FPOx (x=1, 2 and 3). A single chemical environment for the phosphorous nucleus was indicated as only one main peak was shown in each spectrum for FPOx (x=1, 2 and 3). The peaks for ^{31}P were at 16.3, 14.4 and 13.9 ppm respectively for FPOx (x=1, 2 and 3). Overall, the analysis of NMR spectra clearly shows that the synthesis of FPOx (x=1, 2 and 3) was successful.

Fig.3-6 ^{31}P NMR spectra for FPO1, FPO2 and FPO3

3.2.2 FTIR

Fourier transform infrared spectra (FT-IR) collected the information on chemical structure by recording the variation in functional groups. The FT-IR spectra for FPx and FPOx (x=1, 2 and 3) for this study are shown in Fig. 3-7 and Fig. 3-8.

The peak assignments for FP1 are as follows: 3200 cm^{-1} (-NH-, *s.v.*); 3010-3080 cm^{-1} (C-H of Ar and $\text{CH}_2=\text{CH}$, *s.v.*); 2889, 2583 cm^{-1} (C-H of $-\text{CH}_2-$, *s.v.*); 1644, 1600, 1492, 1431 cm^{-1} (C=C of C=C and Ar, *s.v.*); 1470 cm^{-1} (Amide I); 1180 cm^{-1} (P=O, *s.v.*); 1120 cm^{-1} (Amide II); 1058 cm^{-1} (C-N, *s.v.*) and 1017 cm^{-1} (P-N-C, *s.v.*).

The peak assignments for FP2 are as follows: 3200 cm^{-1} (-NH-, *s.v.*); 3083, 3061 cm^{-1} (C-H of Ar, *s.v.*); 2891, 2853 cm^{-1} (C-H of $-\text{CH}_2$ and $-\text{CH}_3$, *s.v.*); 1591, 1465, 1440 cm^{-1} (C=C of Ar, *s.v.*); 1470 cm^{-1} (Amide II); 1176 cm^{-1} (P=O, *s.v.*); 1096 cm^{-1} (Amide I); 1068 cm^{-1} (C-N, *s.v.*) and 1006 cm^{-1} (P-N-C, *s.v.*).

The peak assignments for FP3 are as follows: 3200 cm^{-1} (-NH-, *s.v.*); 3061, 3020 cm^{-1} (C-H of Ar, *s.v.*); 2938, 2869 cm^{-1} (C-H of $-\text{CH}_2$, *s.v.*); 1647, 1600, 1480, 1440 cm^{-1} (C=C of Ar); 1470 cm^{-1} (Amide II), 1242 cm^{-1} (P=O, *s.v.*); 1129 cm^{-1} (Amide I); 1056 cm^{-1} (C-N, *s.v.*) and 1015 cm^{-1} (P-N-C, *s.v.*).

Fig.3-7 FT-IR spectra for FP1, FP2 and FP3

The peak assignments for FPO1 are as follows: 3238 cm^{-1} (-NH-, *s.v.*); 3019-3075 cm^{-1} (C-H of Ar and $\text{CH}_2=\text{CH}$, *s.v.*); 2901, 2586 cm^{-1} (C-H of $-\text{CH}_2-$, *s.v.*); 1644, 1600, 1492, 1431 cm^{-1} (C=C of C=C and Ar, *s.v.*); 1456 cm^{-1} (Amide II); 1254 cm^{-1} (P=O, *s.v.*); 1210 cm^{-1} (Ar-O, *s.v.*); 1170 cm^{-1} (Amide I); 1140 cm^{-1} (C-N, *s.v.*); 1046 cm^{-1} (P-N-C, *s.v.*) and 997 cm^{-1} (P-O-Ar, *s.v.*).

The peak assignments for FPO2 are as follows: 3238 cm^{-1} (-NH-, *s.v.*); 3043 cm^{-1} (C-H of Ar, *s.v.*); 2934, 2856 (C-H of $-\text{CH}_2-$ and $-\text{CH}_3$, *s.v.*); 1600, 1500, 1450 cm^{-1} (C=C of Ar, *s.v.*); 1470 cm^{-1} (Amide II); 1260 cm^{-1} (P=O, *s.v.*); 1215 cm^{-1} (Ar-O, *s.v.*); 1167 cm^{-1} (Amide I); 1160 cm^{-1} (C-N, *s.v.*); 1025 cm^{-1} (P-N-C, *s.v.*) and 1006 cm^{-1} (P-O-Ar, *s.v.*).

The peak assignments for FPO3 are as follows: 3238, 3216 cm^{-1} (-NH-, *s.v.*); 3069, 3033 cm^{-1} (C-H of Ar, *s.v.*); 2934, 2861 cm^{-1} (C-H of $-\text{CH}_2-$, *s.v.*); 1600, 1587, 1490, 1423 cm^{-1} (C=C of Ar, *s.v.*); 1453 cm^{-1} (Amide II); 1253 cm^{-1} (P=O, *s.v.*); 1225

$\text{cm}^{-1}(\text{Ar-O}, s.v.)$; $1197 \text{ cm}^{-1}(\text{Amide I})$; $1167 \text{ cm}^{-1}(\text{C-N}, s.v.)$; $1080 \text{ cm}^{-1}(\text{P-N-C}, s.v.)$
and $975 \text{ cm}^{-1}(\text{P-O-Ar}, s.v.)$.

Fig.3-8 FT-IR spectra for FPO1, FPO2 and FPO3

3.3 Summary

Tab.3-1 The P' chemical shifts and IR peaks of P=O of P-FRs

P-FRs	δ^a (P, ppm)	IR peak (P=O, cm^{-1})
FP1	19.8	1176
FP2	20.4	1180
FP3	20.0	1242
FPO1	16.3	1254
FPO2	14.4	1215
FPO3	13.9	1253

a meant chemical shift

Two series of P-FRs (FPx and FPOx, x=1, 2 and 3) with varied P' chemical environments were designed and synthesized successfully as described in Section 3.1 and 3.2. In Tab. 3-1, the P' chemical shifts showed sequences: “FP1<FP3<FP2” and

“FPO3<FPO2<FPO1”. Those of FPx were showed at higher chemical shift than those of FPOx (x=1, 2 and 3). The IR peaks of P=O in FPx and FPOx (x=1, 2 and 3) were at different wavenumbers as well in FTIR spectra. The results revealed that the P' chemical environments were modified due to the different number of oxygen atoms and side groups connected with P in synthesized P-FRs. Both FPx and FPOx (x=1, 2 and 3) were phosphamide compounds, while FPx showed a lower oxidation extension compared with FPOx (x=1, 2 and 3). The impact of side groups varied from alkyl, allyl and phenyl groups was not as strong as that of number of oxygen atoms connected with P in each P-FR series.

CHAPTER 4

P_{REPARATION AND PROPERTIES OF THE FLAME-RETARDANT EPOXY RESIN}

“Energy and persistence conquer all things.”

~Benjamin Franklin

4.1 Introduction

Two series of P-FRs (FP_x and FPO_x, x=1, 2 and 3) were synthesized and characterized as described in Chapter 3. The number of oxygen atom connected with P were 0 and 1 in FP_x and FPO_x, (x=1, 2 and 3), respectively. The oxidation state of P varied due to the different number of oxygen atoms. The steric hindrances around P in the structures of FP_x varied due to the different side groups as did those in the structure of FPO_x (x=1, 2 and 3). The impacts of FP_x and FPO_x (x=1, 2 and 3) on thermal stability, flame retardancy and mechanical properties were studied in Chapter 4. The reactivity between EPC and FP_x/FPO_x (x=1, 2 and 3) were studied using DSC and VT-FTIR. LOI, UL 94 and cone calorimetry tests were employed to investigate

the impacts of FPx and FPOx (x=1, 2 and 3) on the flame retardancy of epoxy resins; TGA was used to study the thermal stability of the flame retardant epoxy resins. In addition, the mechanical properties of the flame retardant epoxy resins were characterized using a tensile test and DMA.

4.2 Reactivity of FPx and FPOx (x=1, 2 and 3) with the epoxy groups

The secondary amine (-NH-) group in the structures of FPx and FPOx (x=1, 2 and 3) was expected to be reactive with the epoxy groups in the structure of the epoxy resins during the curing behavior. In this section, DSC and VT-FTIR were employed to study the reactivity of -NH- with the epoxy groups from 100 °C to 220 °C. FP1 and FPO1 were chosen as being representative of FPx and FPOx (x=1, 2 and 3). The mole ratio of the N-H groups and the epoxy groups was a stoichiometric ratio (1:1) in DSC and VT-FTIR.

4.2.1 DSC analysis

DSC measures the heat phenomenon of a material under a certain temperature range. The reaction between -NH- and the epoxy groups was exothermic, which was revealed by the DSC thermograms. Fig. 4-1 shows the DSC thermograms for EPC, FP1, FPO1, EPC/DDS, EPC/FP1 and EPC/FPO1 from room temperature (RT) to 220 °C.

In Fig. 4-1(A), EPC and FP1 showed no visible exothermic peaks on their thermograms. It means that both of them were thermally stable from RT to 220 °C.

The curing behavior of EPC/DDS started around 140 °C along with a strong exothermic phenomenon. On the DSC thermogram for EPC/FP1 a remarkable exothermic peak started from around 110 °C. The intensity of the exothermic phenomenon was comparable with that of EPC/DDS. The above information showed that the –NH– in the structure of FP1 was able to react with the epoxy groups and the reaction started at a lower temperature than that for EPC/DDS.

Fig.4-1 (A): DSC thermograms for EP, EPC/FP1, EPC/DDS and FP1; (B): DSC thermograms for EP, EPC/FPO1, EPC/DDS and FPO1.

In Fig. 4-1 (B), the DSC thermogram for FPO1 showed an exothermic peak from 150 °C to 210 °C. The peak value was at 190 °C. The DSC thermogram for EPC/FPO1 also showed an exothermic peak from 150 °C, while the peak value was at around 170 °C. The exothermic phenomenon for EPC/FPO1 appeared again from 190 °C. The intensity was comparable to that of EPC/DDS. The different peak positions of the first peak indicated that different phenomena were showed in FPO1 and

EPC/FPO1. Curing reaction was considered to occur in EPC/FPO1. These results showed that the –NH– in the structure of FPO1 was reactive with the epoxy groups in the structure of the epoxy resins as well.

4.2.2 VT-FTIR analysis

A series of FT-IR spectra for EPC/FP1 (or FPO1) were collected regularly from RT to 220 °C using VT-FTIR. Fig. 4-2 shows the contour maps for the peak at 921 cm⁻¹ vs T for EPC (a), EPC/FP1 (b) and EPC/FPO1 (c). The peak at 921 cm⁻¹ was the characteristic IR absorption peak of an epoxy group. The peak at 1110 cm⁻¹ was characteristic of the IR absorption peak of an ether group. In order to show the variation in the epoxy groups during heating, one ratio $R (i_{\text{(epoxy group)}}/i_{\text{(ether group)}})$ was defined, in which *i* means IR peak height of functional group. Since the ether group in the EPC structure was thermally stable from RT to 220 °C, the R-value should decrease if the epoxy groups reacted with the –NH– in the structures of FP1 or FPO1; otherwise the R-value would be maintained as a constant throughout the heating. Fig. 4-3 shows $R (i_{\text{(epoxy group)}}/i_{\text{(ether group)}})$ values vs T curves for EPC, EPC/FP1 and EPC/FPO1 from VT-FTIR.

