Department of Mechanical, Materials
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Bio-sourced Epoxy Matrix Composites with Natural Fibre Reinforcement

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Abstract

The increasing concern about environment and pollution issues caused by disposal of petroleum-based waste lead to requirement for green composite which is sustainable and eco-friendly. Fibre reinforced composite with natural fibre reinforcement or bio-sourced resin matrix may be a feasible answer to the demand of green material. To fabricate fully-green composite, this work selected ramie fabric (RF) and rosin-sourced epoxy (rEP) resin as reinforcement and matrix respectively. To improve the fire safety performance of the rEP/RF composite, ammonium polyphosphate (APP) and organic phosphate (OP) were applied to modify the rEP and RF respectively, and the combined effect of simultaneously modification to fibre and matrix on inflammability of composite was investigated. Secondly, to furtherly study the combined flame retardant effect, different flame retardant (FR) additives including APP, aluminum trihydrate (ATH), zinc borate (ZnB) and expandable graphite (EG) were applied to modify rEP respectively and then reinforced by OP modified ramie fabric (OP@RF). Furthermore, a concept-proof study of liquid composite molding (LCM) process was carried out to fabricate RF/rEP composite, this section is to solve the high viscosity problem of rEP system in resin transfer molding (RTM) process. At last, a preliminary study about bio-sourced itaconic acid based epoxy (IABE) resin was carried out, the mechanical performance of glass fibre (GF) reinforced IABE (IABE/GF) composite and carbon fibre (CF) reinforced IABE (IABE/CF) composite was characterized. The specific information of each part of work was as follows.

To begin with, a fully-green composite composed of RF and rEP was developed. The RF and rEP were modified by OP and APP, respectively. Correspondingly, four groups of samples (rEP/RF, APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF) were manufactured via vacuum bag assisted compression molding process. Thermal properties, flammability, heat release behavior, and mechanical properties of the samples were characterized. The preliminary results shows that both the FR modification to the fabric and the resin improved the fire safety performance of the composite. The APP@rEP/OP@RF composite achieved self-extinguishing in vertical burning test and a limit oxygen index of 33.2%, the peak heat release rate (PHRR) and average heat release rate (HRR) were reduced by 79% and 57% respectively than those of rEP/RF composite. However, the mechanical properties of the samples with FR modified matrix or FR modified ramie fabric behaved unfortunately inverse.

Secondly, on the basis of first part of work, to furtherly investigate the combined effect of OP@RF with rEP modified by different FR additives, the RF was still modified by OP and rEP was modified by APP, ATH, ZnB, and EG, respectively. Six formulations of composite groups: control (rEP/RF), rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF, were fabricated. Thermal gravimetric analysis (TGA), flexural and tensile tests, UL-94 vertical burning and limit oxygen index (LOI) tests, and scanning electron microscope (SEM) were carried out to evaluate the influence of different FR additives on composite performance. The results proved that the combination of OP@RF with rEP modified by different FR additives improved the inflammability of composite with different extent. The APP@rEP/OP@RF and EG@rEP/OP@RF composites achieved V0, V0 inflammability in UL-94 category, 71.4% and 42.7% reduction in peak heat releasing rate, 46.6% and 21.1% reduction in heat releasing rate compared with rEP/OP@RF composite and 35.0%, 41.5% in limiting oxygen index test, respectively. However, the introduction of OP@RF into composites showed obviously negative influence on composite mechanical performance.

Furthermore, in a concept-proof study, a preform-based resin transfer molding (RTM) process was presented that was characterized by first pre-loading the solid curing agent onto the preform, and then injecting the liquid nonreactive resin with an intrinsically low viscosity into the mold to infiltrate and wet the pre-loaded preform. The separation of resin and hardener helped to process inherently high viscosity resins in a convenient way. Rosin-sourced, anhydrite-cured epoxies that would normally be regarded as unsuited to liquid composite molding, were thus processed. Rheological tests revealed that by separating the anhydrite curing agent from a formulated RTM resin system, the remaining epoxy liquid had its flowtime extended. C-scan and glass transition temperature tests showed that the preform pre-loaded with anhydrite was fully infiltrated and wetted by the liquid epoxy, and the two components were diffused and dissolved with each other, and finally, well reacted and cured. Composite laminates made via this approach exhibited roughly comparable quality and mechanical properties with prepreg controls via autoclave or compression molding, respectively. These findings were verified for both CF and RF composites.

Finally, itaconic acid, as a natural-sourced product with enough production and acceptable price, its unsaturated double bond and carboxyl group endows it potential as precursor of epoxy monomer, some IABE systems was designed and synthesized. To furtherly extend the application of IABE resin, GF and CF were applied to reinforced the IABE resin respectively. The IABE/GF and IABE/CF composites were fabricated via compression molding process and the mechanical performance was characterized. The current work was preliminary and the aim was to provide some fundamental information about mechanical properties of IABE/GF and IABE/CF composites.

The current work tried the possibility of combining natural fibre and bio-sourced epoxy to form fully-green composite. The influence of FR treated RF on flame retardancy of fibre reinforced composite was investigated. The combined effect of fibre treated by OP with matrix treated by different FR additives was discussed. This work also tried to find a solution for RTM process for high viscous rosin-sourced resin. In addition, the mechanical performance of IABE/GF and IABE/CF composites were evaluated as the extension of future work about bio-sourced epoxy resin composite.

List of Publications

Journal papers:

1. **Sicong Yu**, Xufeng Zhang, Xiaoling Liu*, Chris Rudd, Xiaosu Yi*, A Conceptional Approach of Resin-Transfer-Molding to Rosin-Sourced Epoxy Matrix Green Composites [J]. Aerospace, 2020, 8(1): 5.

2. Study on Flammability And Mechanical Properties of A Fully-Green Composite, in preparation.

3. Influence of Different Flame Retardant Additives on Ramie Fibre Reinforced Rosin-sourced Epoxy Composite, in preparation.

Book Chapter:

1. **于思聪**, 张旭锋, 刘晓玲, 益小苏. 植物纤维增强树脂基复合材料研究进展. 《绿色航空技术创新与发展：中欧携手应对未来挑战论文集，航空工业出版社，2020/11，北京，ISBN978-7-5165-2403-9.

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Abbreviations

APP: Ammonium polyphosphate

APP@rEP: Ammonium polyphosphate modified rosin-sourced epoxy

ASTM: American Society of Testing and Materials

ATH: Aluminum trihydrate

ATH@rEP: Aluminum trihydrate modified rosin-sourced epoxy

BC-120: A Lewis acid, is a confidential catalyst agent for curing of epoxy system

CCT: Cone calorimeter test

CF: Carbon fibre

DMA: Dynamic mechanical analysis

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

EG: Expandable graphite

EG@rEP: Expandable graphite modified rosin-sourced epoxy

FAR: Federal Aviation Regulations

FR: Flame retardant

GF: Glass fibre

HRR: Heat release rate

IABE/GF: Glass fibre reinforced itaconic acid based epoxy

IABE/CF: Carbon fibre reinforced itaconic acid based epoxy

ILSS: Interlaminar shear strength

ISO: International Standard Organization

LCM: Liquid composite molding

NFRP: Natural fibre reinforced polymer

OP: Organic phosphate

OP@RF: Organic phosphate modified ramie fabric

PHRR: Peak heat release rate

PLA: Poly(lactic acid)

PU: Polyurethane

RAM: Maleopimaric acid

rEP: Rosin-sourced epoxy

RF: Ramie fabric

RIM: Reaction injection molding

RTM: Resin transfer molding

SEM: Scanning electron microscopy

SPR: smoke production rate

THR: Total heat release

TGA: Thermogravimetric analysis

TMA: benzenetricarboxylic anhydride

TSP: total smoke production

TTI: Time to ignition

VARI: Vacuum-assisted resin injection

vol%: Volume per cent

wt%: Weight per cent

ZnB: Zinc borate

ZnB@rEP: Zinc borate modified rosin-sourced epoxy

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Chapter 1. Introduction and Literature Review

1.1 Introduction

1.1.1 Research background

With the advancement of industry, people's living is also changing day by day. However, the fast growing industrial development and large population also cause some negative issues such as greenhouse effect, pollution arising from petroleum-based solid waste disposal and depletion of non-renewable resources. Therefore, considering the environmental and sustainable development reasons, many countries have proposed goals and plans to achieve carbon neutrality within a certain period, and the development and utilization of green materials (i.e. eco-friendly, sustainable, recyclable or bio-sourced materials) is an important path to achieve carbon neutrality.

Natural fibre, especially for cellulosic fibre sourced from botanic plant, is exactly one potential green material which acts as competitive alternative to conventional synthetic fibres represented by glass fibre (GF) and carbon fibre (CF). Natural fibres possess comparable specific strength than glass fibre while having the advantages of high availability, biodegradability, light-weight and favorable cost-effectiveness [1].

As fibrous material, the structure of natural fibre makes it not suitable for application in many situations. To expand the application range of natural fibre, a common used approach is to combine natural fibre with polymer. Thus natural fibre reinforced polymer (NFRP) composite has gained popularity as an important topic in green material field. The fibre reinforcements in fibre reinforced polymer system can act as medium for load transfer and bridge the cracks of polymer matrix during failure, thus enhancing the mechanical performance of composites. The potential application of NFRP composites involves construction material, non-structural part of automobiles or shell of equipment [2].

In the cases of NFRP composites, another viable method to increase the content of green components in composite system is replacing conventional petroleum-based polymer matrix with bio-sourced polymer. The bio-sourced polymers are synthetized from natural feedstocks such as plant oils, derives of natural carbohydrate, natural resins. Among the bio-sourced polymers, bio-sourced epoxy resins have promising mechanical property, good chemical resistance and shape stability, which enables epoxy resins to be applied in various engineering fields. However, the development of novel bio-sourced resin may encounter some problem, for instance, the high viscosity of rosin-sourced epoxy (rEP) resin leads to bad processability during manufacturing process.

In addition, a primary drawback of both natural fibre and epoxy resin are their high flammability in NFRP composite system because there are serious human and property damage caused by fire hazard annually. No matter in the automotive, aircraft or construction fields, there are different fire safety standards for involved composites. A universal method to improve the inflammability of material is using flame retardant (FR) additive to modify the material. In the cases of studies relevant to FR composites, most of the studies focus on development of novel FR additives or evaluating the effectiveness of FR additive modified polymer matrix. There are numerous studies correlated with the flame retardancy of fibre reinforced composite, but few studies consider the role of fibre on the anti-flammable performance for fibre reinforced composites. Therefore, it is significant to investigate the influence of FR modified fibre on fire safety performance of NFRP composite.

This work focuses on the manufacture optimization and FR modification of NFRP composite composed of natural fibre reinforcement and bio-sourced epoxy matrix. Firstly, the ramie fabric (RF) reinforced rosin-sourced epoxy composite was fabricated, the ramie fabric and rosins-sourced resin were modified by organic phosphate (OP) and ammonium polyphosphate (APP) respectively and the combined effect of two FR modification was investigated. Secondly, different FR additives including APP, aluminum trihydrate (ATH), zinc borate (ZnB) and expandable graphite (EG) were applied to modified the rosin-sourced resin respectively and the influence of different FR additives on composites was evaluated. Thirdly, an ex-situ liquid composite molding (LCM) method was proceeded to solve the high viscosity problem of rosin-sourced anhydride hardener to make the resin system more suitable to resin transfer molding (RTM) process. At last, a novel bio-sourced epoxy, itaconic acid based epoxy (IABE), was reinforced by GF and CF respectively, the mechanical performance of glass fibre reinforced itaconic acid based epoxy (IABE/GF) and carbon fibre reinforced itaconic acid based epoxy (IABE/CF) composites were characterized.

1.1.2 Aims and objectives

The current work aims to develop fully green composite composed of natural fibre reinforcement and bio-sourced epoxy matrix. The manufacturing process and fire safety performance of composite are optimized to extend the application to automobile even aircraft field. The objectives of the current study include:

(1) To develop a fully green NFRP composite with bio-sourced epoxy resin matrix. Specifically, this objective involves selection of raw materials and optimization of manufacturing process.

(2) To improve the fire safety performance of previous NFRP composite, the natural fibre and bio-sourced resin are simultaneously modified by different FR additives respectively, the combined effect of simultaneously FR modification to fibre and polymer on mechanical and fire safety performance of composite is evaluated. Furthermore, keeping the FR modified fibre unchanged, different FR additives are applied to modify the resin matrix respectively and the influence of different FR additives on combined effect is compared.

(3) To extend the application of bio-sourced epoxy system as matrix for fibre reinforced composite. The manufacturing process is developed and optimized. Some preliminary composites with different manufacturing process, bio-sourced resins or

fibre reinforcements are prepared and compared.

In order to fabricate FR and green composite, ramie fabric and rosin-sourced epoxy resin are chosen as fibre reinforcement and bio-sourced epoxy matrix. RF and rEP are modified by different FR additives with proper process. According to characteristics of RF and rEP, the manufacturing process and relevant parameters are determined and optimized. At last, the fabricated composite samples are characterized to investigate their mechanical and inflammability performance.

1.1.3 Thesis outline

Totally six chapters are included in this work.

Chapter 1 reviews the overall background, research gap, aim and objectives of this research as well as the outline of this thesis.

Chapter 2 adopts RF as reinforcement, rEP resin as matrix. The RF is treated by organic phosphate via dip coating process, while APP is mixed with rEP to improve the inflammability of resin. The fully green rEP/RF composite is fabricated by a two-step process: firstly rEP/RF prepreg is prepared by painting rEP solution (the solvent is acetone) on RF, then the composite is fabricated by vacuum bag assisted compression molding process. To investigate the combined effect of OP modified fabric (OP@RF) and APP modified rEP (APP@rEP), composites with four formulas (rEP/RF, APP@rEP/RF, rEP/OP@RF, APP@rEP/OP@RF) are prepared. The mechanical properties and inflammability of composites are characterized.

Chapter 3 investigates the influence of typical FR additives: APP, ATH, ZnB and EG on the combined effect of rEP/OP@RF system. The fabrication process and test methods are similar to Chapter 2. The difference is that four typical FR additives (APP, ATH, ZnB and EG) are applied to modify rEP respectively with same weight fraction. The mechanical performance and flame retardancy of rEP/RF, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites are tested to evaluate the influence of different FR additives on combined flame retardant effect as well as mechanical performance of composite.

Chapter 4 exploits a concept-proof preform-based resin transfer molding process to fabricate rEP/RF and rEP/CF composite. In this process, the rosin-sourced curing agent is preloaded on fabric preform, and then nonreactive resin with low viscosity is injected to infiltrate the pre-treated fabric preform in RTM process. Compared with compression molding, the preform-based RTM solve the high viscosity problem of rosin-sourced resin system by separating the curing agent and epoxy monomer. The mechanical performance and resin infiltration are characterized to compare the effectiveness of preform-based RTM process with compression molding.

Chapter 5 is a preliminary study about itaconic acid based epoxy (IABE) composite reinforced by GF or CF. This chapter is an extension of fibre types and bio-sourced resin types to find more possibilities of fibre reinforced composite based on bio-sourced resin. The IABE/GF and IABE/CF composites are fabricated via similar compression molding process as previous chapter, the tensile, flexural, interlaminar and compressive properties of the composites are investigated.

Chapter 6 summarizes the research results and proposes possible future research topics on the basis of the current work.