Fig.4-2 The contour maps for the peak at 921 cm^{-1} vs T for EPC (a), EPC/FP1 (b) and EPC/FPO1(c)

In Fig. 4-2, the peak at 921 cm^{-1} for EPC (a) showed a constant intensity color as T increased from 100 to 220 °C. In Fig. 4-3, the R-value for EPC was constant from 110 to 220 °C as well. Both epoxy and ether groups were thermally stable from 110 °C to 220 °C. Compared with EPC, the peak at 921 cm^{-1} showed a clearly variation of intensity color as T increased, this was the case both in EPC/FP1 and EPC/FPO1. It suggested that the concentration of epoxy groups in EPC/FP1 and EPC/FPO1 might reduce from 100 to 220 °C. Furthermore, R-values for EPC/FP1 and EPC/FPO1 showed a clear decrease from 110 to 220 °C in Fig. 4-3. The varied intensity colors and decrease of R-values was due to the epoxy groups being reacted with -NH- in EPC/FP1 and EPC/FPO1.

Fig.4-3 R ($i(\text{epoxy group})/i(\text{ether group})$) vs temperature curves for EP, EPC/FP1 and EPC/FPO1 from VT-FTIR tests

On the basis of the results from DSC and VT-FTIR, the reaction between the -NH- groups in the structure of FP1 or FPO1 and the epoxy groups in the EPC structure was evidently verified. It was suggested that FP_x and FPO_x ($x=1, 2$ and 3) were incorporated into the cured structures of EP via chemical bonds. They might be in the middle of the chain or at the end of the chain. Fig. 4-4 describes the proposed molecular chain structures of EPC/DDS/ FP_x (or FPO_x) ($x=1, 2$ and 3). The migration issue of FP_x (or FPO_x) ($x=1, 2$ and 3) in EPC/DDS was avoided due to incorporation by chemical bonding.

Fig. 4-4 The proposed molecular chain of EPC/DDS/FPx (or FPOx) (x=1, 2 and 3)

4.3 Preparation of flame retardant epoxy

The epoxy equivalent weight of EPC was 185. The stoichiometric amount of curing agent DDS in weight parts per 100 g epoxy resin (phr) was calculated using the following equation (4-1):

$$phr = \frac{\text{Equivalent weight of amine}}{\text{Equivalent weight of epoxy resin}} * 100 \quad 4-1$$

In which: equivalent weight of epoxy resin (EEW) was 185 and equivalent weight of amine (AEW) was calculated from equation (2):

$$AEW = \frac{\text{Molecular weight of amine}}{\text{number of active hydrogen atoms of amine}} \quad 4-2$$

The phr of DDS was calculated as below:

$$phr \text{ of DDS} = \frac{\frac{248.3}{4}}{185} * 100 = 34 \quad 4-3$$

Therefore, the mass ratio of EPC/DDS was 100 g/34 g.

The preparation of EPC/DDS/FPx (EFPx, x=1, 2 and 3) and EPC/DDS/FPOx (EFPOx, x=1, 2 and 3) followed the general procedure described below. First, the appropriate amount of P-FR (FP1-1, 3, 5 wt%; FPO1-1, 3, 5, 30 wt%; FP2 and FPO2-7.5 wt%; FP3 and FPO3-7.7 wt%) was mixed with EPC at 100 °C and stirred

for 5 minutes. Then the stoichiometric amount of curing agent DDS was slowly added into the EPC/P-FR mixture at 130 °C with continual stirring until the mixture was totally transparent. The EPC/DDS/P-FR mixture was poured into a pre-heated polytetrafluoroethylene (PTFE) mold at 160 °C. The curing temperature profile was set as 160 °C for 1 h, 180 °C for 2 h and 200 °C for 1 h. The preparation of EPC/DDS (EP) was similar but missing the first step. All the formulas for EP, EFP_x and EFPO_x (x=1, 2 and 3) were listed in Tab. 4-1.

Tab. 4-1 The formulas for prepared EP, EFP_x and EFPO_x (x=1, 2 and 3)

Samples	EPC/DDS (wt: wt)	FP _x (wt%)	FPO _x (wt%)	P ^a (wt%)
EP	74.6:25.4	--	--	0
EFP1-1	73.9:25.1	1	--	0.14
EFP1-3	72.4:24.6	3	--	0.40
EFP1-5	70.9:24.1	5	--	0.67
EFPO1-1	73.9:25.1	--	1	0.14
EFPO1-3	72.4:24.6	--	3	0.40
EFPO1-5	70.9:24.1	--	5	0.67
EFPO1-30	52.2:17.8	--	30	4.00
EFP2-7.5	69.0:23.5	7.5		0.67
EFPO2-7.5	69.0:23.5	--	7.5	0.67
EFP3-7.7	68.9:23.4	7.7		0.67
EFPO3-7.7	68.9:23.4	--	7.7	0.67

a = the phosphorous content in the prepared EP and flame retardant EP

4.4 Flame retardancy

4.4.1 LOI and UL 94 tests

LOI and UL 94 tests are two typical tests used to study the flammability of polymer materials. The LOI test measures the minimum oxygen concentration which is able to support the burning of a polymer. The vertical rating test in the UL 94 test is used to study the extinguishing ability of a polymer. In this section, the LOI and UL 94 tests were used to investigate the impact of FPx and FPOx ($x=1, 2$ and 3) on the flammability of EP. The results are showed in Tab. 4-2.

EP showed an LOI value of 22% and was burnt out in the UL 94 test, showing that EP was high flammable. In Tab. 4-2, the LOI values of EFPx and EFPOx ($x=1, 2$ and 3) clearly increased compared with that of EP. First of all, the LOI of EP increased with the increasing loading of FPx and FPOx ($x=1, 2$ and 3). EFP1 showed LOI values of 28%, 29% and 31% respectively at a 1, 3 and 5 wt% FP1 loading. However, the increase of LOI was not proportionally related with the FP1 loading in EP. EFPO1 also showed a similar change in comparison to EP when the FPO1 loading was increased. In a horizontal comparison with EFPOx, the LOIs for EFPx ($x=1, 2$ and 3) were higher respectively for a constant P content. The LOI for EFPO1-3 was 26%, while that for EFP1-3 was 29%; the LOI for EFPO2-7.5 was 33%, while that for EFP2-7.5 was 37%. With a 30 wt% FPO1 loading, EFPO1-30 showed a LOI value of 28% which was equal to that for EFP1-1. In addition, EFPx ($x=1, 2$ and 3) showed different LOI values as the side group changed in the structures of FP1,

FP2 and FP3 at a constant P content, 0.67 wt%. The LOIs of EFPx (x=1, 2 and 3) showed a sequence: $\text{EFP1-5} < \text{EFP2-7.5} = \text{EFP3-7.7}$. The LOIs of EFPO x (x=1, 2 and 3) showed a sequence of $\text{EFPO1-5} < \text{EFPO2-7.5} < \text{EFPO3-7.7}$. The results showed that the varied number of oxygen atom and side group connected with P influenced the impact of P-FRs on LOI of EP: A higher LOI was obtained when the number of oxygen atom was lower; the LOI became higher as the steric hindrance of the side group increased.

In the UL 94 test, EFPx and EFPOx (x=1, 2 and 3) showed a significant difference. With a 0.67 wt% P content, EFPOx (x=1, 2 and 3) showed no rating. EFPO1-5 showed no extinguishing ability and burnt out as thoroughly as EP in the test. EFPO2-7.5 and EFPO3-7.7 showed extinguishing ability, whereas neither of them reached a rating either. Their burnt lengths were long (90 ± 5 mm and 100 ± 5 mm respectively). EFPO1 achieved a V-1 rating at a 30 wt% loading of FPO1. In contrast, EFPx (x=1, 2 and 3) was classified as having a V-0 rating in the UL 94 test, demonstrating that EFPx (x=1, 2 and 3) has a strong self-extinguishing ability at a 0.67 wt% loading of P content. EFP1-1 and 3 showed self-extinguishing phenomena which were stronger than EFPO1-1 and EFPO1-3. The burnt lengths of EFP1-1 and EFP1-3 were 50 ± 5 and 40 ± 5 mm shorter than those of EFPO1-1 and EFPO1-3, respectively. In addition, EFP1-3 achieved a V-1 rating.

Tab. 4-2 Results for LOI and UL 94 tests of EP, EFPx and EFPOx (x=1, 2 and 3)

Samples	LOI (%)	UL 94 (3.2 mm)	
		Rating	Burnt length (mm)
EP	22	NR ^a	130
EFP1-1	28	NR ^a	50±5
EFP1-3	29	V-1	40±5
EFP1-5	31	V-0	15±5
EFPO1-1	25	NR ^a	130
EFPO1-3	26	NR ^a	130
EFPO1-5	27	NR ^a	130
EFPO1-30	28	V-1	40±5
EFP2-7.5	37	V-0	15±5
EFPO2-7.5	33	NR ^a	90±5
EFP3-7.7	37	V-0	15±5
EFPO3-7.7	34	NR ^a	100±5

a: No rating

Above all, the impact of FPx was more significant compared with that of FPOx (x=1, 2 and 3) in reducing the flammability of EP with the same P content. The LOI increases for EFPx were much higher than those for EFPOx (x=1, 2 and 3) respectively compared with the results for EP. FPOx (x=1, 2 and 3) showed almost no impact with a 5 wt% loading, while FPx (x=1, 2 and 3) endowed EP with a strong

self-extinguishing ability in the UL 94 test even at a 1 wt% loading. It is noteworthy that the impact of FPO1 at a 30 wt% loading was comparable with that of FP1 at a 3 wt% loading in reducing the flammability of EP. In the following research, FP1 and FPO1 were chosen as being representative of FP_x and FPO_x (x= 1, 2 and 3) for further detailed study on the flame retardancy of EP, EFP_x and EFPO_x (x= 1, 2 and 3).

4.4.2 Cone calorimeter test

Cone calorimetry measures the different parameters (such as material ignitability, heat release and smoke production) in a manner generally relevant to real fires. Fig. 4-5 presents the characteristic curves for heat release rate (HRR) vs time (A) and mass vs time (B) for EP, EFP1-y and EFPO1-y (y=1, 3 and 5) in cone calorimetry testing. Fig. 4-6 showed smoke production curves. The main performance parameters such as time to ignition (TTI), peak heat release rate (pHRR), effective heat of combustion (EHC), total heat release (THR), total smoke production (TSP) and the residue after the test are presented in Tab. 4-3.

The TTI for EP was 55 ± 2 s. Compared with EP, the TTIs for EFPO1-y (y=1, 3 and 5) were shorter. EFP1-3 and EFP1-5 were ignited at 52 ± 2 s and 50 ± 2 s, respectively. The TTI of EFP1-y (y=1, 3 and 5) were as long as that of EP. EFP1-3 and EFP1-5 were ignited at 54 ± 3 s and 55 ± 3 s, respectively. This shows that FPO1 clearly reduced the ignitability of EP, whereas FP1 did not. The HRR curve for EP shows a sharp and high peak in Fig. 4-5(A). The pHRR for EP was 1079 ± 20 kW/m².

The THR and EHC for EP were $97 \pm 3 \text{ MJ/m}^2$ and $22.0 \pm 1.5 \text{ MJ/kg}$ respectively.

After cone calorimetry testing, the residue of EP was around $9 \pm 3 \text{ wt\%}$, indicating that EP showed a low charring ability in forming a polycyclic aromatic hydrocarbon residue during the burning. The TSP value for EP was $35.1 \pm 2 \text{ m}^2$.