1.2 Natural fibres

1.2.1 Introduction of natural fibres

In recent years, the extensive application of petroleum-based materials has led to nonnegligible environmental problems such as ecology system damage, land occupation by waste landfill and harm to people health [1]. These problems lead to the ever-increasing environmental concern for exploration of green, biodegradable or recyclable materials. In response to this demand, researchers and engineers have conducted massive work about bio-sourced and sustainable materials [3]. Natural fibres, especially for cellulosic plant fibres, have been widespread utilized as green reinforcements within composites [4]. Material industry have taken advantage of natural fibres owing to the cost-effectiveness and low density for a long period, for instance, the ancient Egyptians mixed straw fibre with clay as the raw material of wall [5]. It is noteworthy that some innovative studies are established to study natural fibres as the reinforcements for polymer-based composites, the incorporation of natural fibres into polymer matrix can improve the mechanical performance of composite, the embedded cellulosic fibres have load transfer effect during deformation thus reducing the cracks of polymer matrix and enhance toughness of the composite [6]. As a result, natural fibre reinforced polymer composite becomes a crucial branch of green material development whether in industry or academia. In industrial field, the European Union has consumed 43,000 tons of natural fibres as reinforcement in 2003 [7]. This annual consumption was furtherly increased to 315,000 tons in 2010, the NFRP composites approximately accounted for 13% of total fibre reinforced composites. According to the forecast report, the annual consumption of natural fibres will increase to 83,000 and take up 28% of all reinforcement composites [8]. The United States Department of Agriculture has constructed a bio-based materials development plan, which aims to use at least 10% of renewable and bio-sourced materials in all basic building materials by 2020, this percentage will increase to 50% by 2050 [9]. In academic field, the number of literatures with “natural fibre” as keyword in title has significantly increased from 2015 to 2021 (As Figure. 1-1 showed), which implied the scholars' interest in natural fibres. The development of industries related to natural fibres can reduce growing risk of greenhouse effect, the biodiversity and waste disposal problem can also be ameliorated [10].

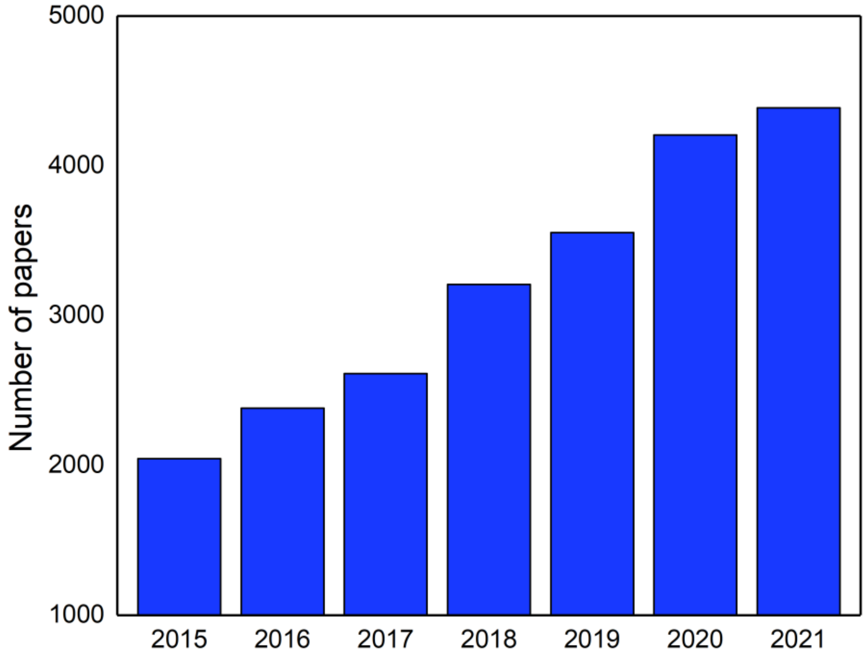


Figure. 1-1 Number of papers with “natural fibre” keyword in title (From Web of Science)

In general, natural fibres are fibrous material produced from natural. The natural fibres can be roughly divided into three groups: animal-sourced fibre (silk, wool, hair), mineral fibre (asbestos, basalt) and cellulosic fibre depending on their sources.

In general, although animal fibres and plant fibres are both from natural sources, the strengths and stiffnesses of plant-based fibres are higher than those of animal fibres except for silk fibre, also the silk fibre is more expensive and with lower stiffness. The availability, yield and widely distribution of plant fibres are also acceptable. Therefore, plant fibres are more suitable for composites utilization compared to animal fibres. As for mineral fibres, the sustainability is not so ideal, which is not in the line with demand for green materials. In this work, the word “natural fibres” is mainly referred to cellulosic fibres from plant and the work is focus on the cellulosic fibres as composite reinforcement.

A universal classification method for cellulosic fibres is according to their botanical origin. As Figure. 1-2 showed, the cellulosic fibres mainly come from bast (jute, flax, ramie, hemp, kenaf), seed (cotton, milk weed), leaf (sisal, banana, abaca), fruit (oil palm) or stalk (race, wheat) of plants [2]. Figure. 1-3 displays some representative plants in their growing environment.

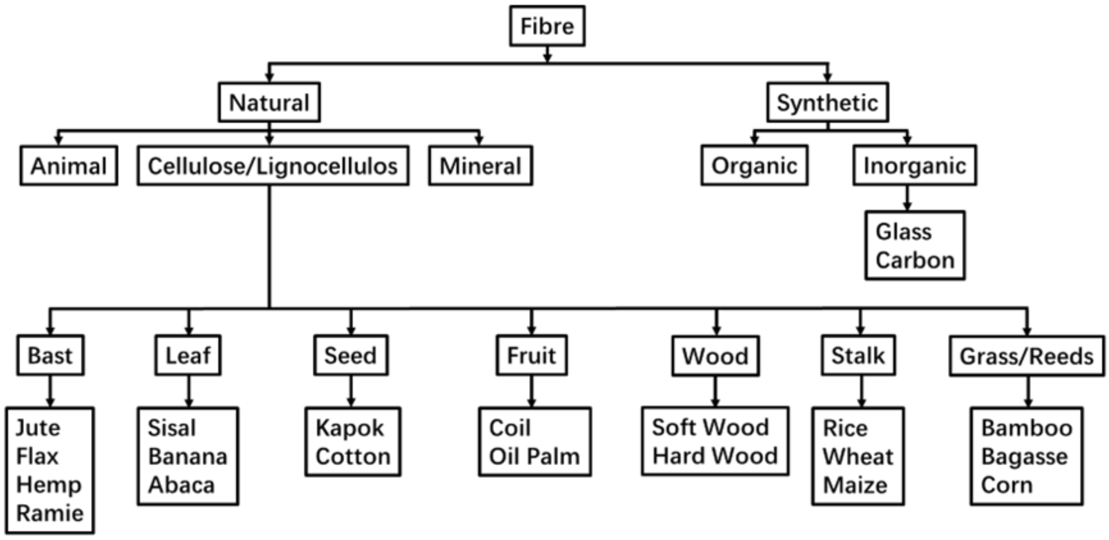
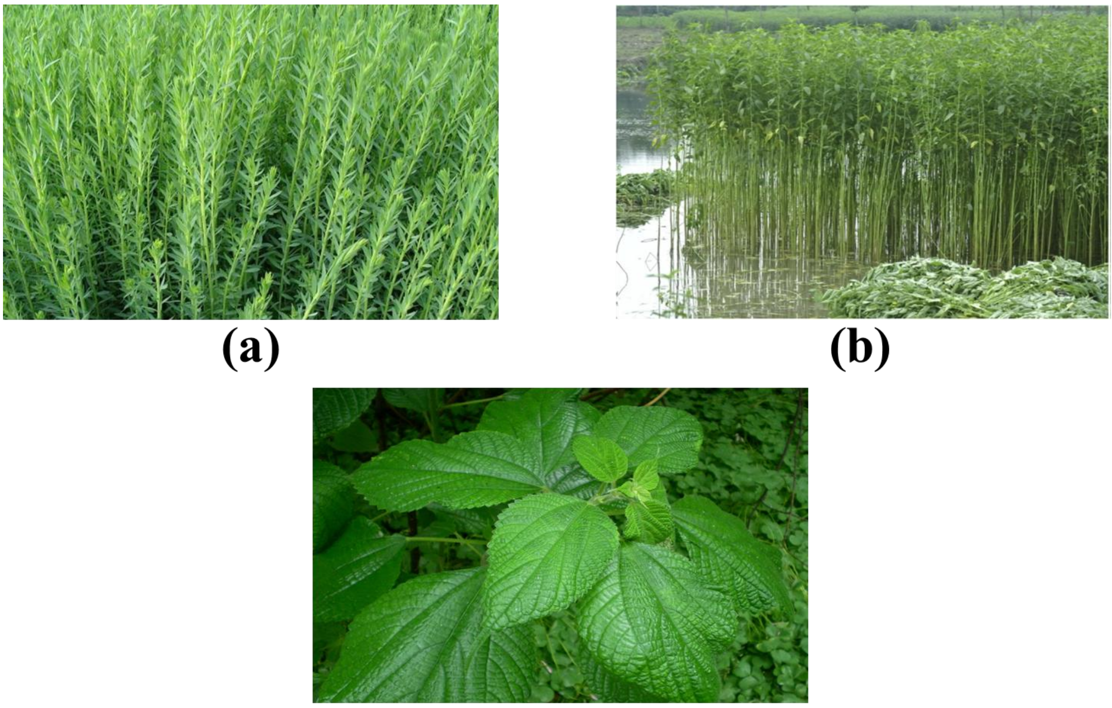


Figure. 1-2 The category of fibres [11]



(a) (b)

(c)

Figure. 1-3 (a) Flax (b) Jute and (c) Ramie plants in their growing environment [2]

For past decades, synthetic fibres are primary reinforcements for fibre reinforced polymer composites. Compared with synthetic fibres, the advantages of natural fibres exhibited in following aspects: First of all, the biodegradability, renewability and non-toxicity of natural fibres correspond to the consensus of developing eco-friendly materials [12]. In addition, as fibre reinforcement for composites, the specific mechanical properties of natural fibres are comparable to traditional fibres such as glass fibre [13]. Meanwhile, natural fibres are also notable from the light-weighting and cost reduction perspective. Compared the energy consumption, the production of natural fibres will save 40% energy than that of glass fibres [14]. Furthermore, based on the unique hierarchical and lumen structure of natural fibres, NFRP composite also showed positive improvement on sound absorption [15] and vibration damping [16] properties of polymer composites. On the basis of above reasons, natural fibre have gradually took place of synthetic fibres in composite industry such as interior of transportation, construction or furniture.

As natural-sourced feedstock, natural fibres are widely planted around the world with high yield. A global yield of various natural fibres in 2014 is displayed in Table. 1-1. As the natural fibre with largest yield, the total global production of cotton fibre is as high as 25 million tons per year. Some bast fibres such as flax or jute also have relatively large annual yield. China and India are the major agriculture areas for many kinds of natural fibres, the yield is also considerable. The high availability and wide distribution of natural fibres guarantee their application in NFRP composite materials [2].

Table. 1-1 Averages of global production of different natural fibres in 2014 [13]

Fibre type	Production per year (Million tons)	Primary producer country
Cotton	25	China, USA, India, Pakistan
Coir	0.45	India, Sri Lanka
Flax	0.5-1.5	China, France, Belgium
Hemp	0.1	China
Jute	2.5	India, Bangladesh
Kenaf	0.45	China, India, Thailand
Ramie	0.15	China
Sisal	0.3	Brazil, China, Tanzania

However, there are some limitations in practical application of NFRP composites: (1) Insufficient durability. Normally there is a basic requirement for durability of commercialized fibre reinforced polymer composites. Before the broad acceptance and utilization of the materials, one crucial challenge of NFRP composites is to collect more relevant data about durability of them [17]. (2) Fluctuation in fibre properties. The generation of natural fibres is affected by a variety of factors such as geography, weather or environment. As a result, natural fibres show quality fluctuation in chemical or physical properties even in a same batch of products. This problem will furtherly influence the stability of mechanical properties of NFRP composites [18]. (3) Low resistance to moisture. The intrinsically hydrophilicity of natural fibres causes water absorption problem. For NFRP composites in wet condition, natural fibre will absorb water, which lead to swelling, delamination or micro cracks between fibre and matrix. These defects will be vulnerable to moisture or bacteria, cause crack propagation and accelerate the degradation [19]. The swelling or delamination caused by moisture absorption problem also affects the interface between fibre and hydrophobic polymer matrix [20]. (4) High flammability. Most of polymer matrix and cellulosic fibres are flammable, the combustion of material may release large amount of heat and toxic smoke, which result in fire propagation, risk to humans and seriously property damage [21], thus a crucial limitation of NFRP composites is their low resistance to fire in transportation or infrastructural applications [22].

Actually, the diversity of naturals fibres lead to their different classifications, chemical compositions, mechanical properties and thermal degradation behaviors, which would be gradually introduced in the followed part.

1.2.2 Chemical compositions and structures of natural fibres

The chemical compositions of various natural fibres are listed in Table. 1-2. Cellulose, hemicellulose and lignin are three primary components of natural fibres while wax, pectin, sugars and starch protein account for a minor amount. The chemical composition of natural fibre is directly relevant to its mechanical properties. As three basic components of natural fibre, cellulose, hemicellulose and lignin play different roles in microstructure of natural fibres and influence mechanical performance of fibres.

Table. 1-2 Chemical compositions of different cellulosic fibres [11]

Natural fibres	**Cellulose (%)**	**Hemi-cellulose (%)**	**Pectin (%)**	**Lignin (%)**	**Wax (%)**
Abaca	62.5	21	0.8	12	3
Alfa	45.4	38.5	-	38.5	2
Bagasse	37	21	10	22	-
Banana	62.5	12.5	4	7.5	-
Bamboo	34.5	20.5	-	26	-
Coir	46	0.3	4	45	-
Cotton	89	4	6	0.75	0.6
Curaua	73.6	5	-	7.5	-
Flax	72.5	14.5	0.9	2.5	-
Hemp	81	20	0.9	4	0.8
Henequen	60	28	-	8	0.5
Isora	74	-	-	23	1.1
Jute	67	16	0.2	9	0.5
Kenaf	53.5	21	2	17	-
Phormium	67	30	-	11	-
Pineapple	80.5	17.5	4	8.3	-
Ramie	72	14	2.0	0.8	-
Sisal	60	11.5	1.2	8	-

As a polysaccharide polymer, cellulose is comprised of linked glucose units and the aligned cellulose molecules form crystalline regions of microfibril [13]. Compared with hemicellulose and lignin, cellulose is more stiffer and stronger, which brings strength, stiffness and stability to natural fibre. However, the cellulose is hydrophilic polymer due to the large amount of hydroxyl group in molecule, the hydrophilicity lead to moisture absorption and interface problem for NFRP composites, especially for hydrophobic polymer matrix [2].

Hemicelluloses have similar molecular structure as cellulose, the difference is the polysaccharides chain of hemicelluloses are relatively short and branching, consequently hemicellulose is fully amorphous. The hydroxyl and acetyl groups on molecular structure of hemicellulose result in the water solubility. These groups form hydrogen bonds with cellulose, therefore hemicellulose acts like binding agent and is bonded to cellulose in microfibril structure of natural fibre [23].

As for lignin, it is three-dimensional aromatic polymer contains p-coumaryl, coniferyl and sinapyl alcohol [24]. Lignin has complex aromatic structure and is amorphous, it acts as an adhesive to bond the cell fibres in microstructure of natural fibre, the rigidity of plants are relevant to lignin. The absence of lignin will reduce the height of a plant [23]. Lignin can be treated as an encrusting agent which encompasses the microfibrils, the content of lignin determines structural and morphology of natural fibre. The pectin and wax account for a low content of natural fibres. The pectin acts like bonding agents while the wax was relevant to wettability and adhesion of fibres [25].

There are significant variation in the chemical composition of different natural fibres. For instance, cotton, flax, hemp, pineapple and ramie fibres have relatively higher cellulose content, the cellulose content of these fibres are over 70 wt%. The high contents in cellulose imparts better mechanical properties to these fibres, their woven fabrics are widely applied as reinforcement in literatures about NFRP composites [13]. Numerous factors such as species, growing environment, climatic variation will influence the chemical compositions of natural fibres, and then affect their properties such as mechanical performance.