Fig.4-5 (A) HRR vs time curves and (B) mass vs time curves for EP, EFP1-y and

EFPO1-y (y=1, 3 and 5)

The addition of FP1 and FPO1 introduced similar impacts on the fire behavior of EP, interesting differences are shown in Fig. 4-5 and Tab. 4-3. First of all, the HRR curves for EFP1-y and EFPO1-y (y=1, 3 and 5) showed two peaks rather than one between 50 s to 500 s. The 1st peaks included shoulder peaks; the 2nd peaks were broad and lower than 600 kW/m^2 for both EFP1-y and EFPO1-y (y=1, 3 and 5). In Fig. 4-5(B), the mass loss rates for EFP1-y and EFPO1-y (y=1, 3 and 5) were lower compared to that of EP, which was consistent with the trends of the HRR curves. The common impacts of FP1 and FPO1 on the combustion of EP were summarized. Both EFP1-y and EFPO1-y (y=1, 3 and 5) showed lower pHRRs, lower THR and higher residue yields in comparison with those for EP; the residue amounts for EFP1-y and

EFPO1-y (y=1, 3 and 5) were similar. Both of them ranged from 20 ± 2 wt% to 25 ± 3 wt%, which increased by 11 wt% ~ 16 wt% in comparison with EP. The shoulder peaks of EFP1-y and EFPO1-y (y=1, 3 and 5) were caused by the residue formed after ignition which was able to protect the matrix. In addition, both FP1 and FPO1 reduced the smoke release of EP as shown in Fig. 4-6.

Fig.4-6 Smoke production curves for EP, EFP1-y and EFPO1-y (y=1, 3 and 5)

Specific differences between EFP1-y and EFPO1-y (y=1, 3 and 5) will now be discussed in detail. TTIs for EFP1-y were longer than those for EFPO1-y (y=1, 3 and 5) with a same loading. From 52 s to 350 s, the shoulder peaks for EFPO1-y (y=1, 3 and 5) were higher than those peaks for EFP1-y (y=1, 3 and 5). The HRR for EFPO1-y (y=1, 3 and 5) increased rapidly again after the shoulder peaks. The pHRR for EFPO1-5 was 702 ± 35 kW/m². However, the HRR for EFP1-y (y=1, 3 and 5) increased slowly after the shoulder peaks. The pHRRs for EFP1-y (y=1, 3 and 5) were lower values in comparison with that for EP and EFPO1-y (y=1, 3 and 5). For instance, the pHRR for EFP1-5 (419 ± 47 kW/m²) was 61% and 40% lower than those for EP and EFPO1-5, respectively. On the HRR curves, the 2nd broad peak for EFP1-y

were higher than those for EFPO1-y (y=1, 3 and 5), indicating that the residue for EFP1-y formed from 50 s to 350 s were less stable than those for EFPO1-y (y=1, 3 and 5). In addition, the impacts of FP1 and FPO1 on the EHC for EP were different. EFPO1-y (y=1, 3 and 5) showed EHCs of 21.0 ± 0.4 MJ/kg, 21.5 ± 0.6 MJ/kg and 20.5 ± 0.5 MJ/kg, respectively. The values were close to that for EP. However, the EHCs of EFP-5 clearly decreased from 22.0 ± 1.5 MJ/kg to 16.7 ± 0.5 MJ/kg compared with EP. The decrease in EHC was induced by incomplete combustion behavior. This indicated that FP1 showed gas phase action. The mass loss rates for EFP1-1, 3 and 5 were lower than those for EFPO1-1, 3 and 5 from 50 s to 200 s, as shown in Fig. 4-5 (B). The TSP values for EFP1-1, 3 and 5 were 29.4 ± 1 m², 27.1 ± 1 m² and 25.6 ± 1 m² respectively. Compared with EFP1-y, EFPO1-y (y=1, 3 and 5) showed lower TSP values. For instance, the TSP for EFPO1-5 was 24.7 ± 1 m² which was 0.9 m² lower than that for EFP1-5.

Overall, both EFP1-y and EFPO1-y (y=1, 3 and 5) show improved flame retardancy in cone calorimetry testing compared with EP. Compared with EFPO1-y, EFP1-y (y=1, 3 and 5) showed longer TTIs and lower pHRRs. The THR and TSPs for EFPO1-y were lower than those for EFP1-y (y=1, 3 and 5). The residue amounts were similar for these two systems. These results indicate that both FPx and FPOx (x=1, 2 and 3) show condensed phase action via accumulating charring residue formation to improve the flame retardancy of EP. However, gas phase action was indicated in the EFP1 system as well due to the evident reduction of EHC values.

Tab. 4-3 Data from cone calorimetry testing of EP, EFP1-y and EFPO1-y (y=1, 3 and 5) at 50 kW/ m²

Samples	TTI ^a (s)	pHRR ^b (kW/m ²)	EHC ^c (MJ/kg)	THR ^d (MJ/m ²)	TSP ^e (m ²)	Residue (wt%)
EP	55±2	1079±50	22.0±1.5	97±3	35.1±2	9±3
EFP1-1	54±3	600±45	20.2±0.6	90±2	29.4±1	20±2
EFP1-3	55±3	530±53	18.5±0.8	81±3	27.1±1	23±3
EFP1-5	55±3	419±47	16.7±0.5	75±4	25.6±1	24±2
EFPO1-1	54±2	864±57	21.0±0.4	87±1	27.4±1	22±3
EFPO1-3	52±2	720±52	21.5±0.6	78±3	25.9±1	23±3
EFPO1-5	50±2	702 ±35	20.5±0.5	70±2	24.7±1	25±3

a: time to ignition; b: peak of HRR; c: effective heat of combustion; d: total heat release; e: total smoke release

4.5 Thermal stability

The impacts of FP1 and FPO1 on the thermal decomposition of EP were studied by thermal gravimetric analysis (TGA) under N₂. Figs. 4-7 and 4-8 show the thermal gravimetric analysis (TGA) and derivative thermal gravimetric analysis (DTG) curves for EP, EFP1-y and EFPO1-y (y=1, 3 and 5). The related data from these curves are presented in Tab. 4-4. T_{d5%} is the temperature at 5% weight loss. T_{max} is the temperature at the maximum decomposing rate.

FP1 and FPO1 induced significant impacts on the thermal decomposition of EP. Under N₂, EP went through one-stage decomposition. T_{d5%} and T_{max} were at 393 °C and 422 °C respectively. At 700 °C, the residue of EP was around 14.6%. In Figs. 4-7

and 4-8, EFP1-y and EFPO1-y (y=1, 3 and 5) show one-stage decomposition as well as EP. The initial decompositions occurred at lower temperatures than that of EP. $T_{d5\%}$ s for EFP1-y (y=1, 3 and 5) were at 365 °C, 348 °C and 339 °C respectively. Compared with EP, the $T_{d5\%}$ for EFP1-5 shifted forward by 54 °C. The $T_{d5\%}$ for EFPO1-5 was at 310 °C which was 83 °C lower than that for EFP1-5. The $T_{d5\%}$ shifts for EFPO1-y were larger than those for EFP1-y (y=1, 3 and 5) respectively. Meanwhile, the peaks on the DTG curves for EFP1-y and EFPO1-y (y=1, 3 and 5) shifted to lower temperatures and were much broader compared with EP. T_{max} s for EFP1-3 and EFPO1-3 were at 382 °C and 387 °C respectively which were 40 °C and 35 °C lower than that for EP. In addition, the char residues of EFP1-y and EFPO1-y (y=1, 3 and 5) were increased in comparison with that for EP. The residue amounts for EFP1-1, 3 and 5 were 23.8%, 25.8% and 27.2% which were close to the residue amounts for EFPO1-1, 3 and 5, respectively. The residue increases for EFPO1-3 and 5 were 2.8% and 5.1%, higher than those for EFP1-3 and 5, respectively.

Fig.4-7 TGA curves for EP and EFP1-y (y=1, 3 and 5) under N₂

Fig.4-8 TGA curves for EP and EFPO1-y (y=1, 3 and 5) under N₂

During the thermal decomposition, FP1 and FPO1 produced phosphorous containing acidic substances which accelerated the thermal decomposition of the EP matrix. The acidic substances promoted char residue formation in the EP matrix, indicated by the increased char residue amount. These impacts induced the forward $T_{d5\%}$ and increased char residue in EFP1-y and EFPO1-y (y=1, 3 and 5). Above all, FP1 and FPO1 showed similar impacts on thermal decomposition to EP. The impact of FP1 on char formation in EP was not as strong as that of FPO1. The thermal stability of EFP1-y was better than that of EFPO1-y (y=1, 3 and 5) as shown by the higher $T_{d5\%}$.

Tab. 4-4 Thermal decomposition data for EP EFP1-y and EFPO1-y (y=1, 3 and 5)

under N₂

Samples	T _{d5%} ^a (°C)	T _{max} ^b (°C)	Residue (700 °C,%)
EP	393	422	14.6
EFP1-1	365	396	23.8
EFP1-3	348	382	25.8
EFP1-5	339	374	27.2
EFPO1-1	359	395	24.1
EFPO1-3	345	387	28.6
EFPO1-5	310	368	32.3

a meant the temperature at 5 % weight loss; b meant the temperature at the maximum decomposing rate

4.6 Mechanical analysis

The mechanical properties of EP, EFP1-5 and EFPO1-5 were studied by means of tensile tests and dynamic mechanical analysis (DMA). The results of the tensile tests are shown in Fig. 4-9. These included strain-stress curves (A), tensile strength and Young's modulus (B) results for EP, EFP1-5 and EFPO1-5. The storage modulus (E') and the loss factor (Tan δ) curves from the DMA results are shown in Fig. 4-10 (A and B).

The elastic behavior of EFP1-5 and EFPO1-5 was similar to that of EP and the Young's modulus of EFP1-5 and EFPO1-5 were 2105 MPa and 2110 MPa, respectively. The elongations at break for EFP1-5 and EFPO1-5 were smaller than that for EP. The tensile strength for EP was 82 ± 9 MPa, while those for EFP1-5 and

EFPO1-5 were 78 ± 8 MPa and 78 ± 10 MPa, respectively. The variation was within 5% for both of them. These results show that the influence of FP1 and FPO1 on the tensile properties of EP was negligible at a 5 wt% loading.

Fig.4-9 (A) strain-stress curves; (B) data on tensile strength and Young's modulus for

EP, EFP1-5 and EFPO1-5

E' and $\tan \delta$ were obtained directly from the DMA test in accordance with the test procedure. E' shows the elastic behavior of a material, which is used to evaluate its stiffness. The glass transition temperature (T_g) was chosen as the temperature at which the peak of $\tan \delta$ ($\tan \delta_{\max}$) was found.

Fig.4-10 (A) E' and (B) $\tan \delta$ curves for EP, EFP1-5 and EFPO1-5 from DMA tests.

The E' values for EFP1-5 and FPO1-5 were similar to those for EP in the glass and rubbery states (Fig. 4-10 (A)). The reduction of E' near the glass transition behavior temperature was slightly shifted to higher temperatures compared with EP. This result is related with the cross-linking structures of EP, EFP1-5 and EFPO1-5 but a detailed explanation cannot be given because the ratios of functional groups were not strictly controlled during the preparation of EFP1-5 and EFPO1-5. The peak $\tan \delta$ values for EFP1-5 and EFPO1-5 shown in Fig. 4-10 (B) were very close to that for EP, while the glass transition temperatures for EP, EFP1-5 and EFPO1-5 were almost the same, around 190 °C. This indicates that the densities of cross-linking structures in EFP1-5 and EFPO1-5 were similar to those in EP. Overall, the tensile and viscoelastic properties of EP did not show significant change resulting from the addition of FP1 and FPO1.

4.7 Morphology analysis

In cone calorimetry testing, both EFP x and EFPO x ($x=1, 2$ and 3) formed an intumescent char residue. Fig. 4-11 shows the digital and SEM images for char residues from EFP1-5 (A) and EFPO1-5 (B).

As shown in the digital images in Fig. 4-11, the char residue for EFPO1-5 showed a similar intumescent shape compared with that for EFP1-5. This type of char residue was able to isolate the exchanges of heat and gaseous compounds between the sample exterior and interior in the cone calorimetry testing. This impact induced the

decreased HRR results discussed in Section 4.4. Regarding the SEM images in Fig. 4-11, significantly different micro-morphologies were showed between the char residues from EFP1-5 and EFPO1-5. The inner char residue surface from EFP1-5 was smooth without large cracks. The outer surface was a densely porous structure. However, the char residue from EFPO1-5 showed a cracked inner surface. The outer surface was a large porous structure with cracks as well. The structure of the char residue from EFP1-5 was different to that from EFPO1-5. The char residue from EFP1-5 shows a better effect in relation to isolating the exchanges of heat and gaseous compounds during the burning. The results are consistent with the HRR results discussed in Section 4.4.

Fig.4-11 The micro-morphology of inner and outer char residues for EFP1-5 (A) and EFPO1-5(B)

4.8 Summary

In Chapter 4, the reactivity between EPC/FPx (or FPOx, x=1, 2 and 3) was verified via DCS and VT-FTIR. The exothermic phenomenon visible on the DSC curves for

EPC/FP1 (or FPO1) and the decreased $R(i_{\text{(epoxy group)}}/i_{\text{(ether group)}})$ values for EPC/FP1 and EPC/FPO1 in VT-FTIR clearly showed that epoxy groups in EPC were reactive with the -NH- groups in FPx (and FPOx, $x=1, 2$ and 3). This indicated that FPx (and FPOx, $x=1, 2$ and 3) was chemically incorporated into the molecular chains of EP during the curing. FP1 and FPO1 showed similar impacts on thermal decomposition to EP. The $T_{d5\%}$ values for EFP1-y and EFPO1-y ($y=1, 3$ and 5) showed at lower temperatures; the char residue amounts were increased at $700\text{ }^{\circ}\text{C}$ compared with EP. The $T_{d5\%}$ values for EFP1-y were higher, while the char residues were lower compared with EFPO1-y ($y=1, 3$ and 5). The tensile strengths for EFP1-5 and EFPO1-5 were $78 \pm 8\text{ MPa}$ and $78 \pm 10\text{ MPa}$, respectively, which were similar with that for EP. Tan δ curves from DMA showed that the addition of FP1 and FPO1 did not decrease the T_g s of EP.

With respect to the flame retardancy, FP1 and FPO1 showed similar impacts in EP. The limiting oxygen index of EP was increased significantly. After the addition of FP1 and FPO1, EP had self-extinguishing ability in UL 94 test. The heat release of EP was suppressed during the burning in cone calorimeter test. However, a significant difference was showed in UL 94 test. With $0.67\text{ wt\% P}$ content, EFPOx achieved no rating, while EFPx ($x=1, 2$ and 3) achieved a V-0 rating in the UL 94 test, indicating that FP1 endow EP with a stronger self-extinguishing ability. EFP1-3 achieved a V-1 rating which was shown in EFPO1-30. The efficiency of FP1 in EP was 10 times

higher than that of FPO1. A further study on the flame retardant mechanisms of FP1 and FPO1 in EP was needed to explain the phenomena.

CHAPTER 5

FLAME-RETARDANT MECHANISM

“Man errs as long as he strives.”

~Goethe

5. 1 Introduction

The flaming combustion of polymer materials is a gas-phase process which was induced by the burning of volatile flammable compounds. The flammable compounds are from the thermal decomposition of polymer materials contacting with fire. Thus, to understand the flame-retardant mechanism of FP1 and FPO1 in EP, it is necessary to study the thermal decomposition of EP, flame retardant EP and P-FRs, independently. In this chapter, the evolved gaseous compounds from thermal decomposition are characterized by TGA-MS and TGA-FTIR to study thermal decomposition behavior of FP1 and FPO1; the slide residues in condensed phase and evolved gaseous compounds in gas phase are studied by VT-FTIR and TGA-FTIR, respectively, to investigate the thermal decomposition behaviors of EFP1-5 and EFPO1-5. In addition, an on-line temperature detection was designed to explain the different efficiency of FP1 and FPO1 in EP in a UL 94 test. Flame-retardant

mechanisms of FP1 and FPO1 in EP were analyzed and compared in gas and condensed phases on basis of the above results related with thermal decomposition behaviors.

5.2 Thermal decomposition behaviors of FP1 and FPO1

5.2.1 Thermal decomposition behavior of FP1

In order to study the thermal decomposition behavior of FP1 and FPO1, the gaseous products released during the thermal decomposition of FP1 and FPO1 were characterized by TGA-MS and TGA-FTIR. Figs. 5-1 and 5-3(A) show the main ion current curves *vs* temperature for ion fragments with an *m/e* of 78, 57, 41, 17, 66 and 94 from FP1 as detected by TGA-MS. Fig. 5-2 shows the FTIR spectra for evolved gaseous products from FP1 at different temperatures as detected by TGA-FTIR. Fig. 5-3(B) shows the 923 cm^{-1} IR peak absorbance intensity *vs* temperature curve for FP1 as detected by TGA-FTIR.

From Fig. 5-1 it can be seen that allyamine, allyl and ammonium were the main detected evolved gaseous products in the thermal decomposition of FP1 in the range 200 °C to 350 °C. FTIR spectra verified this information at 250 and 300 °C, as shown in Fig. 5-2. Ion fragments of benzene were detected with *m/e*=78 from 350 °C. Meanwhile, phosphorus-containing compounds were found with an IR peak at 1260 cm^{-1} in FTIR spectra at 350 °C, as shown in Fig. 5-2. This indicates that the P (O)-Ph bond was broken at around 350 °C. In addition, a signal from ion fragments with an

$m/e=94$ appeared at around 400 °C in Fig. 5-3 (A). This fragment was not assigned to the phenol ion fragment due to the lack of a peak at $m/e=66$ at the same time. The ion fragment with $m/e=94$ was considered to be related to a phosphorous-containing structure as the release of allyamine, allyl and ammonium was almost finished above 350 °C. The FTIR spectra in Fig. 5-2 were used to assign this fragment. The IR absorbance peak at 932 cm^{-1} gradually became visible in the FTIR spectra at 450, 500 and 600 °C. According to the structure of FP1, the ion fragments with $m/e=94$ were assigned as being from a P_2O_2 compound as reported by Lope (Lopez, Sarasola et al. *et al.* 1993). Moreover, this P_2O_2 was considered to be formed by a $\text{PO}\cdot$ radical produced during the thermal decomposition of FP1.

Fig.5-1 Ion current of ion fragments with $m/e = 78, 57, 41$ and 17 vs temperature curves from TGA-MS for FP1

Overall, P-N and C-N bonds in the structure of FP1 were broken at around 200 °C to 400 °C. Ammonium, allylamine and allyl compounds were formed and released into the gas phase. Allyl compounds might also bond again with a phenylphosphonyl structure in the condensed phase. The further decomposition of reformed structures in the condensed phase produced a complex mixture of gaseous products such as allylamine, benzene and phosphorus compounds. The P (O)-Ph bond in the FP1 structure dissociated at around 350 °C which was indicated by the release of the benzene structure at 600 °C. It is thought phosphorous acid (H_3PO_3) was formed in the condensed phase. The speculative thermal decomposition of FP1 is shown in Fig. 5-4.

Fig.5-2 FTIR spectra for evolved gaseous products at different temperatures from
TGA-FTIR of FP1

Fig.5-3(A) Ion current of ion fragments with $m/e=66$ and 94 vs temperature curves;

(B) 932 cm^{-1} IR peak intensity vs temperature curves

Fig.5-4 Speculative thermal decomposition route for FP1

5.2.2 Thermal decomposition of FPO1

Fig. 5-5 presents the ion current curves vs temperature for ion fragments with an m/e of 94, 66, 64, 57 and 41, as detected by TGA-MS of FPO1. Fig. 5-6 shows the FTIR spectra for evolved gaseous products at different temperatures as detected by TGA-FTIR.

Fig.5-5 Ion currents for ion fragments with $m/e = 94, 66, 57, 41$ and 17 vs temperature curves from TGA-MS of FPO1

The thermal decomposition of FPO1 was different from that of FP1. From 200 °C to 400 °C, the detected ion fragments were mainly from phenol, allylamine and allyl compounds, as shown in Fig. 5-5. Phenol ion fragments were released from 200 °C to 550 °C. In addition, the FTIR spectra in Fig. 5-6 at 300 °C, 400 °C and 500 °C were virtually the same as the added spectra for phenol and allylamine in the library as shown in Fig. 5-7. The results show that the gaseous compounds evolved from TGA were mainly phenol and allylamine compounds. Notably, the TGA-MS and TGA-FTIR results showed that few phosphorous signals were detected, indicating that phosphorus was mainly kept in the condensed phase between 200 °C and 500 °C. Phosphoric acid (H_3PO_4) is thought to be formed in the condensed phase of FPO1 during thermal decomposition. The possible evolved phosphorus compounds are

considered to be metaphosphorous acid (HPO_2) related with the ion fragment with $m/e=64$ as shown from 475°C in Fig. 5-5.

Fig.5-6 FTIR spectra of evolved gaseous compounds at different temperatures
from TGA-FTIR of FPO1

Overall, FPO1 showed a different decomposition route compared with that of FP1. P-N and N-C bonds broke rapidly from around 200°C , this is indicated by the fact that the fragments of allyamine and allyl compounds were detected between 200°C and 300°C . The breaking of the P-O Ph bond occurred within a wide temperature range as indicated by the broad phenol ion fragment peaks with $m/e=94$ and 66 (from 200°C to 550°C). In addition to these behaviors, a pyrophosphoric acid-like structure was thought to be formed in the condensed phase. Further decomposition of this structure occurred at temperatures above 450°C as indicated by the HPO_2 ion fragment peak with $m/e=64$. A speculative thermal decomposition path for FPO1 is

shown in Fig. 5-8. In the case of FPO1, there was no significant signal indicating the formation of a phosphorus radical at least from 200 °C to 450 °C.

Fig.5-7 Library FTIR spectra for phenol and allyamine, the addition of these two spectra and FTIR spectra for evolved gaseous products at 300 °C, 400 °C and 500 °C from TGA-FTIR of FPO1

Fig.5-8 Speculative thermal decomposition route for FPO1

5.3 Thermal decomposition behaviors of EFP1-5 and EFPO1-5

5.3.1 Study of solid residues from EP, EFP1-5 and EFPO1-5 in the condensed phase

The thermal weight losses of EP, EFP1 and EFPO1 were discussed in Section 4.5 in Chapter 4. EP mainly went through dehydration or dehydrogenation, chain scission, chain stripping and carbonization reactions during thermal decomposition. (Bellenger, Fontaine et al. *et al.* 1984, Braun, Balabanovich et al. *et al.* 2006, Rakotomalala, Wagner et al. *et al.* 2010) The detailed mechanism for EP is described in Fig. 5-9. The influences of FP1 and FPO1 on the thermal decomposition of EP are discussed for the gas and condensed phases respectively. VT-FTIR was used to study the solid residues from EP, EFP1-5 and EFPO1-5 at different temperatures in the condensed phase.

Fig. 5-10 shows the FTIR spectra of EP, EFP1-5 and EFPO1-5 in the condensed phase at $T_{\max}$ from VT-FTIR tests. The solid residues from EFP1-5 and EFPO1-5 did not show any different IR peaks compared with EP. In Section 4.5, $T_{\max}$ values for EFP1-5 and EFPO1-5 were recorded at 374 °C and 368 °C, which were 48 °C and 54 °C lower than those for EP. The char residue amounts for EFP1-5 and EFPO1-5 increased significantly from 14.6% to 27.2% and 32.3% respectively. These results show that FP1 and FPO1 did not alter the main decomposition routes of EP, while the decomposing reactions were catalyzed at lower temperatures compared with EP. The carbonization reaction of EP was catalyzed and accumulated after the addition of FP1 and FPO1 as well. Based on the discussion in Section 5.2, phosphorous containing

acid compounds (H_3PO_3 and H_3PO_4) were the main active compounds in inducing the catalyst effects in EFP1-5 and EFPO1-5.