Different with synthetic fibres, natural fibres have irregular shape, surface and cross-sections. Take sisal fibre as an instance, a typical microstructure of a sisal fibre is shown as Figure. 1-4. The sisal filament has a hierarchical microstructure, a bundle of unidirectional cell fibres with 10-20 μm diameter make up one single sisal filament, while a cell fibre is composed of a lumen encompassed by fibrils with 1-4 nm diameter [15]. In general, natural fibres possess multi-scaled hierarchical microstructures like stacked tubular structures which composed of nano-sized microfibrils. The structure of a natural fibre can be regarded as a composite, hemicellulose and lignin blend and form the matrix while the unidirectional cellulose microfibrils act as reinforcement.

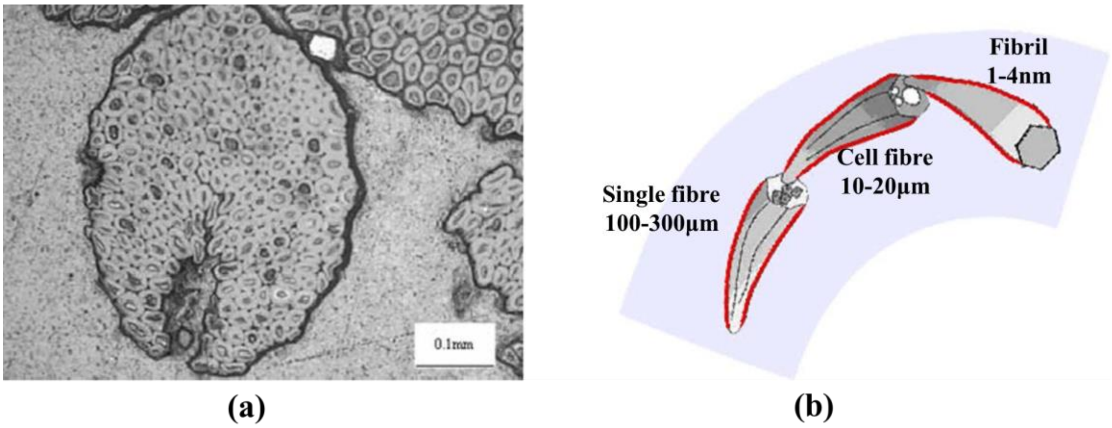


Figure. 1-4 (a) Cross-section of a single sisal filament and (b) sketch drawing of the hierarchical microstructure for sisal fibre

Different with the shape stability of synthetic fibres, natural fibres have irregular shape and rougher surface, there is a huge gap between the structures of different types of natural fibres. The structures of flax, jute and ramie fibres will be introduced afterwards.

As a widespread utilized natural fibre, flax in textile have been found in relics of Egypt and was proved to be produced 7000 years ago. The largest producer of flax are Canada, France and Netherlands, the yield of flax in the EU was 120,000 tons in 2007. A growing cycle of flax begins from sowing in March to cropping in July, the whole process lasts for only 100 days. The flax can be spun to yarns and furtherly fabricated to linen for application such as beddings, furnishing fabric, towels, canvas or decoration. The flax fibres are also utilized as reinforcement elements for NFRP composites [26]. The microstructure of a flax fibre cell and cross-section of a flax filament were exhibited in Figure. 1-5. In the mesoscopic perspective, the cross-section of a flax filament is a bundle contains about 10-40 elementary fibres bonded by pectin. In the microscopic perspective, each elementary fibre processed a structure comprised of primary cell wall, secondary cell wall and lumen in the middle. The primary cell wall coats several layers of secondary cell wall which determine the strength of elementary fibre and the secondary cell wall encompassed the lumen, the lumen is for water transfer of a plant. All the cell walls are consisted of microfibrils which are comprised by crystalline zone (Cellulose) embedded in an amorphous zone (hemicellulose and pectin). The cell wall can be regarded as the reinforcement element for flax fibre, about 70% weight fraction of a flax filament is taken up by microfibrils [27].

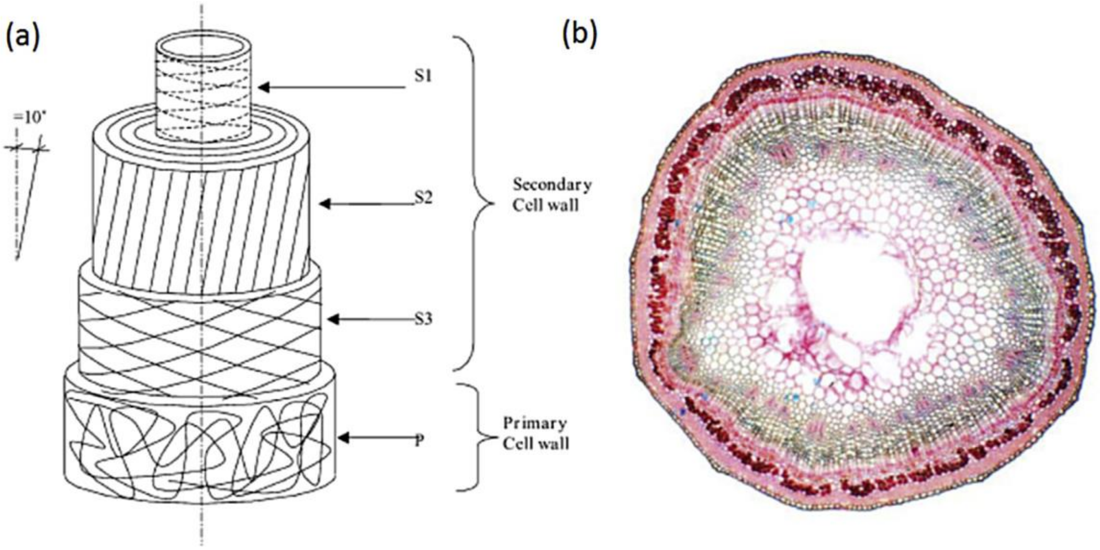
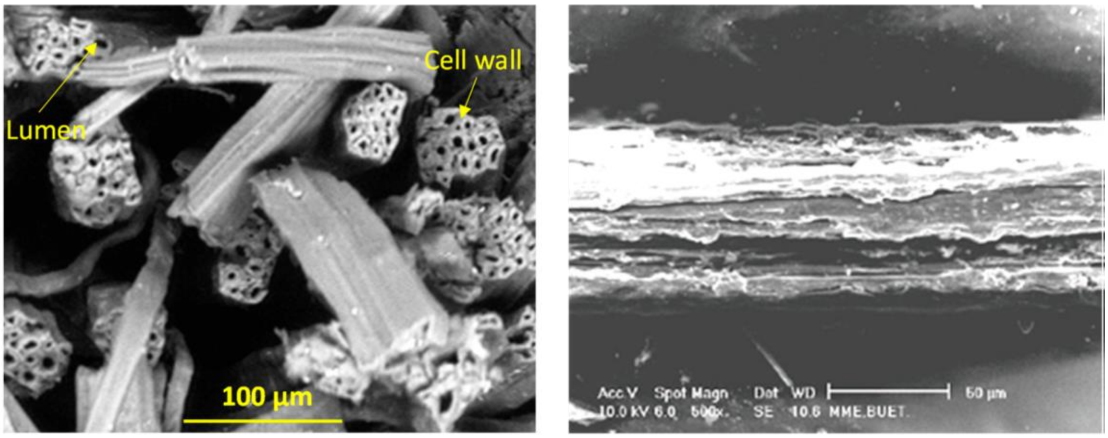


Figure. 1-5 The microstructure of (a) a flax fibre cell and (b) cross-section of flax stem [28]

Jute fibres also yield from the bast of jute plant. An ideal environment for jute includes grassy soil, 125-150 mm precipitation per month and humidity between 70-80%. To extract jute fibres more easily, jute plants will be dipped in water for retting. The SEM images of cross-section and fibre surface are shown in Figure. 1-6. The cross-sectional geometry and fibre surface are generally irregular, the fibre diameters, maturity and micro pores also have significant variation [29]. As Figure. 1-7 exhibited, the cell fibre of jute fibre possesses similar microstructure compared to flax fibre, a bundle of cell fibres form a jute filament and a cell fibre is composed of primary wall, secondary wall which encompassed the lumen [30].



(a) (b)

Figure. 1-6 The SEM images of (a) cross-section (b) surface of jute fibres [31]

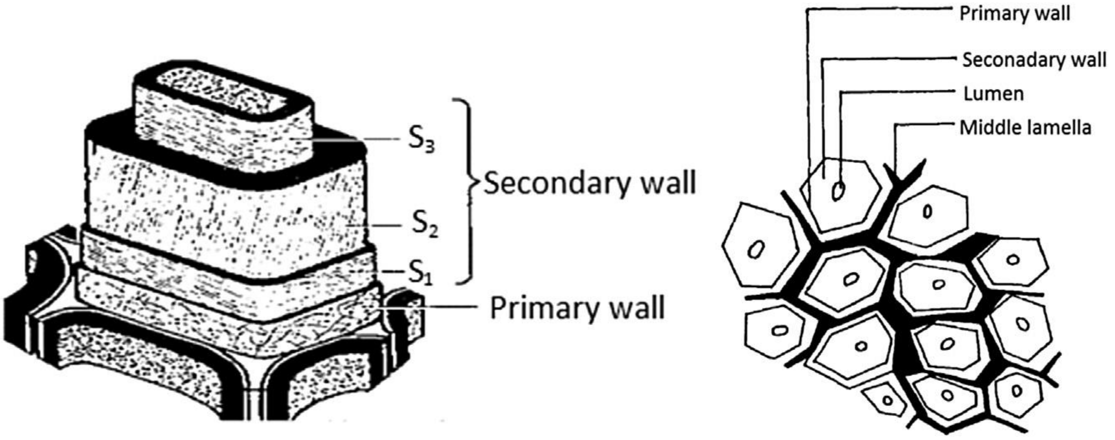


Figure. 1-7 Jute fibre cell wall [30]

Ramie plant, also known as “China grass”, is widely cultivated in the south of China. It is white, smooth and can be dyed easily, thus ramie fabric are still popular raw materials for summer clothes in modern times. Ramie fibres have a short life cycle around 100 days and can be harvested three times annually in the major production in China, with a large yield [32]. The length and diameter of a ramie filament are 60-500 mm and 20-35 µm, respectively. Ramie fibre has relatively higher cellulose content (65-75%) and lower lignin content (1-2%) in comparison to other natural fibres, therefore the mechanical performance of ramie fibre is comparable to several strongest natural fibres such as flax, pineapple leaf, and curaua fibre [33]. Ramie fibre is one of the longest natural fibre, with better thermal stability and resistance to bacteria, mildew and insects than other natural fibres [34]. Figure.1-8 shows the surface and cross-section view of ramie fibres. In comparison to flax and jute fibres, the surface of ramie fibres are more regular and smoother. The cross-section of ramie filament possesses only one cell fibre surrounded by several layers of cell wall, there is a single huge lumen in the middle, which differs from the structure of flax or jute fibre [35].

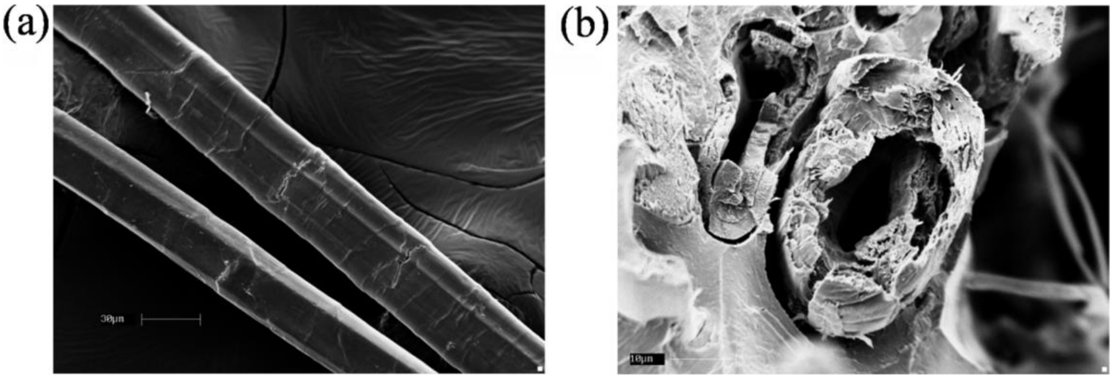


Figure. 1-8 SEM images of (a) surface (b) cross-sectional view of a single ramie fibre [35]

According to the aforementioned descriptions, the typical macroscopic structure of natural fibres (i.e. flax. jute and ramie) is composed of a bundle of tubular cylinders with a lumen in the center of each cylinder. In the microscopic perspective, each cylinder is consists of two cell walls: the primary wall and the secondary wall. The thin primary wall acts as intercellular bonding agent for cell wall bundles while the secondary wall is composed of cellulose micro-fibrils which takes load transfer and provides tensile strength for natural fibres.

1.2.3 Mechanical properties of natural fibres

As aforementioned, all the natural fibres possess similar chemical compositions and varying content of cellulose, hemicellulose and lignin, the different chemical composition of natural fibres lead to different mechanical performance. A. Komuraiah et al. [23] have established a correlation coefficient to evaluate the relation between the chemical compositions and mechanical properties of natural fibres. The results showed that cellulose has a positive correlation with tensile strength, specific Young's modulus and the length of natural fibres. Compared with hemicellulose and lignin, the cellulose presents higher stability and mechanical strength based on the chemical structure. Hence, cellulose can be regarded as major framework component as load transfer for natural fibres. Meanwhile, cellulose has a negative correlation with the microfibril angle, moisture gain and strain at failure of natural fibres. Whereas for hemicellulose, higher hemicellulose content leads to higher specific Young's modulus diameter and moisture gain, it also has a negative correlation with the tensile strength, density, microfibril angle and failure strain of natural fibres. In the case of lignin, it has a positive correlation with the microfibril angle, failure strain, and moisture gain of natural fibres. In addition, the reduction of lignin content will reduce the tensile strength, specific Young's modulus, density, diameter, and length of natural fibres. The natural fibre can be considered as a composite system, the cellulose microfibrils aligned with fibre axis are the reinforcement elements while hemicellulose and lignin act as matrix around the microfibrils. The cellulose microfibrils are the main load-carrying when a load is implemented, the debonding of matrix with reinforcing fibrils and broken of hydrogen bonding of cellulose microfibril will led to final failure of a natural fibre. Therefore, the content of cellulose is the primary factor which influences the tensile strength of natural fibres.

Table.1-3 listed the mechanical properties of natural fibres and synthetic fibres. The specific modulus and density are the average of extreme values found in the literatures [36]. As the table shown, the specific Young's modulus of ramie, flax, curaua, hemp and jute are higher than 30 GPa•cm^3/g, which are higher than that of E-glass fibre. The tensile strength of flax, ramie, kenaf, jute and kenaf are also comparable to E-glass fibre. Comprehensively consider the mechanical strength, yield, cost-efficiency and density of natural fibres, natural fibres represented by flax, ramie, jute and sisal are potential alternatives of glass fibres as reinforcement elements in composite application and civil engineering.