Fig.5-9 The common thermal decomposition routes of EP

5.3.2 Study of evolved gaseous compounds from EP, EFP1-5 and EFPO1-5 in gas phase

TGA-FTIR identified the gaseous compounds evolved from EP, EFP1-5 and EFPO1-5 in the gas phase. Fig. 5-11 shows the FTIR spectra of EP, EFP1-5 and EFPO1-5 in the gas phase at T_{max} from TGA-FTIR tests.

Fig.5-10 FTIR spectra for EP, EFP1-5 and EFPO1-5 in the condensed phase at $T_{\max}$ from VT-FTIR tests

The gaseous compounds evolved from EFP1-5 and EFPO1-5 showed similar IR spectra to those from EP. This showed that the thermal decomposition of EP was not influenced by FP1 and FPO1, which was consistent with results in the condensed phase. The IR peaks at 1100 cm^{-1} and 1508 cm^{-1} were weakened after the addition of FP1 and FPO1 to EP. The assignments of these two peaks were a C-O stretching vibration and a C=C stretching vibration respectively. According to the discussion in the condensed phase, the reduction of C=C containing compounds was induced by the improved formation of char residues in the condensed phase. The weakened C-O IR absorption indicates that the releases of ether or carbonyl compounds were reduced in EFP1-5 and EFPO1-5.

Overall, the thermal decomposition routes and products for EFP1-5 and EFPO1-5 were similar to those for EP in both the condensed and gas phases, which was shown by the VT-FTIR and TGA-FTIR results. The acidic compounds from FP1

and FPO1 accelerated residue formation in the EP matrix which was shown by the increased residue amounts and intensity reduction of C=C and C-O IR peaks for EFP1-5 and EFPO1-5 compared to EP.

Fig.5-11 FTIR spectra for EP, EFP1-5 and EFPO1-5 in the gas phase at $T_{\max}$ from

VT-FTIR tests

5.3.3 Hydrocarbon releases from EFP1-5 and EFPO1-5

Hydrocarbons from the thermal decomposition of polymers are the main fuels in their ignition. (Wilkie and Morgan *et al.* 2009) The hydrocarbons released from EFP1-5 and EFPO1-5 were studied in order to understand the flame retardant mechanism for FP1 and FPO1 in EP. Fig. 5-12 shows the IR absorbance intensity for hydrocarbons vs temperature curves from TGA-FTIR for EFP1-5 and EFPO1-5.

The hydrocarbons were released between 370 °C and 600 °C during the thermal decomposition of EFP1-5. As discussed in Section 5.2.1, benzene and PO· radicals were the main compounds evolved from the thermal decomposition of FP1 within the same temperature range. The above results show that the release of hydrocarbons and

PO· radicals was in the same temperature range in EFP1-5. This indicates that PO· radicals were able to act as a flame inhibitor in EFP1-5 in the gas phase. As for EFPO1-5, the hydrocarbons were released between 350 °C and 500 °C. As discussed in Section 5.2.2, phenol, allylamine and allyl compounds were the main gaseous compounds evolved within the same temperature range during the thermal decomposition of FPO1. No obvious phosphorous signal was shown at the same time. This indicates that no evidence was found that it acted in the gas phase in EP.

Fig.5-12 IR absorbance intensity for hydrocarbons vs temperature curves from TGA-FTIR tests of EFP1-5 and EFPO1-5

5.4 On-line temperature detection for EFP1-5 and EFPO1-5 in UL 94 testing

In recent years, researchers have made considerable efforts to study fire behavior using different tests, such as LOI, UL 94 and cone calorimetry tests. (Dupretz, Fontaine et al. *et al.* 2015, Kempel, Scharrel et al. *et al.* 2015) In this study, the near-to-surface temperature (NTST) and surface temperature (ST) of EFP1-5 and

EFPO1-5 were collected using a thermocouple (TC) and an infrared thermometer (IR thermometer) respectively in a UL 94 test. The on-line temperature detection experiment is shown in Fig. 5-13. The emissivity of the IR thermometer was always set as 0.950. T_{TC} (NTST) vs time curves are shown in Fig. 5-14. T_{IR} (ST) vs time curves are shown in Fig. 5-15. In the vertical burning test (UL 94), EFPO1-5 self-extinguished 25 s after the 1st ignition, once it had burnt out it was subjected to the 2nd ignition. In comparison, EFP1-5 self-extinguished within 5 s after the 1st ignition and would not ignite for the 2nd ignition.

Fig.5-13 Sketch diagram of on-line temperature detection equipment for the UL 94 test

Fig. 5-14 shows that the T_{TC} for EFP1-5 and EFPO1-5 increased continuously during both the 1st and 2nd ignitions. In the 1st ignition, the T_{TC} for EFP1-5 and EFPO1-5 were 211 ± 14 °C and 215 ± 15 °C respectively. Meanwhile, the slopes of the T_{TC} curves are very similar to each other. After the 1st ignition, the T_{TC} for

EFPO1-5 continued increasing until 35 s, while the T_{TC} for EFP1-5 decreased within 5 s. The slopes of the T_{TC} curves are also very similar to each other for EFPO1-5 and EFP1-5 during the 2nd ignition. In the 2nd ignition, the T_{TC} for EFP1-5 and EFPO1-5 were 370 ± 15 °C and 410 ± 15 °C respectively. After the 2nd ignition, the T_{TC} for EFPO1-5 increased to around 500 °C and kept relatively stable until the sample burnt out. However, the T_{TC} for EFP1-5 decreased within 3 s. The trends of the T_{TC} curves are consistent with the burning behavior of EFP1-5 and EFPO1-5.

Interesting differences in the T_{IR} curves for EFP1-5 and EFPO1-5 are shown In Fig. 5-15. Both EFP1-5 and EFPO1-5 presented an up-down trend during 1st and 2nd ignition. However, the T_{IR} increase for EFPO1-5 slowed down when T_{IR} was 400 ± 40 °C, whereas that for EFP1-5 slowed down when T_{IR} was 300 ± 40 °C during the 1st ignition. The maximum T_{IR} difference between EFP1-5 and EFPO1-5 was above 80°C. During the 2nd ignition, the T_{IR} -values for EFPO1-5 and EFP1-5 initially increased with a similar gradient. However, the increase for EFP1-5 kept relatively stable when the value was around 350 ± 40 °C, while the T_{IR} for EFPO1-5 increased up to 550 ± 40 °C during the 2nd ignition at 10s. The maximum difference was up to 300 °C during the 2nd ignition. Following this the T_{IR} for EFPO1-5 increased to around 600 °C until the sample burnt out, whereas that for EFP1-5 decreased immediately after the flame went out.

Fig.5-14 NTST curves for EFP1-5 and EFPO1-5 in UL 94 testing

Basically, the heat energy required to increase T_{IR} (Q_{ST}) is described in equation 5-2, where Q_F represents the heat from the UL 94 test flame; Q_B represents the heat

$$Q_{ST} = Q_F + Q_B - Q_D - Q_C \quad 5-1$$

from burning the sample; Q_D represents the decomposition heat from the samples; Q_C represents the conductive heat of a sample. In this study, we assumed that Q_D was equal to each other for EFP1-5 and EFPO1-5. We also assumed that the Q_F for EFP1-5 and EFPO1-5 were the same values as well because the flame heights in the test were both 20mm and the ignition times were both 10 s in each ignition.

Fig.5-15 ST curves for EFP1-5 and EFPO1-5 in UL 94 testing

From the T_{TC} vs time curves, it can be noted that the slopes of T_{TC} curves from EFP1-5 and EFPO1-5 show similar values during the 1st and 2nd ignitions. This also indicates that Q_C was the same value for the two systems. Under this hypothesis, Q_{ST} depended on Q_B . According to Fig. 5-15, the Q_B for EFPO1-5 was evidently much higher than that for EFP1-5, showing that the burning of EFP1-5 was much weaker than that of EFPO1-5. The results indicate that there was incomplete combustion in EFP1-5, which is thought to be induced by the flame inhibition effect. Considering that the release of hydrocarbons and $PO\cdot$ radicals was in the same temperature ranges in EFP1-5, the low Q_B clearly shows that a flame inhibition effect occurred in the gas phase of EFP1-5.

5.5 Flame retardant mechanism

5.5.1 Gas phase action of FP1 and FPO1 in EP

In the gas phase, the main effective function induced by flame retardants is releasing species that either blanket out the flames with noncombustible gases such as water vapor, or flame inhibitors such as $\text{Cl}\cdot$ and $\text{PO}\cdot$ radicals. (Wilkie and Morgan *et al.* 2009) The gas phase actions of FP1 and FPO1 in EP can be understood based on the results of Section 5.1, 5.2 and 5.3. A clear flame inhibition effect was indicated by the significant decrease in the EHC for EFP1-5 from 22.0 ± 1.5 MJ/kg to 16.7 ± 0.5 MJ/kg compared with EP, as shown in Section 4.4; the overlapped temperature ranges for hydrocarbons release and $\text{PO}\cdot$ radicals release in EFP1-5, as shown in Section 5.3 and the lower Q_B for EFP1-5 compared with EP, as shown in Section 5.4.

The results in Sections 5.2 and 5.3 show that $\text{PO}\cdot$ radicals were evidently released from FP1 above 400 °C. Meanwhile, hydrocarbons were released in the EP matrix from 370 °C to 600 °C. It is believed that hydrogen ($\text{H}\cdot$) and hydroxyl ($\text{OH}\cdot$) radicals from hydrocarbons reacted with $\text{PO}\cdot$ radicals in the gas phase in accordance with the equation below (5-3) (Schartel *et al.* 2010). According to this equation, the $\text{H}\cdot$ and $\text{OH}\cdot$ radicals changed to become less effective or harmless compounds to the flame cycle in the gas phase. Many of the branching and chain reactions of the hydrocarbon flame were slowed down or interrupted. Therefore, the EHC for EFP1-5 was decreased compared to that for EP.

5-3

Fig.5-16 The proposed gas phase actions of EFP1-5 and EFPO1-5 in UL 94 testing

In contrast, FPO1 did not show any ability to induce a flame inhibition effect in EP. Firstly, no active moiety or radicals that were able to capture $\text{H}\cdot$ and $\text{OH}\cdot$ radicals were released from FPO1 into the gas phase over the temperature range for hydrocarbon release in EFPO1-5. Secondly, non-flammable species were clearly released from FPO1 at a 5 wt% loading during the thermal decomposition of EFPO1-5. The allyamine, phenol and allyl compounds released from FPO1 were also flammable. Above all, FPO1 did not show any evident effect in endowing EP with

flame retardancy in the gas phase. The different gas phase actions of EFP1-5 and EFPO1-5 are described in Fig. 5-16.