Table. 1-3 Mechanical properties of cellulosic fibres and synthetic fibres [13]

Fibre Type	Relative density (g/cm^3)	Tensile strength (MPa)	Elastic modulus (GPa)	Specific modulus (GPa•cm^3/g)	Elongation at failure (%)
Abaca	1.5	400-980	6.2-20	9	1.0-10
Alfa	0.89	35	22	25	5.8
Bagasse	1.25	222-290	17-27.1	18	1.1
Bamboo	0.6-1.1	140-800	11-32	25	2.5-3.7
Banana	1.35	500	12	9	1.5-9
Coir	1.15-1.46	95-230	2.8-6	4	15-51.4
Cotton	1.5-1.6	287-800	5.5-12.6	6	3-10
Curara	1.4	87-1150	11.8-96	39	1.3-4.9
Flax	1.4-1.5	343-2000	27.6-103	45	1.2-3.3
Hemp	1.4-1.5	270-900	23.5-90	40	1-3.5
Henequen	1.2	430-570	10.1-16.3	11	3.7-5.9
Isora	1.2-1.3	500-600	-	-	5-6
Jute	1.3-1.49	320-800	30	30	1-1.8
Kenaf	1.4	223-930	14.5-53	24	1.5-2.7
Piassava	1.4	134-143	1.07-4.59	2	7.8-21.9
Palf	0.8-1.6	180-1627	1.44-82.5	35	1.6-14.5
Ramie	1.0-1.55	400-1000	24.5-128	60	1.2-4.0
Sisal	1.33-1.5	363-700	9.0-38	17	2.0-7.0
Aramid	1.4	3000-3150	63-67	46.4	3.3-3.7
Carbon	1.4	4000	200-240	157	1.4-1.8
E-glass	2.5	1000-3500	70-76	29	0.5
S-glass	2.5	4570	86	34.4	2.8

1.2.4 Thermal decomposition of natural fibres

The thermal decomposition behaviors of natural fibres are crucial aspect in NFRP composites, especially for researches about flammability of composites.

Thermogravimetric analysis (TGA) is the most typical test to evaluate the thermal stability of natural fibres. The thermal degradation of natural fibres are also relevant to their chemical composition and the main components such as cellulose, hemicellulose, and lignin can be referred to decomposition peak of TGA curve. The main stages of thermal degradation of natural fibres and the reaction corresponded to these stages are summarized as Table. 1-4 [20]

Table. 1-4 The main decomposition stages of natural fibres [20]

Stage 1	Stage 2	Stage 3	Reference
•50-100 ℃: Evaporation of moisture in the fibres	•200-300 ℃: Decomposition of hemicelluloses	•400-500 ℃: Degradation of cellulose and lignin	[37]
•300 ℃: Thermal decomposition of hemicellulose and the glycosidic links of cellulose	•360 ℃: Decomposition of α-cellulose	•200-500 ℃: Degradation peak of lignin	[38]
•250-300 ℃: Characteristic pf low molecular weight component, such as hemicelluloses	•300-400 ℃: Thermal degradation of cellulose	•420 ℃: Lignin decomposition	[39]
•220-315 ℃: Pyrolysis of hemicelluloses	•315-400 ℃: Pyrolysis of cellulose	•160-900 ℃: Pyrolysis of lignin	[40]

As temperature increases, the thermal degradation of cellulose can be divided as followed steps: (1) Evaporation of absorbed moisture (2) Cross-linking of cellulose chains due to dehydration then form dehydrocellulose (3) Degradation of the dehydrocellulose then generate char and volatiles (d) Formation of and degradation of levoglucosan, generate gases, tar and char [41, 42]. The schematic diagram of the decomposition process for cellulose is exhibited in Figure. 1-9. As for hemicellulose, the decomposition temperature occurs between 200-260 °C, most of the products are incombustible gases such as CO_2. Moreover, lignin has a wider decomposition range from 160-400 °C due to different chemical bonding, it was also proved that lignin can promote dehydration and char formation of cellulose. For instance, the lignin content of bast fibres are higher than those of leaf fibres, and the heat release rates of bast fibres were observed to be lower compared to leaf fibres [43].

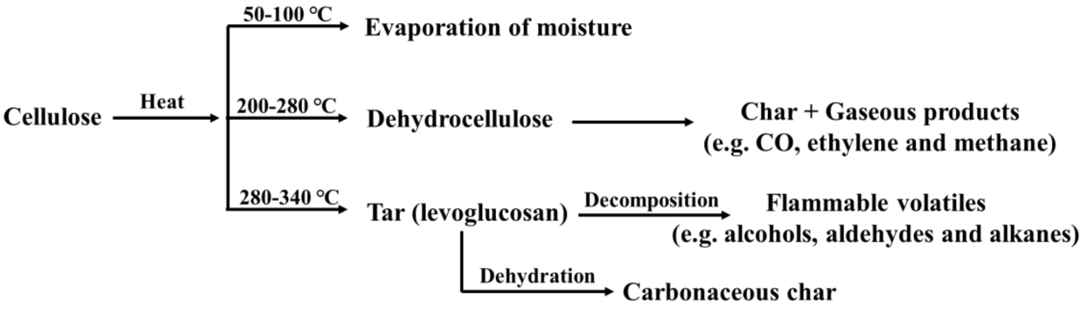


Figure. 1-9 The schematic diagram of thermal decomposition for cellulose [43]

The introduction of natural fibres into NFRP composite system will significantly influence the thermal stability and flammability of composites. The thermal decomposition behavior of natural fibres is important information for these studies relevant to NFRP composites.

1.3 Natural fibre reinforced polymer composites

To utilize the benefits of natural fibres, a reliable solution is to adopt natural fibres as reinforcements for NFRP composites. There is an increasing trending to replace conventional syntactic fibres with natural fibres for fibre reinforced composites, Figure. 1-10 displays the market share of NFRP composites with different application field, it can be seen that the primary applications of NFRP composites are civil and non-structural materials [44]. However, in order to extend the application of NFRP composites to structural or aerospace field, there are some problems to be coped with, such as the durability or insufficient strength compared to carbon fibre reinforced composite.

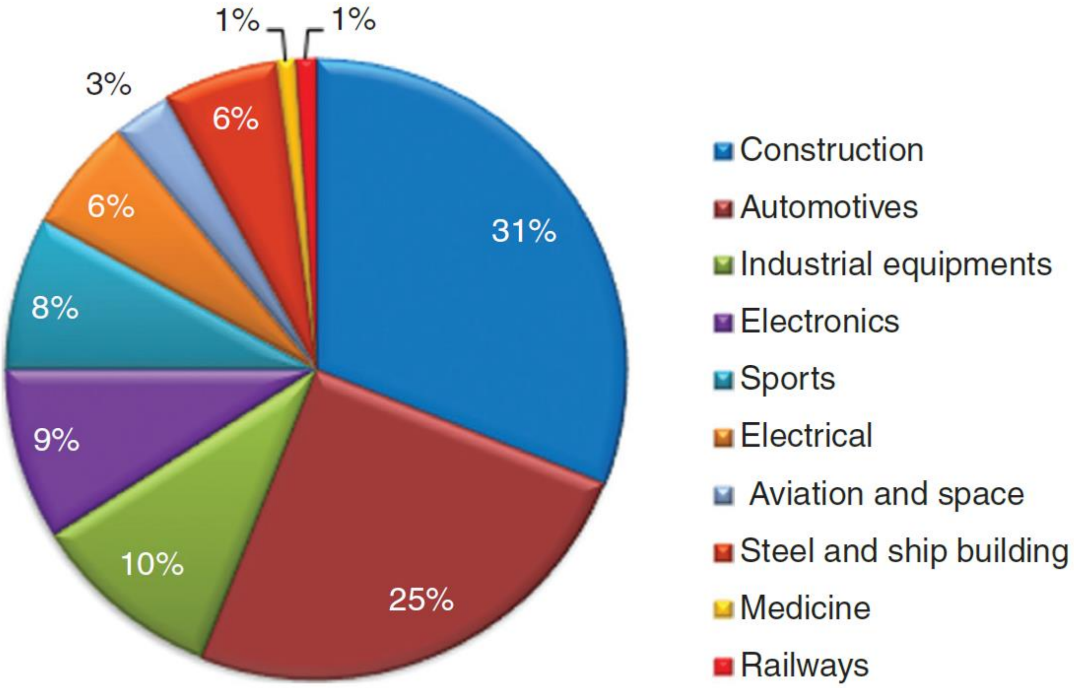


Figure. 1-10 Market share of NFRP composites [44]

1.3.1 Factors influencing the mechanical performance of natural fibre reinforced polymer composites

In the previous part, the reason why natural fibres can be applied as reinforcement elements for composites has been introduced. In comparison to synthetic fibre reinforced polymer composite, the advantages and disadvantages of NFRP composites are summarized as Table. 1-5. NFRP composites are potential replacement for synthetic fibre reinforced polymer composites, especially suitable for requirement of sustainable and eco-friendly materials.

Table. 1-5 Advantages and disadvantages of NFRP composites [45]

Advantages	Disadvantages
•Light weight and high specific strength	•Low durability
•Renewable and eco-friendly resource	•High moisture absorption
•Cost-effectiveness	•Low strength compared to synthetic fibre composites
•Low hazard manufacturing process	•Unstable properties
•Biodegradable, cause less pollution in the end of life	•Lower thermal stability compared to synthetic fibre composites

There are many factors which affect the final mechanical performance of NFRP composites. The followed factors are primary ones: (1) natural fibre selection, (2) matrix selection, (3) interfacial strength and fibre treatment, (4) parameters of fibres (including fibre aspect ratio, fibre content, structure of fibre preform, fibre dispersion and orientation etc.,), (5) composite manufacturing process and (6) porosity.

(1) Natural fibre selection

As mentioned in previous introduction of natural fibres, the mechanical performance of NFRP composites are significantly influenced by the fibre reinforcement, while the mechanical performance of natural fibres are depending on their source in natural. Different plant types (flax, jute, ramie), plant sources (bast, seed, leaf) or growing environment (temperature, moisture, soil) will lead to their different chemical compositions and structures, which furtherly affect the strength and stiffness properties of natural fibres. Compared with glass fibres, the strength of natural fibres is lower. However, considering the lumen in the center takes a proportion of fibres, the specific strength and specific stiffness of natural fibres are comparable or higher than those of E-glass fibres.

(2) Matrix selection

The selection of resin matrix is also a crucial factor for fibre reinforced composites. In a fibre reinforced composite system, matrix can protect fibre surface from abrasion and transfer loading between fibres. Natural fibres can be used to reinforce both thermoplastic and thermoset resins [46]. Considering the thermal stability of natural fibres and the processing temperature of different polymers, the fabrication of NFRP composites should better be performed below 200 ℃. However, a short time processing at higher temperature is acceptable for natural fibres in some cases [47]. Result from this limitation, some thermoplastics with lower melting temperature such as polyethylene, polypropylene, polyvinyl chloride and polystyrene are commonly used matrices for NFRP composites. Regarding thermoset matrix, polyurethane, unsaturated polyester, phenolic resin and epoxy resin are the most commonly adopted ones. The relevant parameters of various resins are listed as Table. 1-6.

Table. 1-6 Parameters of polymers applied in NFRP composite [13]

Resins	**Density (g/cm^3)**	**Tensile strength (MPa)**	**Elastic modulus (GPa)**	**Processing temperature (℃)**
Polypropylene	0.90-0.92	26-41.4	0.95-1.77	160-176
Low-density polyethylene	0.91-0.93	40-78	0.06-0.38	105-116
Polystyrene	1.04-1.06	25-69	4-5	110-135
Polyester	1.2-1.5	40-90	2-4.5	25-200
Phenolic	1.29	35-62	2.8-4.8	25-200
Epoxy	1.1-1.4	35-100	3-6	25-200

(3) Interfacial strength and fibre treatment

The interface between fibre reinforcement and polymer matrix is key factor in determining mechanical performance of NFRP composites. When a stress is applied to fibre reinforced composite, the interface can transfer the loading between fibre and matrix. A weak interface means that the bonding between matrix and fibre is easier to be debonded and generate crack, thus reducing the mechanical properties of composite. However, owning to the sufficient hydroxyl groups of cellulose and hemicellulose, the hydrophilicity of natural fibres is high, whereas most of the polymer matrices are hydrophobic. As consequence, the interfacial bonding between hydrophilic natural fibre and hydrophobic matrix is normally weak. Another problem is the infiltration, poor interface will result in inadequate infiltration for most of fabrication process. The infiltration of matrix to fibre has been proved to significantly influence mechanical properties of composites [48]. Furthermore, because natural fibre tend to absorb moisture from environment, once the interface fails, the debonding occurs and micro-cracks generate around interface, the micro-crack will absorb more moisture and have a propagation [19]. To improve the interface and wettability of natural fibres, some physical or chemical modifications were performed on natural fibres and the effectiveness was evaluated [49]

Numerous physical or chemical treatments have been proposed to evaluate the influence of treatments to the interfacial bonding of NFRP composites. The frequently-used physical treatments to natural fibres include plasma, corona discharge and steam explosion treatments. While the commonly used chemical treatments to natural fibres include alkali, acetylation, silane, benzoylation, maleated coupling agents and peroxide treatments. In addition, some biological treatments represented by enzyme treatment has also attracted the interests from researchers. These treatments can improve the natural fibre/matrix interface primarily due to four mechanisms: removing the impurities, increasing surface roughness of fibre, reducing fibre hydrophilicity and improving chemical interaction [50]. The specific effects of chemical, physical, and biological treatments of natural fibres are illustrated in Table. 1-7.

Table. 1-7 Effects of different treatments of natural fibres

Treatments	Effects	References
Physical		
Plasma	A clean and dry fibre treatment method which can increases surface roughness of flax fibre. Some new functional groups (O-C=O) generated on fibre surface. The increased roughness is dominant factor of improved interface.	[51]
Corona discharge	It is a green treatment method, the miscanthus fibre after treatment showed chemical (oxidation) and physical (etching) variation after treatment. The Young's modulus of the composites was increased by 10-20%, indicating the improvement of interface.	[52]
Steam explosion	The banana stem fibre was violently discharge into a collector at high temperature and pressure. The treatment resulted in increased surface area and decreased stiffness.	[53]
Chemical		
Alkali	The alkali treatment removed impunities and part of non-cellulose compositions from fibre, as a result the mechanical properties of natural fibre increased due to the increased proportion of cellulose. The fibre bundle was broken and the fibre diameter decreased. The increased mechanical properties and thermal stability of composite indicated the improved interface.	[54]
Acetylation	The acetyl group reacted with hydroxyl group on flax fibre surface. The composite reinforced by acetylated fibre showed 30% strength increase than composite reinforced by untreated fibre.	[55]
Silane	It is one of most effective treatment to improve fibre/matrix interface. The silane coupling agent acted as a linkage between pineapple leaf and matrix. After silane treatment, some non-cellulose proportion was removed, the hydrophilicity was reduced and the interface shear strength increased.	[56]
Benzoylation	Benzoyl chloride was used to decrease hydrophilicity of sisal fibre and improve interfacial bonding. The treatment eliminated lignin and wax from fibre surface, some hydroxyl groups were replaced by benzoyl groups. The mechanical performance and thermal stability of composite was improved after benzoylation treatment.	[57]
Maleated coupling agents	The treatment improved fibre/matrix interface but reduced thermal stability and stiffness of fibre due to the exist of carboxyl group. This approach is usually applied in study related to natural fibre reinforced polypropylene composites.	[58]

Peroxide	The peroxide groups decomposed and generated free radicals, which reacted with cellulose. The interfacial interaction, thermal stability and hydrophilicity of jute fibre were improved. The peroxide treatment caused increase of tensile and flexural properties while reducing impact strength for composite.	[59]
Biological		
Enzymatic treatment	Some amorphous portions on the fibre surface were removed with very less damaging to plant fibre after enzymatic treatment. The interface between fibre and matrix, modulus, failure strains and strength of composite were all improved. The enzymatic treatment was in mild condition and the enzyme was specific catalyst. However, the cost-effectiveness of this method is a problem due to high price of enzyme.	[60]

The incompatibility between hydrophilic natural fibre and hydrophobic polymer matrix results in weak fibre/matrix interface. To solve the interface problem, different treatments have been carried out to modify natural fibres and the influence has been comprehensively investigated by numerous studies. Many papers have summarized the research progress about the effectiveness of these treatments in NFRP composite system [1, 2, 49].

(4) Parameters of fibres (including fibre aspect ratio, fibre content, structure of fibre preform, fibre dispersion and orientation etc.)