5.5.2 Condensed phase action of FP1 and FPO1 in EP

A classical action mode of a P-FR in polymer is to promote char formation in the condensed phase during the burning. (Wilkie and Morgan *et al.* 2009) As can be seen from the cone calorimetry and TGA test results, the char residue formation in EP was significantly increased after the addition of both FP1 and FPO1. This showed that both FP1 and FPO1 acted effectively in the condensed phase by promoting char residue formation. Furthermore, the char residues of EFP1-5 and EFPO1-5 were intumescent after burning. This type of char residue acts as an excellent isolating layer for the gas and heat exchange during the burning. (Wilkie and Morgan *et al.* 2009) The intumescent char residue formation in EFP1-5 and EFPO1-5 were as below: the acid compounds (H_3PO_3 and H_3PO_4) from the thermal decomposition of FP1 and FPO1 acted as acids; the EP matrix acted as a char former; the gaseous products from the thermal decomposition of EFP1 and EFPO1 acted as blowers to form the intumescent char residue. Therefore, the combustion behaviors of EFP1-y and EFPO1-y (y=1, 3 and 5) were depressed on release of heat and mass loss of samples in the cone calorimetry testing. However, the temperature ranges of the acid compounds and evolved gaseous products released and the charring rate of the epoxy matrix affected the formation of intumescent char residues in EFP1-5 and EFPO1-5. For instance, the char residue of EFP1-5 was denser than that of EFPO1-5, although

their mass and the intumescent shape were similar to each other. As can be seen in Fig. 4-5(B), EFP1-y (y=1, 3 and 5) showed less mass loss than EFPO1-y (y=1, 3 and 5) did before 200 s in the cone calorimetry testing. The same thing occurred below 400 °C in the TGA test, as shown in Figs. 4-7 and 8. This shows that the charring rate for EFPO1-y (y=1, 3 and 5) was lower than that for EFP1-y (y=1, 3 and 5) at the initial stage of heating. In addition, the char residue structure from EFP1-5 was higher than that from EFPO1-5. Both these two differences induced the lower pHRRs for EFP1-y than those for EFPO1-y (y=1, 3 and 5) in the cone calorimetry testing.

5.5.3 Flame retardant mechanism

Based on the results and discussion in Section 5.2 to 5.4, the flame retardant mechanism of FP1 and FPO1 in EP is summarized here.

FPOx (x=1, 2 and 3) mainly acted as an effective char promoter in EP in the condensed phase at low loadings (< 10 wt%). H_3PO_3 was the main active compound formed by the thermal decomposition of FPOx (x=1, 2 and 3). The result of this effect had three aspects: (i) catalyzing the carbonization reaction in EP to increase the charring rate; (ii) increasing the char residue amount of the EP matrix; (iii) promoting intumescent char residue formation during the burning.

FPx (x=1, 2 and 3) acted effectively in EP both in the gas and condensed phases at low loadings (<10 wt%). In the gas phase, the flame inhibition effect was clearly shown in the results for the overlapped temperature ranges for $\text{PO}\cdot$ radicals and hydrocarbons release, as well as in the lower Q_B for EFP1-5 compared with EFPO1-5. In the condensed phase, FPx (x=1, 2 and 3) showed a similar effect in EP to that of FPOx (x=1, 2 and 3). As a whole, the following two factors induced the highly

efficient flame retardancy of FP_x ($x=1, 2$ and 3) in EP: (i) a flame inhibition effect in the gas phase; (ii) catalyzing of the charring process in the condensed phase. It is believed that the flame inhibition effect was the main factor to endow EP with a strong self-extinguishing ability. Due to the effects of flame inhibition and catalyzing of char formation, FP1 imparted EP with a UL94 V-0 rating, a high LOI value and low HRR at a loading of only 5 wt%.

CHAPTER 6

INFLUENCE OF HALOGEN-FREE PHENYLPHOSPHONIC AMIDE ON THE PROPERTIES OF CARBON FIBER/RTM6 COMPOSITES

“Failure is the mother of success.”

~Thomas Paine

6.1 Introduction

Carbon fiber reinforced RTM6 epoxy composite (CFR) is widely used in the aerospace industries owing to its characteristics such as easy of processing, excellent mechanical properties and low water absorption. The on-going development of CFR is extending its application into more fields such as the train and automobile industries. (Perez, Sandler et al. *et al.* 2007, Li, Kang et al. *et al.* 2013, Sprenger, Kothmann et al. *et al.* 2014) However, the RTM6 matrix is highly flammable, leading to a fire hazard during its application, especially in the transportation sector. It has

been a standing issue that the flame retardancy of CFR has to be improved. (Li, Kang *et al. et al.* 2013,)

In numerous journal articles, three methods are considered to be effective in endowing epoxy resin and its composites with flame retardancy. One is to incorporate non-reactive flame retardant additives (red phosphorus (Levchik and Weil *et al.* 2006), ammonium phosphates (Wang, Liu *et al. et al.* 2009, Lim, Mariatti *et al. et al.* 2012), aluminum hydroxide (Zammarano, Franceschi *et al. et al.* 2005, Formicola, De Fenzo *et al. et al.* 2009), intumescence-based (Kandola, Horrocks *et al. et al.* 2003, Levchik and Weil *et al.* 2006, Chapple and Anandjiwala *et al.* 2010, Gao and Yang *et al.* 2010), zinc-based (De Fenzo, Formicola *et al. et al.* 2009, Formicola, De Fenzo *et al. et al.* 2009) and boron-based (Yu, Xing *et al. et al.* 2016, Zhang, Liu *et al. et al.* 2016) flame retardants, etc.). Another one is to develop reactive flame retardants (organophosphorous compounds). (Gao, Yang *et al.* 2010) The third one is to coat a flame retardant layer on the surface of the materials. For instance, the peak heating release rate (pHRR) of a glass fiber reinforced epoxy composite was decreased by 71% when the surface was coated with an intumescent flame retardant coating which was a mixture of P-FRs (DOPO, triphenyl phosphate, zinc borate, tetraethylpentamine and 3-aminopropyltriethoxysilane. (Chapple *et al.* 2010)

In the literature review, few studies were found that related to improving the flame retardancy of CFR. The research group of A. De Fenzo reported that zinc hydroxystannate (ZHS), zinc borate (ZB) and aluminum trihydroxide (ATH) were

effective flame retardants as they decreased the pHRR for RTM6. At a 30 wt% loading, the pHRRs for RTM6/ZHS (De Fenzo, Formicola *et al. et al.* 2009) and RTM6/ZB (Formicola, De Fenzo *et al. et al.* 2009) were 46% and 44% less respectively compared with that for RTM6. In terms of the requirements of industrial processes, a high loading with these flame retardants always increases the viscosity of RTM6 resins and decreases the mechanical properties of CFR. B. Scharrel's research group studied the influence of DOPO (9, 10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide)-based flame retardants on improving the flame retardancy of RTM6 and CFR. (Perret *et al.* 2011, Perret *et al.* 2011) For instance, oligomeric star-shaped DOPO-based flame retardants DOPP (ground body tetra-[(acryloyloxy) ethyl] pentarythrit) and DOPI (ground body [(acryloyloxy) ethyl] isocyanurate) were used in CFR. DOPP and DOPI are soluble in RTM6. CFR/DOPP (6 wt%) and CFR/DOPI (7 wt%) achieved V-0 ratings in the UL 94 test. Their LOI values were 12.1% and 14.5% higher than that of CFR, respectively. Interlayer shear strength (ILSS) decreased after the addition of DOPP and DOPI in CFR. (Perret *et al.* 2011)

In this chapter, the use of FP1 to develop a novel flame retardant for CFR is discussed. The influence of FP1 on the processing of resin transfer molding was investigated using rheological tests. DSC testing was performed to study the influence of FP1 on the T_g and curing degree of CFR. Flexure and in-plane shear tests were used to study the influence of FP1 on the interlayer share strength (ILSS) and the

in-plane shear strength (IPSS) of CFR. Limiting oxygen index (LOI), UL 94 and cone calorimetry tests were used to study the influence of FP1 on the flame retardancy of CFR. In addition, the influence of FP1 on water absorption by CFR was studied.

6.2 Materials and Experimental Techniques

6.2.1 Materials

The synthesis of FP1 is described in Section 3.1.1. HexFlow® RTM6 epoxy resin was supplied by the FIDAMC institute in Spain.

6.2.2 Preparation of RTM6 and flame retardant RTM6

The preparation of flame retardant RTM6 followed the following procedure: firstly, the loading amount (4, 6 and 8 wt%) of FP1 was dissolved in RTM6 at 70 °C; then the mixture was poured into preheated rubber modules to cure at 170 °C. The curing temperature profile was 170 °C, 1h; 190 °C, 2h. The reference RTM6 material was cured with the same temperature profile. The formula of the prepared RTM6 and RTM6/FP1 is shown in Tab. 6-1.

6.2.3 Preparation of CFR and flame retardant CFR

The preparation of CFR and flame retardant CFR was done by FIDAMC institute. Resin transfer molding (RTM) technology was used to manufacture CFR and flame retardant CFR panels. An RTM tool is composed of two mold halves. First, the perform is positioned on the bottom half and then the tool is closed and sealed by means of two rubber lines as indicated in Fig.6-1. Both panels comprise 6 layers of dry carbon fiber fabric with lay-up $[+ 45^{\circ}]_{3s}$. Theoretically, the weight of the fiber

content of the panels is 67.4%, given a layer thickness of 0.37 mm. Thus, the theoretical panel thickness is 2.22 mm. The formula for the prepared CFR0 and CFR3 are shown in Tab.6-1.

Fig. 6-1 RTM tool inlets and outlet.

During the injection process the RTM6 resin was initially degassed for 30 minutes in the resin pot at 80 °C. Then the RTM6 was injected at an approximately 3 bar pressure into the mold which was preheated to 120 °C. Once the injection was finished, the temperature of the mold was increased to 180 °C and maintained for 2 hours to complete the curing cycle. Finally, the panels are de-molded and inspected using the non-destructive pulse-echo technique. No reportable defects were found on inspection of both panels.

Tab. 6-1 The formula of prepared flame retardant RTM6 and CFR

Samples	RTM6 (wt%)	CF (wt%)	FP1 (wt%)
R0	100	--	--
R1	96	--	4
R2	94	--	6
R3	92	--	8
CFR0	33	67	--
CFR3	29	68	3

6.2.4 Characterization

DSC test

The DSC test was performed on a DSC Q2000 (TA, USA). The T_g temperature and curing degree (α) of CFR0 and CFR3 were examined with a heating rate of 10 °C/min and a nitrogen flow of 50 mL/min.

Volume density test

The fiber, resin and void volume contents were determined by using a XP205DR Precision Scale (Mettler Toledo, Spain). The mass densities of the fiber (1.77 g/cm³), R0 (1.14 g/cm³) and R3 (1.10 g/cm³) were used for the volume content calculations. The specimen size was 20 x 10 x 2 mm.

Rheological test

Oscillatory tests of RTM6 and RTM6/FP1 (10 wt%) were performed on an AR-G2 Rheometer (TA, USA) using a parallel plate geometry from 40 °C to 200 °C. The heating rate was 10 °C/min. Isothermal flow tests were carried out at different temperatures (50 °C, 100 °C, 120 °C and 160 °C) in order to examine the viscosity of RTM6 and RTM6/FP1 (10 wt%).

Mechanical tests

Flexural testing of CFR0 and CFR3 was carried out to determine the interlaminar shear strength (ILSS) in accordance with the PREN2563 standard by using an AllroundLine Z01OTH Universal Testing Machine (Zwick, Germany) equipped with a 10 kN load cell. The specimen size was 20 x 10 x 2 mm. The crosshead speed was 1 mm/min. The values reported were an average value from five tests.

In-plane-shear (IPS) testing of CFR0 and CFR3 were performed on a MTS 370.1 Universal Testing Machine equipped with a 100kN load cell in accordance with PREN 6031. The specimen size was 230 x 25 x 2 mm. Longitudinal and transversal extensometers were used to acquire the deformation values. Five samples were tested to obtain average values.

Limiting oxygen index (LOI)

LOI was tested on an Oxygen Index Meter (FTT, UK) in accordance with ASTM D2863-97. The sample size of R0, R1, R2 and R3 was $130 \times 6.5 \times 3.2$ mm. The specimen size of the CFR0 and CFR3 composites was $130 \times 6.5 \times 2.2 (\pm 0.1)$ mm.