Except for factors such as fibre selection, matrix selection and interface, some fibre physical or morphological factors such as fibre aspect ratio, fibre content, structure of fibre preform, fibre dispersion and orientation are also relevant to mechanical properties of NFRP composites.

The aspect ratio of natural fibre plays important role on mechanical performance of fibre reinforced composites. Take short fibre reinforced composite as an instance, when a tensile load is applied, the loading is mainly transferred via shear deformation at interface between fibre and matrix. The shear deformation causes tensile deformation of fibre and the tensile stress is transferred along the fibre orientation, the end of fibre carries nearly no tensile stress and the tensile stress increases along the fibre length. Therefore, the length of a fibre should be higher than a critical length (L_c) to ensure tensile fracture of fibre when the composite is broken by tensile loading [61].

Generally, because stress will not be evenly transferred to the whole system, the fibre length should better to be much higher than critical length to guarantee effective reinforcement for a NFRP composites. The L_c can be denoted as follows equation:

$$\frac{L_c}{d} = \frac{\sigma_f}{2\tau_i}$$

where d is fibre diameter, σ_f is fibre tensile strength and τ_i is the fibre/matrix interfacial strength. However, if the aspect ratio of fibres are too high, the tangle of fibres during mixing process will led to weak dispersion and reduce the mechanical performance of composites [62]. Obviously, the value of L_c is correlated with many elements such as fibre type, matrix type, fibre treatment, fibre content and fabrication process. All these elements determine the strength of fibre and fibre/matrix interface, finally determining the value of L_c. Higher strength and better interface result in shorter critical length of fibre. However, since there are too many factors which influence the result, it is difficult to find an optimal critical fibre length exactly [63].

The fibre content of NFRP composite is also a crucial factor which influences the mechanical behavior of composites. Normally, the mechanical properties of fibre reinforced composite will increase with increased fibre content because the strength and stiffness of fibres are generally higher than those of polymer matrix. However, this proportional relation between fibre content and mechanical properties depends on reasonable interface and good wettability of matrix to fibre. When the fibre content is too high, the processibility during fabrication process becomes challenging due to the agglomeration of fibres, the moisture absorption and porosity problem are also inevitable. The fibre contents in most of the studies about NFRP composites are typically around 40-55% [64, 65].

The structure of fibre preform is another factor which affects the mechanical performance of NFRP composite. Additionally, the structure of fibre preform is correlated with the dispersion and orientation of fibre in composite. As reinforcement elements, natural fibres are not only applied in the form of monofilament, the monofilament fibres [66] will be furtherly fabricated into preforms such as mats[67], rovings [68], yarns [69] and fabrics [70] to meet different demand conditions of composites (Figure. 1-11).

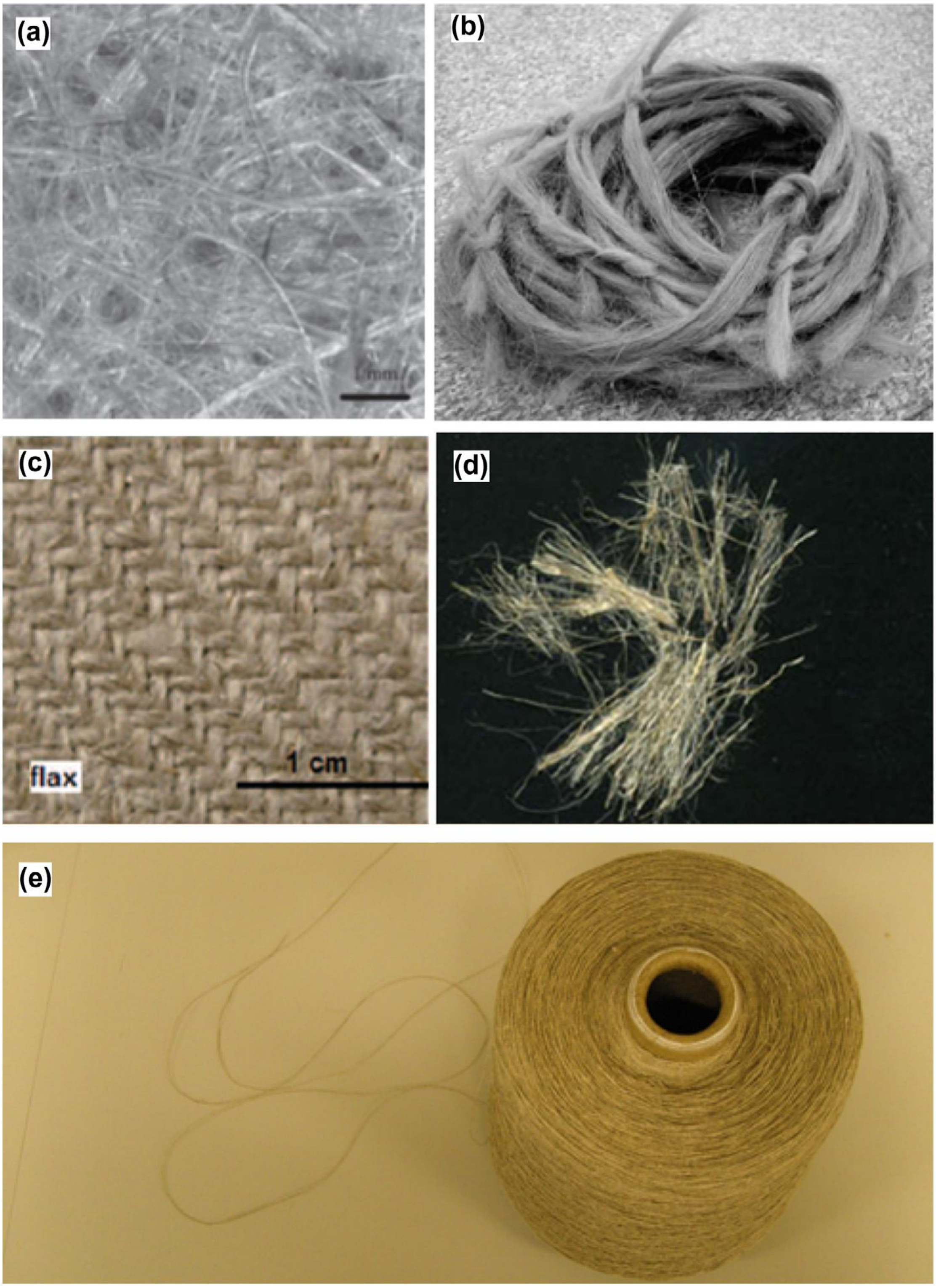


Figure. 1-11 Preforms of natural fibre (a) mat, (b) roving, (c) fabric, (d) monofilament fibre and (e) yarn [13]

Monofilament fibres are twisted to get yarns or rovings, and the yarns or rovings are furtherly woven or knitted into fabrics. Compared a bundle of monofilament fibres with a yarn, when a tensile loading is applied, the movement of twisted filaments in yarn lead to closer packing of them. Whereas for monofilament fibre bundle, some monofilament fibres will break and the rest will slip when the tensile failure is close [71]. In fact, most of the applications of natural fibres in real-world are based on fabric preform. Compared with fibre monofilaments or yarns, fabrics are easier to handle by engineers or researchers for composite material, the interaction between fibres in fabric structure makes the fabric more stable. By standardizing the fabrication process, the natural fabric ensures the control of fibre orientation, formula reproducibility and high yield [2]. Figure. 1-12 displays several types of natural fabric structure.

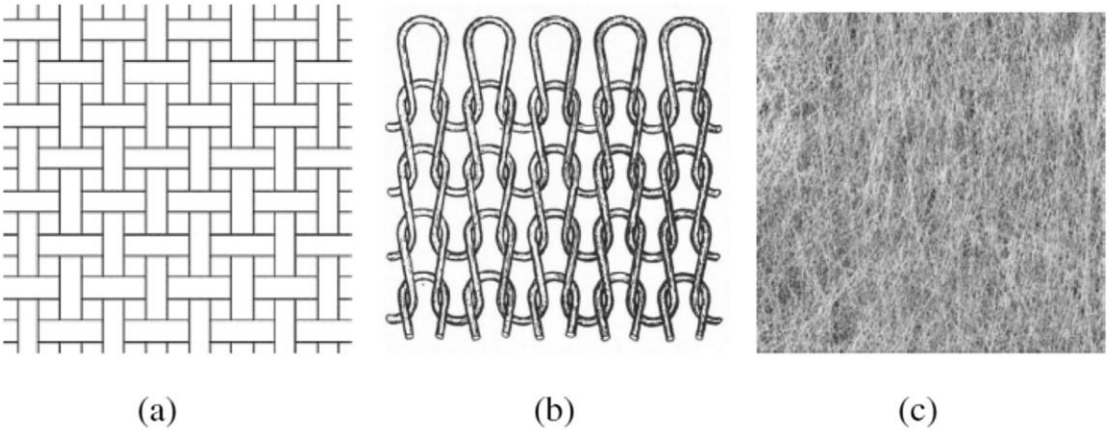


Figure. 1-12 Structures of natural fabric: (a) woven, (b) knitted and (c) non-woven fabrics [72]

Another morphological factor influencing the properties of NFRP composites is the dispersion and orientation of fibres in composite. An even dispersion of natural fibres in matrix promotes better interfacial adhesion, better fibre wettability and lower porosity for composites [73]. As aforementioned, the factors such as processing parameters, fibre aspect ratio, structure of fibre preform will all influence the fibre dispersion in composite. For example, too dramatic processing like internal mixing can lead to even dispersion, but the fibre damage and reduction are inevitable [74]. High fibre aspect ratio results in increasing mechanical properties, but long fibres are easier to twisted during processing. As for fibre orientation, commonly the best mechanical performance of composites is achieved when the fibre orientation is parallel to the direction of applied loading. Nevertheless, the alignment of natural fibres is difficult to get than synthetic fibres due to the irregular shape. The researchers have explored some method to get higher degrees of fibre alignment, for example, carding fibre prior to processing, applying unidirectional and continuous fibre yarns [75] or using continuous fibre tape [76].

(5) Composite manufacturing process

To determine the fabrication technique of NFRP composites, some parameters (i.e. expected properties, size and structure of product, characteristics of raw materials and cost) should be comprehensively take into consider [77].

As aforementioned discussion, the selection of manufacturing method of NFRP composites is depending on structure and characteristics of polymer matrices and natural fibre reinforcements. For NFRP composites with thermoset matrix, the commonly used techniques are hand lay-up, compression molding, resin transfer molding, pressure bag molding, pultrusion and vacuum assisted resin transfer molding. As for thermoplastic-based NFRP composites, the typical fabrication methods include extrusion, injection molding, cold pressing, compression and filament winding. Before the fabrication, some parameters such as purposed properties, size and geometry of composite sample and cost problem should also be taken into consider [13]. The size of composite is directly relevant to the difficulty of manufacturing. For instance, injection and compression moldings are facile and with short processing time, but the size of sample is limited by fabrication equipment, so these two methods are mainly applied to fabricate composite with small size for lab-scale testing. Resin transfer molding and hand lay-up methods are more proper to composite sample with large size. The resin transfer molding offers better matrix infiltration and higher shape accuracy, this process is also easy to be industrialized. While hand lay-up is a manual and cost-effective process which is widely utilized in civil infrastructure. More detailed information can be referred to some other works [77].

Extrusion, injection molding, compression molding and resin transfer molding are several most applied manufacturing method for NFRP composites. Parameters represented by temperature, processing speed, pressure and selection of mold should be thoroughly optimized to achieve composite with best performance. The weak thermal stability of natural fibres restrains their combination with polymer matrices with high processing temperature.

Extrusion and injection molding are typical fabrication process for thermoplastic-based composites. In extrusion process, thermoplastic pellets and natural fibres are mixed by single or two rotating screws, the mixture is then extruded by the force of the screw. Usually, the extruded mixture will be cut up and used as precursor for injection molding. Figure. 1-13 exhibits the structure of a typical injection molding machine. The pellets are firstly added to the hopper, the screw conveys the melted pellets through the heated barrel, at last the material is injected into the mold through a nozzle for cooling and finalizing the shape. However, the size of the mold and the scale of injection molding machine limit the size of composite sample. Reinforcements with high aspect ratio such as long fibre or continuous fibres are also difficult to process in injection molding. Normally, injection molding is adopted for short fibres reinforced thermoplastic composites.

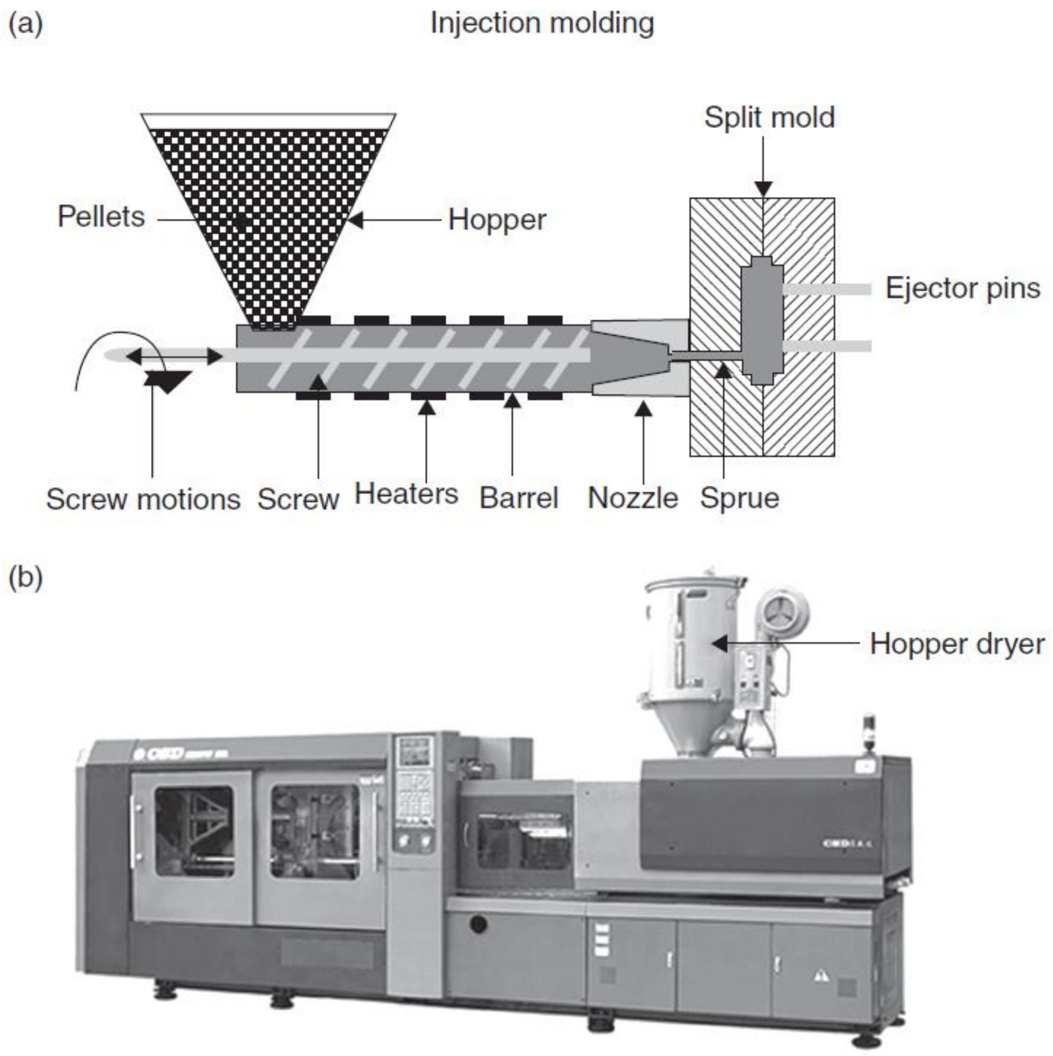


Figure. 1-13 (a) Schematic view of a typical injection molding equipment (b) Photo of an injection molding equipment (with hopper dryer) [78]

Both thermoplastic and thermoset NFRP composites can be fabricated via compression molding. Different to injection molding, compression molding allow the incorporation of reinforcements with high aspect ratio. Near all kinds of fibre preforms such as short chopped fibres, long aligned fibres, yarns or fabrics can be applied in compression molding and it is more easy to achieve higher fibre content via this technique. As Figure. 1-14 shown, the fibre preforms and polymer matrix sheets are normally stacked between two heating stages of compression molding equipment, the pressure and heat are then applied to ensure the infiltration of matrix. Experimental parameters such as temperature, pressure and dwelling time should be determined according to characteristics of natural fibre and matrix [77]. There is a balance between the matrix viscosity and thermal degradation of natural fibre, as a consequence it is essential to control the temperature exactly for both better matrix infiltration and less fibre degradation.

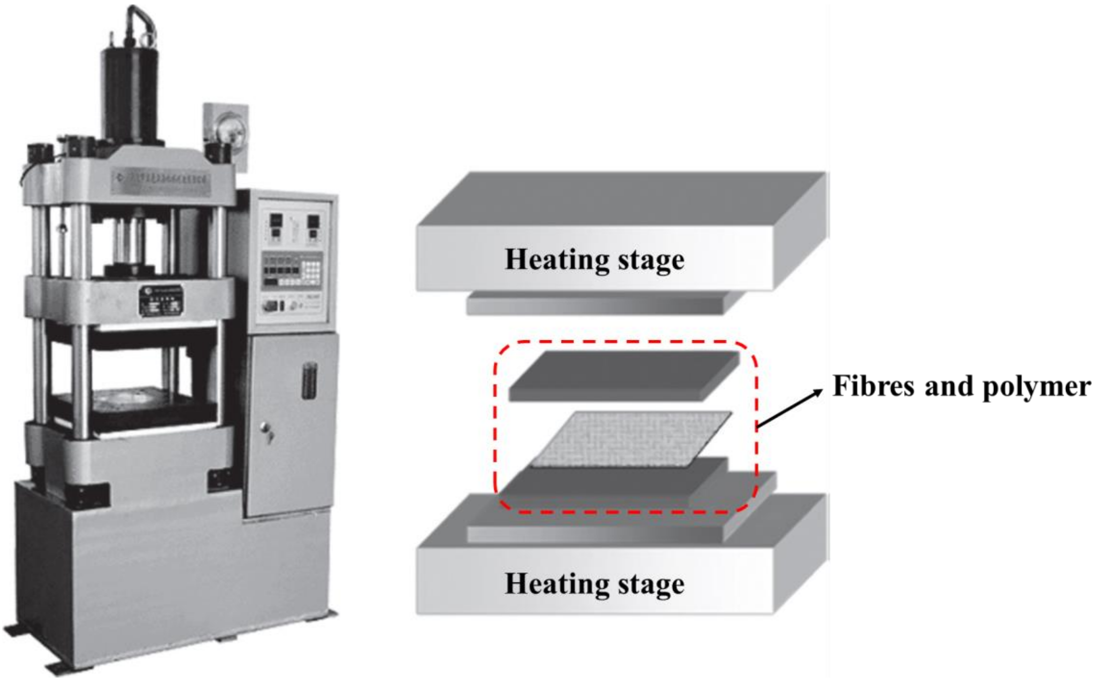


Figure. 1-14 A graphical view of compression molding equipment [78]

The sketch map of resin transfer molding process is displayed in Figure. 1-15, the natural fibre preforms are stacked in a mold which can be closed and with good finishes on all dimensions, after closing, the liquid resin matrix is injected into the chamber of the mold. The primary factors which influence the composite product are temperature, pressure, structure of fibre preform, rheological behavior of resin and mold design [77]. In comparison to other fabrication methods, the advantages of this method include high fibre content, low porosity, good dimensional tolerance and smooth surface finishing [79]. It is worth noting that the resins and fibre reinforcements are kept separately before the transfer of resin, therefore the thermal degradation time of natural fibre is reduced. Composites manufactured by resin transfer molding are utilized as high-strength structural materials owning to the high fibre content and low porosity of them.

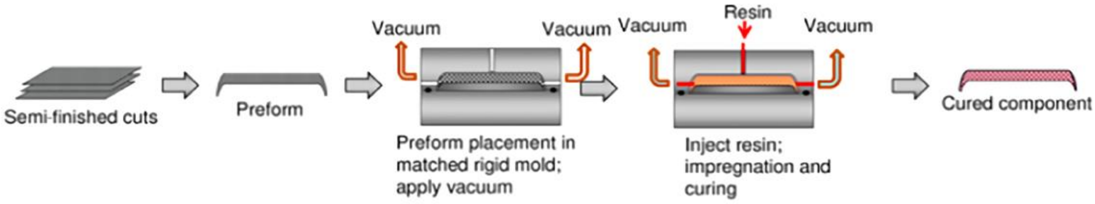


Figure. 1-15 Sketch map of resin transfer molding process [80]

The selection of manufacturing technique for NFRP composites is determined by characteristics of natural fibre reinforcement and polymer matrix. The influence of processing parameters and specific application of final product on composite performance should also be comprehensively considered.

(6) Porosity

The porosity can be regarded as defects in composite, obviously the exist of defects will promote crack propagation when the failure happens and undermine the mechanical properties of composite. For NFRP composite, the porosity problem is more serious due to the moisture absorption property of natural fibre. Also it is more difficult to achieve good infiltration of matrix to the fibre due to the rough surface and unstable size of natural fibre. The generation of porosity in NFRP composite is relevant to air bubble in matrix during fabrication, insufficient infiltration of fibres, lumen structure of natural fibres and voids within fibres or fibre bundles [65]. As mentioned earlier, the increased fibre content will cause poor fibre wettability, thus increasing the porosity of composite. To get better mechanical performance, it is necessary to reduce the porosity of the composites.

This part has introduced the influence of (1) natural fibre selection, (2) matrix selection, (3) interfacial strength and fibre treatment, (4) fibre aspect ratio, fibre content, fibre dispersion and orientation, (5) composite manufacturing process and (6) porosity on the mechanical properties of NFRP composites. These factors interact with each other and researcher should comprehensively consider these factors before manufacturing of NFRP composite.

1.3.2 Mechanical properties of natural fibre reinforced polymer composites

Numerous literatures have been reported to detail the mechanical properties of NFRP composites. Shah et al., [81] has summarized an materials selection chart for NFRP composites (Figure. 1-16). The selection chart listed properties of NFRP composites for a range of (1) forms of reinforcement (short-random fibres, nonwoven fabric, long-aligned fibres, multiaxial fabrics and unidirectionals) (2) polymer matrices (thermoplastic with unfilled balloons and thermoset with filled balloons) and (3) fabrication processes (injection molding, compression molding, hand lay-up, vacuum infusion, resin transfer molding and pre-pregging). This figure will provide a guide for the selection of suitable fibre form, fabrication route and polymer matrix in NFRP composite fabrication process.

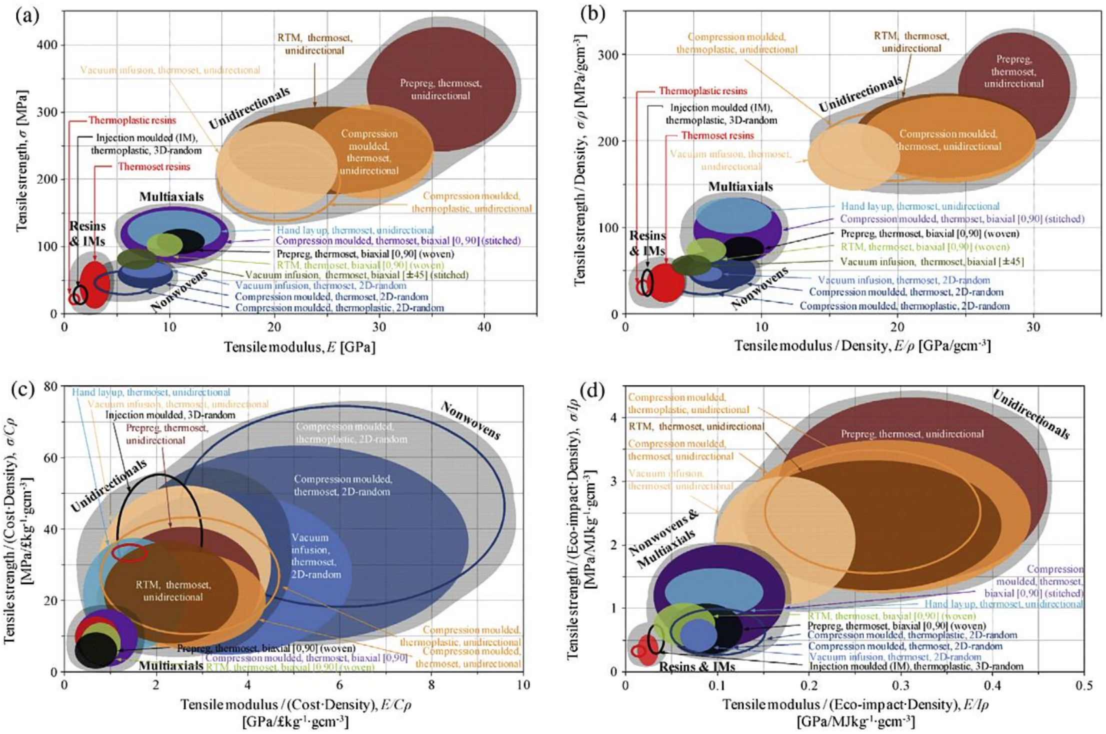


Figure. 1-16 Materials selection chart for NFRP composites. Charts show the range of (a) tensile strength and modulus, (b) specific strength and modulus, (c) tensile strength and modulus per unit cost, and (d) tensile strength and modulus

per unit eco-impact for NFRP composite manufactured with different fibre form, polymer matrix and fabrication process [81]

Figure. 1-16 (a) illustrates the range of tensile properties for NFRP composite. It can be found that the tensile strength is proportional to the tensile stiffness, approximately 10 MPa strength is corresponded to 1 GPa stiffness. In general, the preforms of natural fibre have significantly influence on the tensile properties of composite. NFRP composites reinforced with unidirectional fibre preforms achieve highest tensile properties. The tensile properties of NFRP composites decrease gradually when the reinforcements are multiaxial fabrics, nonwoven fabrics and short random fibres, respectively. Obviously, the preform of fibres, which is related to the fibre length and orientation, has determining influence on mechanical properties of NFRP composite, the influence is caused by the variation of length and orientation efficiency factors based on different structures of fibre preform. The effects of matrix selection and fabrication process are not so evident as that of fibre preform. It can be seen that the composite with thermoset matrix possess higher mechanical properties than composite with thermoplastic matrix. The fabrication process mainly affects the porosity of final composite product, the porosity content increases as following order: hand lay-up, vacuum infusion, resin transfer molding, compression molding and pre-pregging. As a result, the tensile properties of composites decrease in similar order [82].

Figure. 1-16 (b) indicates the range of specific strength and modulus for composites. The tendency of specific properties shows no evident shift compared to the tendency of absolute properties in Figure. 1-16 (a). It is noteworthy that the excellent mechanical performance of NFRP composites reinforced with long aligned fibre (multiaxial and unidirectional) makes them suitable for light weight and quasi-structural materials [15]. However, owning to the additional processing steps of long aligned fibre, the cost of long aligned fibre reinforced NFRP composite should also be considered.

Figure. 1-16 (c) depicts tensile properties per cost unit of different NFRP composites. It can be found that the spread of balloons in Figure. 1-16 (c) is much larger than those in Figure. 1-16 (a) and Figure. 1-16 (b), indicating the difference in cost between various natural fibres. By and large, the tensile properties per cost unit of thermoplastic-based composites are higher than those of thermoplastic-based composites reinforced by similar reinforcements. The NFRP composites reinforced by nonwoven fibre preform shows higher cost-effectiveness compared to NFRP composites reinforced by unidirectional and multiaxial fibre preforms.

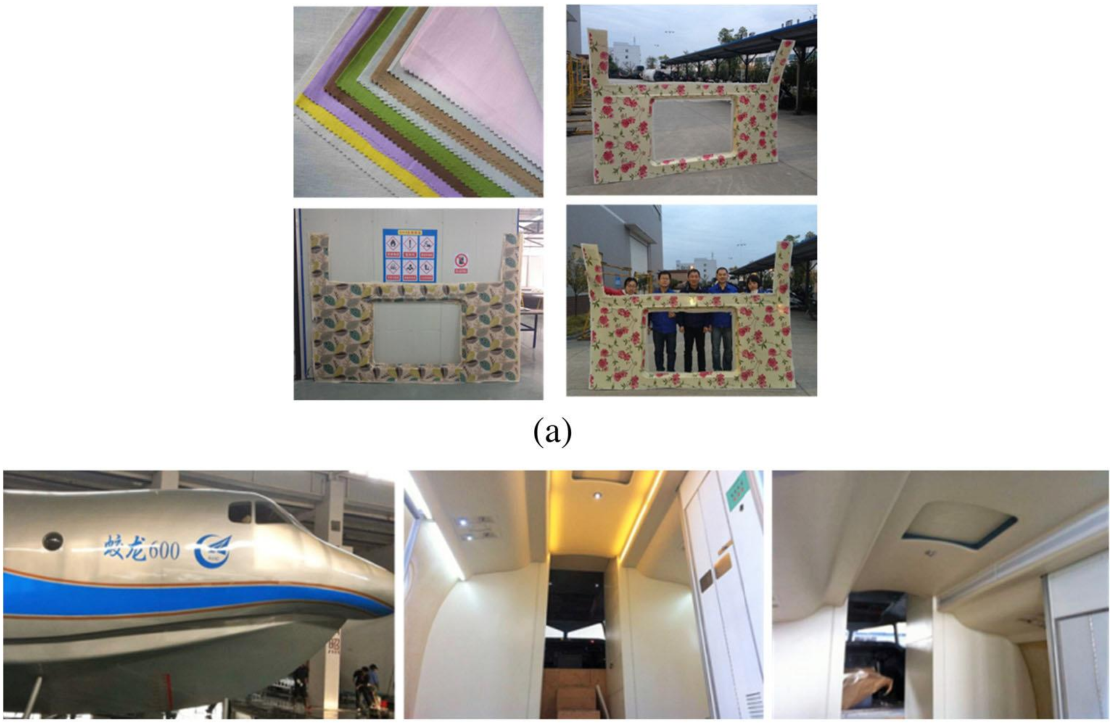
The tensile properties per unit eco-impact of various NFRP composites are displayed in Figure. 1-16 (d). The distribution of balloons in this figure is similar to those in Figure. 1-16 (a) and Figure. 1-16 (b). The tensile properties per unit eco-impact of NFRP composites are in order from highest to lowest: unidirectional > nonwoven and multiaxial > short fibre reinforced composites. However, different from absolute and specific properties, the tensile properties per unit eco-impact of composites reinforced by nonwoven, multiaxial and unidirectional natural fibre preforms have less difference in value.

The materials selection charts in Figure. 1-16 give an example that shows how to select proper raw materials and manufacturing method for NFRP composites according to different requirement.

1.3.3 Application of natural fibre reinforced polymer composites

The requirement of renewable and sustainable materials lead to the development of NFRP composites. The advantages of NFRP composites are their low density, low price, eco-friendship and favorable specific strength, which makes them potential alternatives of traditional composites reinforced by synthetic fibres. However, drawbacks represented by limited mechanical durability, moisture absorption problem, insufficient mechanical properties and low thermal stability may restrain their application [12]. Overall considering the advantages and drawbacks of NFRP composites, the materials are especially suitable for application in non-structural, decorative or civil materials.