UL 94 test

Vertical rating tests were undertaken in a UL 94 Horizontal/Vertical Flame Chamber (FTT, UK) in accordance with the UL 94 standards. The height of the burning flame was 20 mm. The sample size of R0, R1, R2 and R3 was $120 \times 12.7 \times 3.2$ mm in this work. The sample size of the CFR0 and CFR3 was $120 \times 12.7 \times 2.2$ mm.

Cone calorimetry test

Cone calorimetry tests were carried out in accordance with the ISO 5660-1 standard with a Cone Calorimeter (FTT, UK). Square specimens (100×100 mm) were irradiated at a heat flux of 50 kW/m^2 . The thickness of R0, R1, R2 and R3 samples was 4.5 mm and that of the CFR0 and CFR3 samples was $2.2 (\pm 0.1)$ mm.

Water absorption test

The water absorption testing was carried out in accordance with the ASTM D570 standard: 1) the specimens were dried at 50°C for 2 hours and then placed in a desiccator until they had cooled down to room temperature; 2) the dried specimens

were weighed immediately after they were taken out of the desiccators; 3) the weighed specimens were initially immersed in de-ionized water for 24 h and they were then re-weighed after being dried with a clean dry cloth; 4) all the specimens were weighed using the same methods after 1, 2, 3, 4, 7, 8, 9, 10, etc. days exposure until the weight of the samples reached a constant level. Water absorption was expressed as the percentage increase in weight:

$$\text{weight gain (\%)} = \frac{W_t - W_i}{W_i} \times 100\%$$

where W_t and W_i represented the weight during the exposure and the initial weight respectively.

6.3 Basic parameters of CFR0 and CFR3

The T_g temperature and curing degree (α) for CFR0 and CFR3 are showed in Tab.6-2 from the DSC test. The volume contents of fiber, resin and void in Tab. 6-2 were calculated from the volume density test. For the calculation of α , the reference enthalpy was obtained via the DSC result of RTM6 with a heating rate of 10 °C/min.

The α for CFR0 and CFR3 was $99 \pm 1\%$ and $100 \pm 0\%$, respectively, showing that both the panels were cured completely with the curing temperature profile. Nevertheless, the T_g for CFR0 decreased after the addition of FP1 to the RTM6 resin. The T_g of CFR3 was 185.4 ± 1.4 °C which was 18 °C lower than that of CFR0. The decrease of T_g temperatures was caused by the lowered cross-linking density due to the reactive amino group in the FP1 structure. The void volume content (V_{void}) for CFR3 was zero, showing that there were no pores in this panel. CFR0 showed a $1.2 \pm$

0.1% V_{void} which was considered to be too low to significantly influence the mechanical properties of CFR0. The fiber volume content (V_{fiber}) for CFR0 and CFR3 were $56.0 \pm 0.1\%$ and $52.0 \pm 0.2\%$, respectively, which were similar to each other. The resin volume content (V_{resin}) for CFR0 was slightly lower than that for CFR3 due to the existence of pores. Overall, the addition of FP1 into RTM6 decreased the T_g for CFR0, while the curing process and the cured panel composition were not significantly affected.

Tab. 6-2 Results for DSC and volume density testing of CFR0 and CFR3

Samples	T_g ($^{\circ}\text{C}$)	α (%)	V_{fiber} (%)	V_{resin} (%)	V_{voids} (%)
CFR0	203.9 ± 7.8	99 ± 1	56.0 ± 0.1	42.8 ± 0.1	1.2 ± 0.1
CFR3	185.4 ± 1.4	100 ± 0	55.7 ± 0.2	44.3 ± 0.1	0.0 ± 0.0

6.4 Rheological properties

The influence of FP1 on the rheological properties of RTM6 was studied in order to show the influence of FP1 on the injection process of CFR0. Oscillatory tests were used to examine the viscosity profile and the minimum viscosity region. The viscosity curves for RTM6 (R0) and RTM6 containing 10 wt% of FP1 (R4) obtained from non-isothermal oscillatory tests are shown in Fig.6- 2. In addition, flow tests were performed at 50 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$, 120 $^{\circ}\text{C}$ (injection temperature) and 160 $^{\circ}\text{C}$ (minimum viscosity temperature region) in order to compare the viscosities of R0 and R4. The

viscosity of R4 from oscillatory and flow tests as a percentage of that for R0 is plotted in Fig.6-3 at 50 °C, 100 °C, 120 °C and 160 °C.

Fig. 6-2 Viscosity vs temperature curves for R0 and R4

The minimum viscosity temperature regions of R0 and R4 were found around 160 °C (Fig.6-2). The viscosities of R0 and R4 decreased as the temperature increased up to 160 °C. Then, the viscosities increased due to the development of curing reactions in RTM6. The viscosity of R4 was lower below 160 °C but higher at 160 °C and above compared with that of R0. The viscosity of R4 measured in the flow test was also lower than that of R0 at 50 °C, 100 °C and 120 °C (Fig.6-3). However, the viscosity of R4 at 160 °C was higher by more than 150% with respect to that of R0.

Both the oscillatory and flow tests showed that the addition of FP1 decreased the viscosity of RTM6 below 120 °C, but increased its viscosity at 160 °C. FP1 acted as a plasticizer below 120 °C. However, the curing process of RTM6 was accumulated due

to the addition of FP1. The addition of FP1 did not influence the composite formation process because resin viscosity was maintained at a comparable level to that of RTM6 at the injection temperature (120 °C).

Fig. 6-3 The viscosities at different temperatures from oscillatory tests and flow tests of R4 as a percentage with respect to the viscosities of R0

6.5 Mechanical properties

The Load *vs* displacement curves of interlaminar shear test and in-plane-shear test were showed in Fig. 6-4 (A and B) for CFR0 and CFR3, respectively. The interlaminar shear strength (ILSS), in-plane shear strength (IPSS) and in-plane shear modulus (IPSM) of CFR0 and CFR3 were measured and are shown in Tab.6-3.

In Fig. 6-4A, there was no remarkable difference on the slope and maximum load value of the curves for CFR0 and CFR3. The ILSS of CFR0 and CFR3 were 71.6 ± 1.9 MPa and 64.7 ± 5.1 MPa, respectively. The reduction in the ILSS after the addition of 8 wt% FP1 into RTM6 was less than 10%. In Fig. 6-4B, the load *vs* displacement curves of in-plane-shear test were similar for CFR0 and CFR3 as well as

the interlaminar shear test. The IPSS of CFR3 was 95.3 ± 1.8 MPa, which was 8% lower than that of CFR0. The slight decreases in ILSS and IPSS after the addition of FP1 were not significant. The ILSS and IPSS of CFR3 were almost equal to those in the technical data sheet. In addition, the IPSM of CFR3 was 4.2 ± 0.1 GPa which was close to the values of CFR0 and the technical data sheet. The results showed that the addition of FP1 did not induce a significant reduction in the mechanical properties of CFR.

Fig. 6-4 The load vs displacement curves of CFR0 and CFR3 in interlaminar shear test (A) and in-plane-shear (IPS) test (B)

Tab. 6-3 ILSS, IPSS and IPSM data of CFR0 and CFR3

Sample	ILSS (MPa)	IPSS (MPa)	IPSM (GPa)
Technical data sheet	62	95	4.3
CFR0	71.6 ± 1.9	102.7 ± 0.6	4.1 ± 0.1
CFR3	64.7 ± 5.1	95.3 ± 1.8	4.2 ± 0.1

6.6 Flame retardancy

6.6.1 LOI and UL 94 tests

LOI and UL 94 tests are two common small-scale fire tests to characterize the flammability of polymer materials. The influence of FP1 on the flammability of RTM6 and CFR were studied in these two tests. Tab.6-4 shows the LOI values and UL 94 ratings of the flame retardants RTM6 and CFR.

As shown in Tab.6-4, the LOI of R0 was 27%. The LOI of R1, R2 and R3 were 33%, 36% and 38%, respectively, showing that the addition of FP1 increased the LOI of RTM6. The LOI increase was positively related with the FP1 loading. In the UL 94 tests, the thickness of the R0, R1, R2 and R3 samples was 3.2 mm. R0 showed no rating and the R0 sample was burnt out once ignited in the 1st ignition. No self-extinguishing ability was shown by R0. R1 showed no rating as well as R0. However, the burnt length (BL) of R1 was 34 ± 3 mm, showing that the self-extinguishing ability of R1 was improved compared to that of R0. The improvement was enhanced when the FP1 loading was increased in RTM6. R2 achieved a V-1 rating and R3 achieved a V-0 rating with a 8 wt% FP1 loading. The BL of R2 and R3 were 26 ± 2 mm and 22 ± 3 mm, respectively. The LOI and UL 94 test results indicated that FP1 had a significant influence in reducing the flammability of RTM6.

The thickness of CFR0 and CFR3 was 2.2 ± 0.1 mm. The LOI values of CFR0 and CFR3 were 31% and 43%, respectively. The increase in LOI was 12% between CFR0 and CFR3, while that between R0 and R3 was 11%. This indicates that a

synergistic effect was shown between carbon fiber and FP1 in RTM6. In the UL 94 test, both CFR0 and CFR3 were classified as having no rating and the samples were burnt out. After the 1st ignition, CFR0 did not reignite. However, CFR0 was burnt out once ignited in the 2nd ignition. Compared with R0, the ignition time of CFR0 was delayed, indicating that carbon fiber had an influence on the burning of RTM6. Unfortunately, CFR3 showed the same phenomenon as CFR0 in the UL 94 test. The influence of FP1 on improving the self-extinguishing ability of RTM6 was not showed in CFR. Considering that sample thickness was positively related with the UL 94 test results, it is possible to understand the UL 94 results of CFR3. At a thickness of 2.2 ± 0.1 mm, the influence of FP1 on self-extinguishing ability was not shown in CFR.

Tab. 6-4 LOI and UL 94 results of flame retardants RTM6 and CFR

Sample	LOI (%)	UL 94	
		Rating	BL (mm)
R0	27	NR	BO
R1	33	NR	34±3
R2	36	V-1	26±2
R3	38	V-0	22±3
CFR0	31	NR	BO
CFR3	43	NR	BO

BL meant the burnt length; NR meant no rating; BO meant burnt out

6.6.2 Cone calorimetry test

A Cone Calorimeter is a well-known instrument for studying the flame retardancy of polymer materials by measuring heat release, mass loss, smoke release and carbon monoxide/carbon dioxide release from burning materials. The influence of FP1 on the burning of RTM6 and CFR were studied using this test. The heat release rate (HRR) and mass curves for R0, R1, R2 and R3 are shown in Fig.6-5 (A and B, respectively). The HRR and TSP (total smoke production) curves for CFR0 and CFR3 are shown in Fig.6-6 (A and B, respectively). The values for TTI (time to ignition), pHRR (peak of HRR), THR (total heat release), TSP (total smoke production), EHC (effective heat of combustion) and residue amounts for the flame retardants RTM6 and CFR are shown in Tab.6-5.