NFRP composites show potential as non-structural construction materials which can be used as window frames, floor boards or insulating wall panels [83]. The favorable mechanical properties, sound abatement and light weight of NFRPs also makes them replace of laminates made from wood, steel or concrete [84]. Another popular application of NFRP composites is decorative units in transport vehicles. Along with the evolution of new energy vehicle industry, NFRP composites are utilized as door panels, headrests, internal engine covers and parcel shelves. Even some quasi-structural parts such as seat backs and underfloor paneling are based on NFRP composites. The application of NFRP composites in automobile can effectively reduce the environmental impact and structural weight, meanwhile saving energy needed for production [13]. Figure. 1-17 has exhibited the quasi-structural side panels based on NFRP composite in a railcar and a seaplane. Except for non-structural and decorative application, performance of the NFRP composites in all aspects corresponds to the requirement in some civil fields, i.e. furniture, sport, packaging and construction infrastructure. In 2010, the global market of NFRP composites was around 2.1 billion US dollars and there will be 10% increase annually [77].



(a)

(b)

Figure. 1-17 Proof-of-concept exhibition of a decorative, quasi-structural NFRP composite side panel of (a) railcar and (b) a seaplane [15]

1.4 Bio-sourced epoxy resin

Except for employment of natural fibre, another strategy to achieve green fibre reinforced composite is to use bio-sourced polymer as matrix. Bio-sourced resin is polymer derived from natural-sourced feedstock, replacing petroleum-based polymer with bio-sourced resins is an important research direction in the field of green materials.

As matrix, thermosetting polymers are broadly applied in engineering fields owning to their favorable performance such as strength, durability as well as thermal and chemical stability. These characteristics make them suitable to various applications, i.e. bonding and adhesives for transportation industry, coating materials for construction or electronic device, matrices in composite field. A market research in 2009 reported that thermosets took up 14% of the whole polymer production [85].

Epoxy resins are crucial branches among the most applied thermosetting systems based on crosslink reaction between epoxy group and active hydrogen compound, which account for about 8% of the whole thermosets production [86]. The thermosetting industry is in the same line of searching for sustainable and green materials. Similar to the natural fibre reinforcements, the ever-increasing demand for green materials has also promoted researchers to explore the possibility of green epoxy matrix sourced from natural feedstock. Except for non-structural applications in automobile industry, composites based on bio-sourced resin may act as quasi-structural materials in aircraft field, which takes the place of fibre reinforced composites based on petroleum-based matrix [87].

The performance of an epoxy resin system is relevant to the epoxy resin, curing agent, their formulation and the parameters during curing process [88]. Compounds represented by polyamines, acid anhydrides, polyphenol or Lewis acids can be employed as curing agent, or hardener of epoxy resins. In the case of epoxy resin industry, most of traditional epoxy resin system are based on petroleum-sourced epoxies and curing agents. To develop eco-friendly and sustainable epoxy systems, some studies have searched for epoxy based on bio-sourced components. The representative bio-sourced epoxy resins developed in recent years are rosin based resins, itaconic acid based epoxy resins natural oil-based epoxies, isosorbide based epoxy resins, furan based epoxy resins, polyphenolic epoxies and epoxy lignin derivatives [85].

This work mainly involve two epoxy resin matrices: rosin-sourced and itaconic acid-based epoxies, which would be introduced in following section. Whereas the other bio-based epoxy resins will be briefly introduced.

1.4.1 Rosin-sourced epoxy resin

Rosin is the primary component extracted from exudate of various species of pine. Isomeric abietic and pimaric acids are two main acids of the rosin, which possess cycloaliphatic, aromatic and carboxylic groups. Therefore, rosin derivatives such as fumaropimaric acid, acrylicpimaric acid and maleopimaric acid can been used as alternatives to petroleum-based hardener for epoxy systems. The hydrogen multiple ring structure of rosin-based curing agent endow resin with improved thermal and mechanical performance [89]. In recent studies, numerous researchers have applied rosin acids as raw materials for bio-sourced and thermoset polymers. Rosin derivatives can be used as curing agents of anhydride type, carboxylic acid type, amine type, rosin-derived epoxies and rosin-derived monomers [87].

Zhang et al., [90] developed a novel rosin-sourced epoxy system based on anhydride-type harder, the hardener is a maleopimaric acid anhydride synthesized from abietic acid (the chemical structure of the hardener was shown in Figure. 1-18). Glass fabric reinforced rosin-sourced epoxy composites were manufactured by hot-melt prepreg followed by hot-press process. When the volume fraction of glass fabric was 47%, the rosin-sourced epoxy/glass fabric composite showed comparable thermal and mechanical performance to glass fibre reinforced composite with petroleum-based matrix.

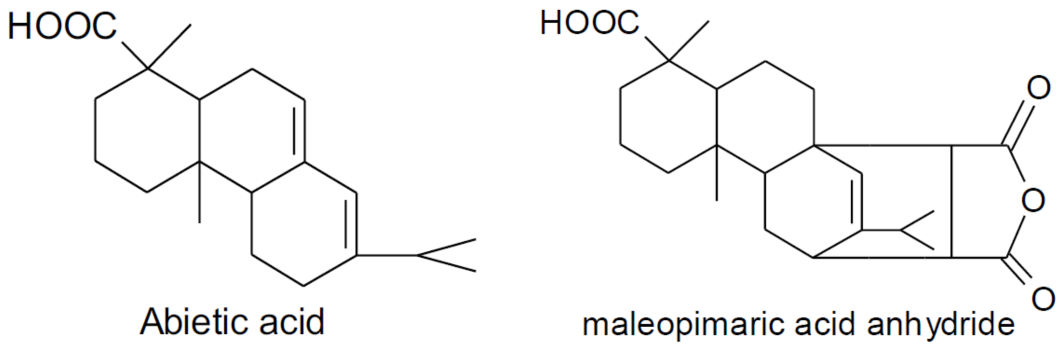


Figure. 1-18 Chemical structure of abietic acid and maleopimaric acid anhydride [90]

1.4.2 Itaconic acid derived epoxy resin

Itaconic acid based epoxies have gained growing popularity over the last years. Itaconic acid, or methylenesuccinic acid, is produced from saccharine by fermentation reaction catalyzed by Aspergillus terreus. Itaconic acid contains two carboxylic acid groups and an α,β-unsaturated double bond, which enables it to be potential precursor for bio-sourced epoxies. The carboxyl groups can react with epichlorohydrin to form epoxy monomer with unsaturated double bond, the double bond of itaconic acid can be converted into epoxy group as well. When the carboxyl groups is epoxidized, the unsaturated double bond can be furtherly modified by rigid or soft comonomer to control the toughness of epoxy network [91].

Songqi Ma et al., [92] used epichlorohydrin to epoxidize itaconic acid and synthesized a novel itaconic acid derived epoxy via esterification reaction (The synthetic route was as Figure. 1-19 shown). Methyl hexahydrophthalic anhydride was then applied as curing agent for itaconic acid derived epoxy. After curing, the glass transition temperature, tensile strength, flexural strength and modulus of itaconic acid based epoxy were 130.4 °C, 87.5 MPa, 152.4 MPa and 3.4 GPa, respectively. The performance of the itaconic acid verify its potential as alternative to petroleum-based epoxy resin.

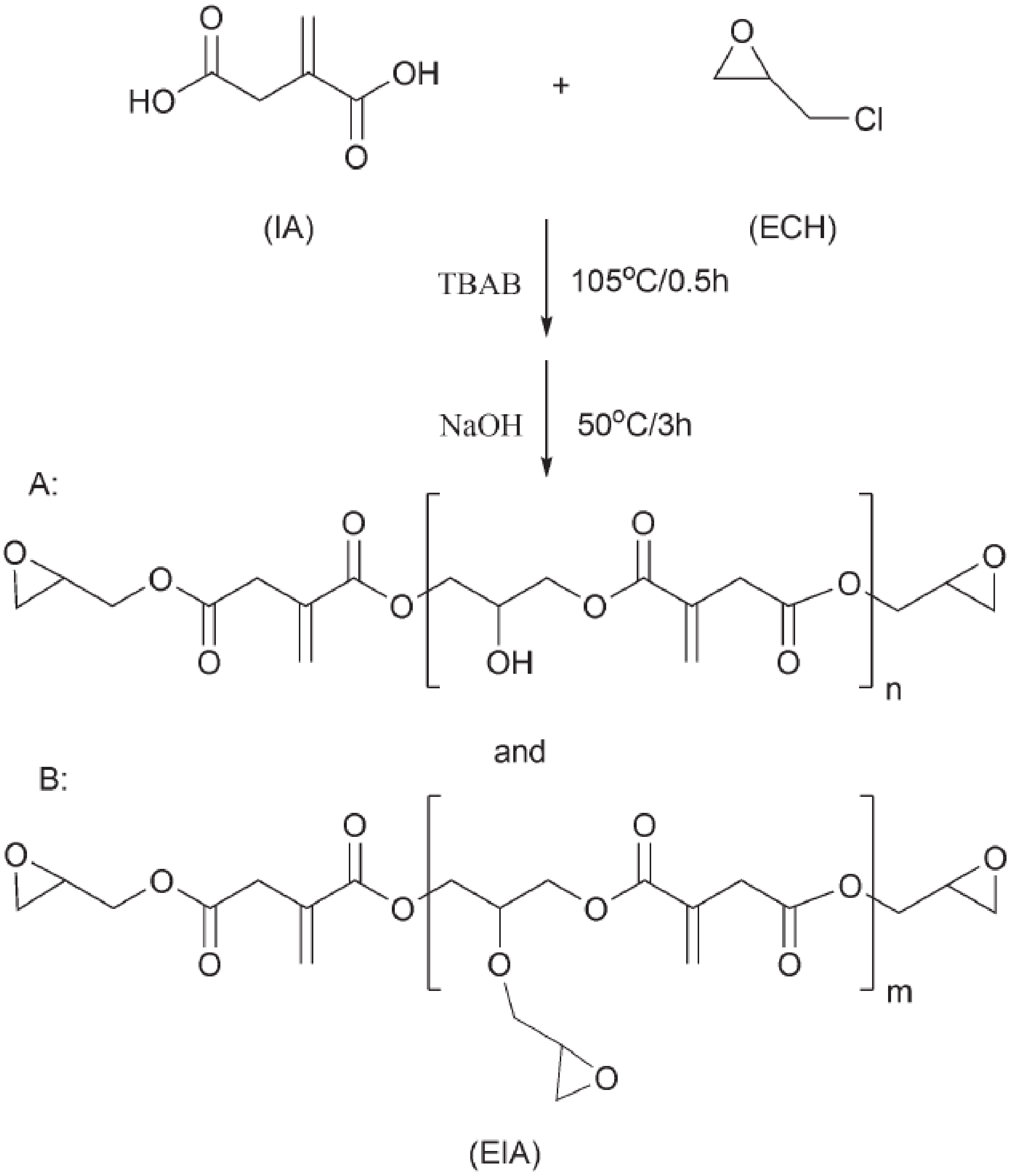


Figure. 1-19 The synthetic route to itaconic acid based epoxy resin (EIA) from Itaconic acid (IA) and epichlorohydrin (ECH) [92]

1.4.3 Other bio-based epoxy resins

Natural oil-based epoxies are based on the epoxidation of vegetable oils such as soybean oil, linseed oil, canola oil, castor oil or grapeseed oil. Normally, the unsaturated double bonds of vegetable oil are oxidized and generate oxirane groups, the epoxidation of the vegetable oils makes them possible to be used as bio-sourced epoxies [93]. Epoxidized soybean oil and epoxidized linseed oil are universal vegetable oils with large yield, there are numerous unsaturated groups existed in the structure which are able to be epoxidized. However, the mechanical performance of natural oil-based epoxies is not so ideal due to their aliphatic structure.

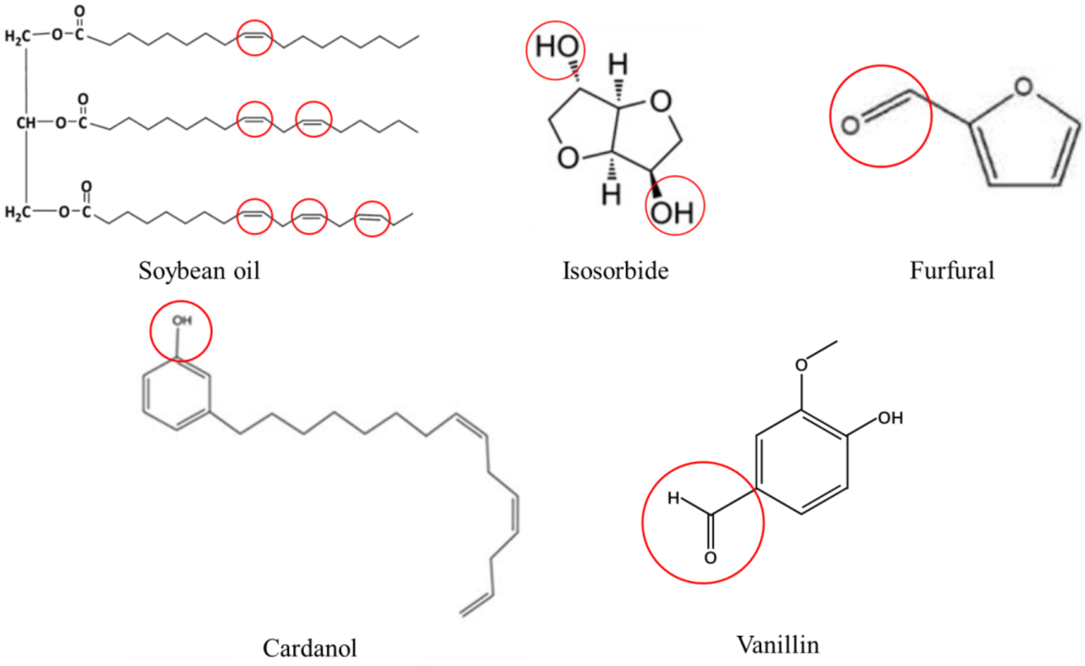
Isosorbide based epoxy resins can be prepared from isosorbide derivatives such as diglycidyl ethers of isosorbide or isosorbide diamine. Isosorbide is a bio-sourced diol generated from starch with a structure contains two fused furan rings. The versatility of hydroxyl groups in isosorbide structure are easy to be derivatized and opens a new opportunity for application as bio-sourced epoxies. The chemical structure of isosorbide results in molecular rigidity and thermal stability which allows diglycidyl ether of isosorbide to be an alternative monomer to bisphenol-A in epoxy system [94].

Another potential bio-sourced epoxy systems are furan based epoxy resins. The origin of furanyl building blocks are usually generated from the hydrogenation of furfural. While furfural is bio-based compounds derived from dehydration of five carbon carbohydrates (i.e., xylose and arabinose generated from fractionation of hemicellulose from bagasse) [95]. The furan based epoxy resins show promising properties which meets requirement of the automobile and aircraft applications. However, the performance of resins should be furtherly studied to ensure that the resins can be employed in the industrial field.

Phenolic and polyphenolic epoxies are important branches of bio-sourced epoxy resins as well. As large molecules with multiple phenol structures, bio-sourced polyphenols can be roughly divided to flavonoids and nonflavonoids according to chemical structure. Flavonoids are compounds with molecular structure containing two phenyl rings and a heterocyclic ring while nonflavonoids do not possess the multiple ring structure (i.e., simple phenols, phenolic acids and tannin) [96]. In polyphenolic epoxy network, natural polyphenolic and phenolic structures provide promising mechanical performance and thermal stability, which makes natural polyphenolic epoxies to be competitive bio-sourced epoxies. Epoxy resins based on tannins and cardanol are representative natural-sourced polyphenolic epoxies [86].