Tab. 6-5 Data for flame retardants RTM6 and CFR at 50 kW/ m² from cone calorimetry tests

Sample	TTI ^a (s)	pHRR ^b (kW/m ²)	THR ^c (MJ/m ²)	TSP ^d (m ²)	EHC ^e (MJ/kg)	Residue (wt%)
R0	49±2	1477±70	118±4	43.8±3	28.2	10.2±1.9
R1	46±3	831±65	106±3	44.6±3	24.8	21.6±1.3
R2	42±2	500±70	115±4	41.7±3	25.3	32.4±2.6
R3	40±1	587±56	109±4	31.4±3	25.0	35.5±2.3
CFR0	53±1	387±30	24.3±0.3	10.0±0.5	21.5	71.5±0.6
CFR3	49±1	423±20	20.4±0.1	8.7±0.2	20.1	71.6±0.6

a: time to ignition; b: peak of HRR; c: total heat release; d: total smoke production ; e:

effective heat of combustion

In Fig.6-5A, the HRR curve for R0 shows one main peak along with a shoulder peak. The pHRR was $1477 \pm 70 \text{ kW/m}^2$ and THR was $118 \pm 4 \text{ kW/m}^2$. Meanwhile, a large amount of smoke was released during the burning of R0. The TSP was up to $43.8 \pm 3 \text{ m}^2$. The mass residue of R0 was $10.2 \pm 1.9 \text{ wt\%}$. The addition of FP1 showed a significant influence on the burning behavior of R0. The TTI of R0 was shortened: those of R2 and R3 were $42 \pm 2 \text{ s}$ and $40 \pm 1 \text{ s}$ respectively. The HRR peak for R0 showed a lower shoulder peak and a lower pHRR in comparison to that of R0. The shoulder peak of R1 was lower than 500 kW/m^2 , while that of R0 was higher than 700 kW/m^2 . The HRR curves for R2 and R3 were very similar to each other. The pHRR was much lower than that of R1. For instance, the pHRR of R2 was 500 kW/m^2 which was 40% and 66% lower in comparison with those for R1 and R0 respectively. The pHRR of R3 was $587 \pm 56 \text{ kW/m}^2$, indicating that the influence of FP1 on the HRR of R0 was not proportional with the loading. The THR of R0 showed a similar variation in HRR after the addition of FP1. At an 8 wt% loading with FP1, the THR of R3 decreased from $118 \pm 4 \text{ MJ/m}^2$ to $109 \pm 4 \text{ MJ/m}^2$. In addition, the smoke production of R1, R2 and R3 was suppressed compared with R0. TSP results showed a sequence of: $R3 < R2 < R1 < R0$. The TSP of R3 was $31.4 \pm 3 \text{ m}^2$. The mass residue of R0 increased significantly after the addition of FP1. The increase in mass residue was proportional to the FP1 loading in R0. At an 8 wt% loading with FP1, R3 showed $35.5 \pm 2.3 \text{ wt\%}$ which was 25.3 wt% higher than that of R0. The above results

show that flame retardant FP1 is a good choice to improve the flame retardancy of RTM6.

Fig. 6-5 HRR (A) and mass (B) curves for R0, R1, R2 and R3 at 50 kW/m²

When RTM6 was reinforced with a high CF loading, the burning behavior of CFR0 showed different results in cone calorimetry testing. The TTI of CFR0 was 53 ± 1 s which was slightly longer than that of R0. The pHRR and THR results were 387 ± 30 kW/m² and 24.3 ± 0.3 MJ/m² respectively which were much lower than those of R0. The TSP of CFR0 was 10.0 ± 0.5 m². The mass residue of CFR0 was 71.5 ± 0.6 wt%. The charring ability of RTM6 was reduced slightly compared to R0. In Tab.6-3, FP1 unfortunately shows that the influence on CFR3 is less than that on R0 at an 8 wt% loading in RTM6. The TTI of CFR3 was 49 ± 1 s which was 4 s slower than that of CFR0. The HRR curve for CFR3 showed a higher and more intense peak in comparison to the curve for CFR0. The pHRR of CFR3 was 423 ± 20 kW/m² which was even higher than that for CFR0. However, the THR for CFR3 was still lower. The value decreased from 24.3 ± 0.3 m² to 20.4 ± 0.1 m². Meanwhile, the TSP of CFR3 was also lower and the reduction was up to 13% in comparison with that of CFR0.

The mass residue of CFR3 was 71.6 ± 0.6 wt% which was almost the same as that of CFR0. The above results show that the influence of FP1 on the burning behavior of CFR0 was much lower than that of RTM6. Surprisingly, the suppression of HRR was the opposite in CFR0. The improvement in charring ability also disappeared. Seen from the results of UL 94 and cone calorimetry tests, FP1 improved the flame retardancy of R0 with a high efficiency, while this efficiency was non-existent in CFR0. However, the increase in the LOI of CFR0 was comparable to that of R0.

Fig. 6-6 HRR (A) and TSP (B) curves for CFR0 and CFR3 at 50 kW/m²

6.7 Water absorption

Water exposure is able to induce stress in the mechanical properties of CFR owing to the water absorption of RTM6. In this section, the influence of FP1 on the water absorption of RTM6 was studied at room temperature. Fig.6-7 shows the weight gain (%) plots for CFR0 and CFR3 as a function of time (day) in the water absorption tests.

In Fig.6-7, the weight gain of CFR0 and CFR3 increases continuously over time. At 30 days, the weight gain values for CFR0 and CFR3 were 0.56% and 0.57%, respectively. Compared with CFR0, the weight gain values for CFR3 were slightly higher at the same time throughout the whole test, as shown in Fig.6-7. Nevertheless, the increase in weight gain was too low to show that the water absorption ability of CFR0 was enhanced after the addition of FP1.

Fig. 6-7 Percentage weight gain curves for CFR0 and CFR3 as a function of time during water absorption testing

6.8 Summary

A halogen-free flame retardant CFR was developed by modification with FP1. The thermal, rheological and mechanical properties of the CFR did not decrease significantly after the addition of FP1. The T_g of CFR3 was 18 °C lower than that of CFR0, while the curing degree and the cured panel composition were not significantly affected. The viscosity of RTM6 decreased the injection temperature after the addition

of 10 wt% FP1, therefore, the addition of FP1 did not affect the processability of RTM in the manufacture of CFR. The ILSS, IPSS and IPSM values of CFR3 were 64.7 ± 5.1 MPa, 95.3 ± 1.8 MPa and 4.2 ± 0.1 GPa, respectively, which were close to those of CFR0, showing that the mechanical properties of CFR were maintained after the addition of FP1. The presence of FP1 improved the flame retardancy of RTM6 to a large extent: the LOI value increased from 27% to 38%. A V-0 rating was achieved in the UL 94 test. pHRR and TSP decreased by 60% and 28%, respectively in cone calorimetry tests; the char residue increased 25.3 wt% with an 8 wt% FP1 loading in RTM6. With regard to the CFR, a synergistic effect between the carbon fiber and FP1 was found in LOI tests. The increase of LOI value for CFR3 with respect to CFR0 was higher than that for R3 with respect to R0. The effect of FP1 on the flame retardancy of CFR led to a reduction in the TSP in cone calorimetry testing.

CHAPTER 7

CONCLUSION AND FUTURE WORK

7.1 Conclusions

The main conclusions of this investigation can be summarized as follows:

- Two series of halogen-free phosphorous-containing flame retardants (FPx and FPOx, x=1, 2 and 3) with different phosphorous (P)' chemical environments were synthesized via nucleophilic addition reaction between acyl chlorides and amines. The significantly different P' chemical shifts in the NMR spectra and the changes in the IR peak positions of P=O groups in the FTIR spectra of FPx and FPOx (x=1, 2 and 3) revealed that the P' chemical environments were modified due to the different number of oxygen atoms and side groups connected with P. FPx and FPOx (x=1, 2 and 3) were chemically incorporated into the epoxy resin since the amide group –NH– in the structure of FPx and FPOx (x=1, 2 and 3) reacted with the epoxide functional group in the epoxy.

- The changes in the P' chemical environments had a significant impact on flame retardancy of epoxy, particularly on the self-extinguishing capacity. The epoxies containing FPOx achieved no rating, while the epoxies containing FPx (x=1, 2 and 3) passed a V-0 rating in UL 94 test. In addition, the limiting oxygen index (LOI) values of the epoxies containing FPx were 3-4 % higher than those of the epoxies containing FPOx (x=1, 2 and 3) with 0.67 wt% P. From the cone calorimeter test, the peak heat release rates (pHRR) of epoxies containing FP1 were 26%-40% lower than those of epoxies containing FPO1. The effective heats of combustion of epoxies containing FP1 were lower than those of epoxy and epoxies containing FPO1, indicating that FP1 was effective in the gas phase during the burning. Both the epoxies containing FP1 and FPO1 showed intumescent char residues and the amounts were higher than that of epoxy after the cone calorimeter test. However, the microstructures of the char residues were different between epoxies containing FP1 and FPO1. The char residue from epoxy containing FPO1 had large porous structures with cracks in the inner surface and cracked outer surface. On the contrary, the char residue of epoxy containing FP1 had dense porous structure in the inner surface and dense outer surface.
- The thermal stabilities of the epoxies containing FP1 and FPO1 were compared. The initial thermal decompositions of epoxies containing FP1 occurred at higher temperatures compared with the epoxies containing FPO1.

Similar amounts of char residues were obtained in the two kinds of epoxy systems at 700 °C.

- The tensile strength, the elastic modulus and the glass transition temperature of the epoxy were maintained after the addition of FP1 and FPO1. The variation of tensile strength was within 5% in both cases.
- The flame-retardant mechanisms of FP_x and FPO_x (x=1, 2 and 3) were different due to the changes in the P' chemical environments due to the different number of oxygen atoms connected with P. FPO_x (x=1, 2 and 3) mainly acted in the condensed phase by the promotion of char during the burning of epoxy. FP_x (x=1, 2 and 3) acted both in the gas and condensed phases during the burning of epoxy. In the gas phase, flame inhibition was indicated by the results of TG-MS and TG-FTIR. In the condensed phase, FP1 also promoted char formation. The self-extinguishing ability of epoxies containing FP_x (x=1, 2 and 3) was obtained due to both of the two phases actions, while the gas phase action was indispensable to the self-extinguishing ability.
- 8 wt% of FP1 was successfully added to an RTM 6 epoxy resin, which was used to manufacture carbon-fiber reinforced composites via resin transfer molding. The resin transfer molding process was not affected since the viscosity of RTM 6 resin was maintained after the addition of FP1. The glass transition temperature of the epoxy decreased by 18 °C. The variations of the

interlaminar shear strength (ILSS), in-plane shear strength (IPSS) and in-plane shear modulus (IPSM) of the carbon-fiber reinforced composite were within 10 % of the values measured in the composites without FP1. In addition, the water absorption of the composite was slightly increased. In terms of RTM 6, its flame retardancy was remarkably improved by the addition of 8 wt% of FP1. However, the fire behavior of the composite manufactured with the RTM6 resin with 8 wt % FP1 only improved moderately. The LOI of the composite with 8 wt% FP1 increased 12 % in comparison with the composite without FP1. The composite with 8 wt% of FP1 showed poor flame retardancy in the UL 94 and cone calorimeter tests.

7.2 Future work

On basis of the results obtained in this thesis, two important areas for future research were found:

- The flame inhibition action of FP1 in epoxy was related to the release of PO₂ from thermal decomposition of FP1 in the same temperature range in which hydrocarbon compounds were released due to thermal decomposition of epoxy matrix. If this mechanism is also active in other epoxy systems, it could be the basis to design a new generation of halogen-free phosphorous-containing flame retardants for polymers. Therefore, this mechanism should be analyzed in different epoxy systems through the analysis of the thermal decomposition

of phosphorous-containing flame retardants and epoxies with phosphorous-containing flame retardants independently.

- Improving the flame retardancy of the epoxy matrix was not enough to improve the fire behavior of the carbon-fiber composite and this is an important issue. Thus, the differences between the epoxy matrix and its composite during combustion have to be better understood. One possible explanation may be due to higher thermal conductivity of the carbon fibers (as compared to the epoxy), which will result in a more intense combustion in the composite. This should be investigated in more detail by comparing the transfer of heat in the epoxy matrix and in the composite during burning as well as the relationship between the surface temperature of flame-retardant composite and the thermal stability of char residue.

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