Lignin is one of the primary components of plants containing rich active groups in molecular structure and shows potential as a precursor of bio-sourced epoxy resin. Lignin is extracted from plants via various technology in pulp and papermaking industries, different extraction technology will affect final chemical structure of lignin. Therefore, the types of lignin can be classified according to extraction technology: kraft lignin, lignosulfonates, soda lignin, organosolv lignin, klason lignin, steam explosion lignin and dilute acid lignin [97]. The amorphous structure and functional groups allow lignin to be functionalized to act as both epoxy components and the hardener [98]. Vanillin, an industrial lignin derivatives, is developed to bio-based epoxy thermoset and shows comparable thermal stability versus commercial epoxies [99]. However, the mechanical performance of lignin-based epoxies should be furtherly investigated and optimized.

In this work, rosin-sourced epoxy and itaconic acid based epoxy are directly applied as matrix, thus the design and optimization of resin formulation are not referred in this section. In general, most of bio-sourced epoxy resins are based on natural-sourced compounds containing characteristic groups (i.e., unsaturated double bond, hydroxyl, aldehyde or phenolic) which can be functionalized. Epoxy groups or groups of curing agent (i.e., amine or anhydride) are introduced to the bio-based compounds and allows the modified compounds to be applied as epoxy monomer or curing agent. The chemical structure of several typical feedstock of bio-based epoxies are shown in Figure. 1-20.



Soybean oil Isosorbide Furfural

Cardanol Vanillin

Figure. 1-20 Chemical structure of typical feedstock of bio-based epoxies (the groups which can be functionalized are denoted by red hollow balloon) [86]

The ever-increasing environmental concern promotes the development of advanced thermoset resins from bio-based feedstock in past years. As aforementioned, various bio-sourced epoxy resins have been exploited based on derivatives of rosin, itaconic acid, natural oil, isosorbide, furan, polyphenolic and epoxy lignin. However, as potential alternatives to thermosets from petroleum, there are still some problems of bio-based resins which should be furtherly improved. Firstly, though the mechanical performance and thermal stability of several bio-based resins are comparable or even better than those commercial petroleum-based ones, the mechanical performance of most bio-sourced resins are not ideal. Secondly, the development of multifunctional bio-sourced resins with unique properties are necessary. In addition, considering the difficulty of synthesis of the bio-sourced resin monomers and price of raw materials, it is a key problem to design more economical and facile synthetic pathway for bio-sourced resins [86, 91].

1.5 Flame retardant composites

1.5.1 Why and how to improve fire safety of composites

In previous sections, the research progress relevant to natural fibres, NFRP composites, and bio-sourced epoxy resin have been reviewed. The significance and advantages of utilization of natural-based materials are denoted. However, as for both natural fibres and polymer matrices, high flammability is a nonnegligible drawback for fibre reinforced composites which restrains the range of application of the materials. Therefore, the improvement of fire safety for fibre reinforced polymer composites becomes an issue which attracts long-term attention in engineering fields [100].

Due to various human errors or natural factors, the fire hazards around the world have caused serious loss of life and property every year. Humans' battle with fire can be traced back to 450 BC, the alum was applied to decrease the flammability of wood by ancient Egyptians [101]. In 2017, there were around 28,000 cases of fire, 1390 deaths, 881 injuries and direct loss of 36,000 million yuan caused by fire hazard in China [102]. The propagation of fire and the release of harmful gases during combustion are two crucial problems which need to be addressed.

Therefore, in order to reduce or even eliminate loss caused by fire hazard, it is necessary to improve the flame retardancy of fibre reinforced composites. The flame retardant composite is defined as a composite material which could reduce or limit the propagation of fire and the generation of toxic in combustion process. To achieve composites with acceptable flame retardancy, the common applied methods can be classified to following four categories [103]:

(1) Direct addition of FR additives into polymer matrix

(2) FR modification to reinforcement elements (mainly for fibre reinforced composite) before manufacture of composites

(3) Adding FR coating on composite surface

(4) Chemical modification to polymers to improve the inflammability of polymers, or directly using intrinsically FR polymers

First of all, the most crucial and facile approach to improve the fire safety performance of composites is direct incorporation of FR additives into the composite system. Compounds containing phosphorus, halogen, boron and silicon, as well as some metal hydroxides or metal oxides are utilized as typical FR additives [104]. The FR additives can be mixed into the polymer matrix via melt blending or solution mixing methods. The FR additive particles are physically dispersed in the polymer matrix and there is no chemical bonding between additive and polymer. Considering most of polymers are organic and most of FR additives are inorganic, the interface between matrix and FR additives will be weak. However, the weak interaction between FR additives and polymer will lead to uneven dispersion and compatibility problem, thus reducing the mechanical performance of composite, especially for composites with relatively higher FR additive content. Direct mixing of FR additives with polymers is the most widely applied method to obtain FR composite because it is a facile and cost-effective process which is easy to be industrialized. Though the incorporation of FR additives shows passive influence on composite performance, the overall performance of the material can meet most requirement in daily life.

The second approach to improve the inflammability of composites is a two-step process which is commonly utilized for fibre reinforced composites. Firstly, the fibre reinforcements are modified with FR chemicals, and then the FR modified fibres are used in the manufacturing of composite materials. Some of representative modification methods to fibre include dip coating, sol-gel coating and layer-by-layer self-assembled coating. Dip coating is a method of dissolving FR additives in a suitable solution, after which the fibre is immersed into the solution and dried to obtain flame retardant fibre [105]. The sol-gel method is a transition from colloidal “sol” to liquid ‘‘gel’’ phase with integrated network, the FR compounds (e.g., metal salts or metal organic) are dispersed in solvent to form a colloid and then condensed to gel on fibre, the FR additives will form a continuous coating on fibre after drying [106]. Layer-by-layer coating is a method depending on electrostatic adsorption between polyanion and polycation on fabric surface. The fabric is alternately immersed into two solutions containing anions and cations respectively to adsorb FR compounds, the thickness of coating is tunable by repeating the immersion process [107]. However, most of the researches about FR modified fabric are limited to evaluate the flammability of fabric, only a minority portion of literatures have applied FR fabrics to composites to study the influence of FR fabrics on flammability of composite.

Another promising method to reduce the flammability of composites is to add a FR coating on the substrate surface of composite. This method is also a facile and available process which is originally developed to protect metal, wood and composite from fire. The FR coatings can be divided as two types: non-intumescent ones and intumescent ones. The non-intumescent coatings usually are the mixture of inorganic particles and adhesives, normally the mixture are directly bonded on the surface of composite to form a protective layer, which could constrain the propagation of fire once the composite is ignited. The intumescent coatings are the complex mixture composed of source of acid, carbonization agent and blowing agent [108]. The intumescent coating on composite surface will expand and form a protective char layer which delays the transfer of heat and flammable volatiles during burning. However, surface coating method is also based on physical interaction between FR coating and composite surface, the weak interface will lead to the separation between coating and composite surface in some situation such as deformation of composite. The thickness of FR coating should be controlled as well, too thick coating will decrease the mechanical performance of composite [109].

The last method to achieve FR composites is improving the fire resistance of polymer matrix through chemical modifications. To solve the weak interaction between FR additives and polymer matrix, some reactive FR additives can be integrated into the polymer molecular chain structure via chemical bonding. This process can be achieved by copolymerization, polycondensation, or grafting reactions between FR chemicals and monomer or polymer precursor. In some cases of thermoset composites, reactive FR additives are used to modify curing agents and then the FR modified curing agents are applied in crosslinking of thermosetting systems to improve the fire safety of composites. A representative instance of reactive FR additive is 9, 10- dihydro-9, 10-oxa-10-phosphaphenanthrene 10-oxide (DOPO) derivative in recent years. DOPO is an H-phosphinate compound, the P(O)-H group show high reactivity to epoxide [110], imine [111] or unsaturated double bond group. Therefore, some DOPO modified polymers are synthesized, the DOPO is integrated into the polymer chain and improve the flame retardancy of polymer [112].

In addition, some of polymers such as polyvinyl chloride, polyether ether ketone or phenolic are intrinsically with acceptable inflammability, the composites based on these intrinsically FR polymer matrices show acceptable fire safety performance. Compared with mechanical mixing FR addtive into polymer, chemical modification can effectively improve the compatibility problem and keep the mechanical properties of the material from decrease. However, chemical modification to polymers may be costly, the synthesis of FR polymer may also be complicated which is difficult to be scaled up.

In general, to obtain composites with promising fire safety performance, FR additives are incorporated into composite systems by various physical or chemical processes. Researchers have exploited various methods to improve anti-flammability of polymer matrices and reinforcements. Problems such as cost-effectiveness, difficulty of the process, yield and requirement for product performance should be comprehensively considered to determine the suitable modification method to improve the FR performance of composite.

1.5.2 Flame retardant mechanisms

In the previous section, the necessity of development of FR composites and how to improve fire safety of composites are discussed. Actually, every FR additives possesses its unique flame retardant mechanism. It is significant to investigate the mechanisms of polymer combustion and flame retardant mechanism of FR additive.

A Triangular combustion cycle of a polymer is exhibited as Figure. 1-21. A cycle of polymer combustion involve three basic elements: the heat generate from the burning of polymer matrix, the combustible volatiles liberated from decomposition of polymer and the oxygen in the air. When the quantity of heat exceeds a certain range by ignition, the polymer is ignited and the degeneration of polymer generates flammable gases which react with oxygen in the air and release more heat, the above process will continue to cycle until the material is burned out [113]. The introduction of FR additives into composite can break a stage in the cycle by some mechanisms, which are the focus to review in this section.

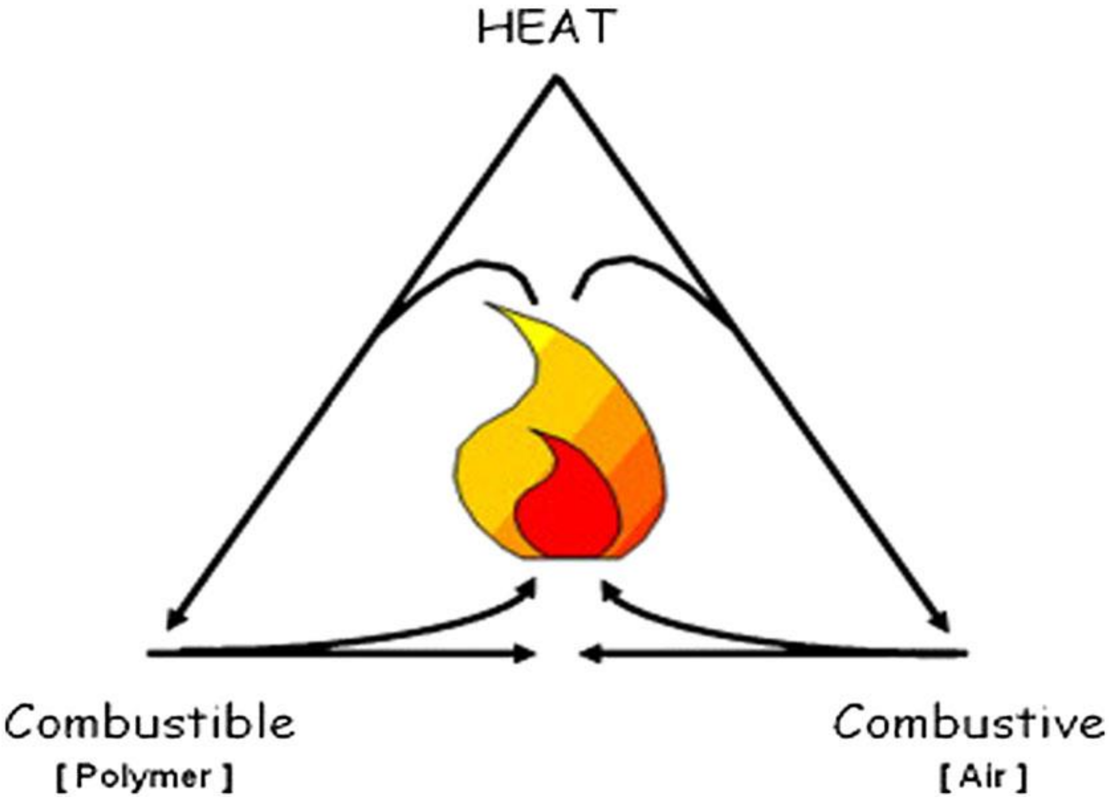


Figure. 1-21 Three basic elements of combustion cycle of a polymer [100]

To furtherly illustrate the cycle of polymer burning, the combustion mechanism of polymer is shown in Figure. 1-22. Understanding the burning mechanism of a polymer is benefit to selection of efficient FR additive. The crucial elements of the combustion cycle are fuel, oxygen and heat. As aforementioned, the cycle of polymer combustion include enough heat to ignite the polymer, flammable and volatile products from depolymerization of polymer and burning between fuels and oxygen. The recycle of polymer burning is on the basis of two primary reactions: the pyrolysis reaction of polymer and the exothermic reaction of volatile gases with oxygen. Therefore, to stop the continuous recycle of burning reaction and improve fire safety of composite, it is crucial to reduce the intensity of these two reactions [114].

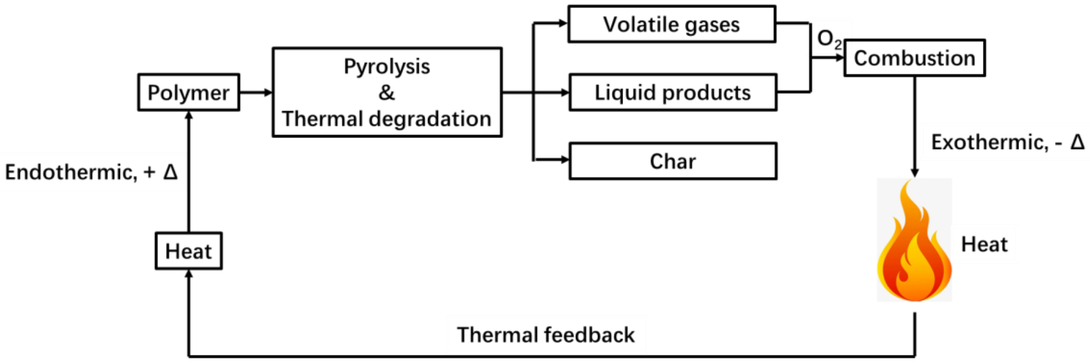


Figure. 1-22 Schematic diagram of combustion mechanism of polymer [115]

Figure. 1-23 (a) has illustrated the strategies to stop the recycle of polymer burning. The recycle of polymer burning behavior can be separated into following stages: heating, decomposition, ignition, combustion and propagation [116]. By interrupting any of these stages, the burning recycle of polymer can be effectively controlled to achieve improved inflammability. First of all, some of FR additives such as metal hydroxide can be introduced into materials, the decomposition of the FR additives is endothermic and reduce the heat release to reach pyrolysis temperature. This method which utilizes endothermic reaction of FR additives is called heat sink effect or endothermic cooling effect. The second method is to interrupt the burning of flammable products with oxygen in the air, there are two effects to achieve this aim:

protective char layer effect and inert gas dilution effect. The protective char layer effect is based on FR additives with the ability to promote the carbonization during pyrolysis of polymer. Due to the influence of FR additives, more and thicker char layer generate on the upper surface of material which functions as an insulating cover. The insulating char cover can effectively inhibit the heat and substrate transfer between air and polymer, thus reduce the intensity of burning. The inert gas dilution effect is relevant to the inflammable gases (e.g., H_2O, CO_2 or NH_3) generated from FR additives. These gases can dilute the oxygen and flammable gases and reduce the scale of burning. The last approach is depended on breaking the stage of fire propagation. The inert gas dilution effect also exists in this approach. Another effect correlated with this stage is radical quenching effect (or radical scavenger effect), this effect is attributed to free-radical quenching reaction between free radicals. The representative FR additives relevant to this effect is halogen-based FR additives, halogen radicals generated from FR additive can capture reactive radicals such as H• or O• free radicals and thus reducing the intensity of combustion [115].

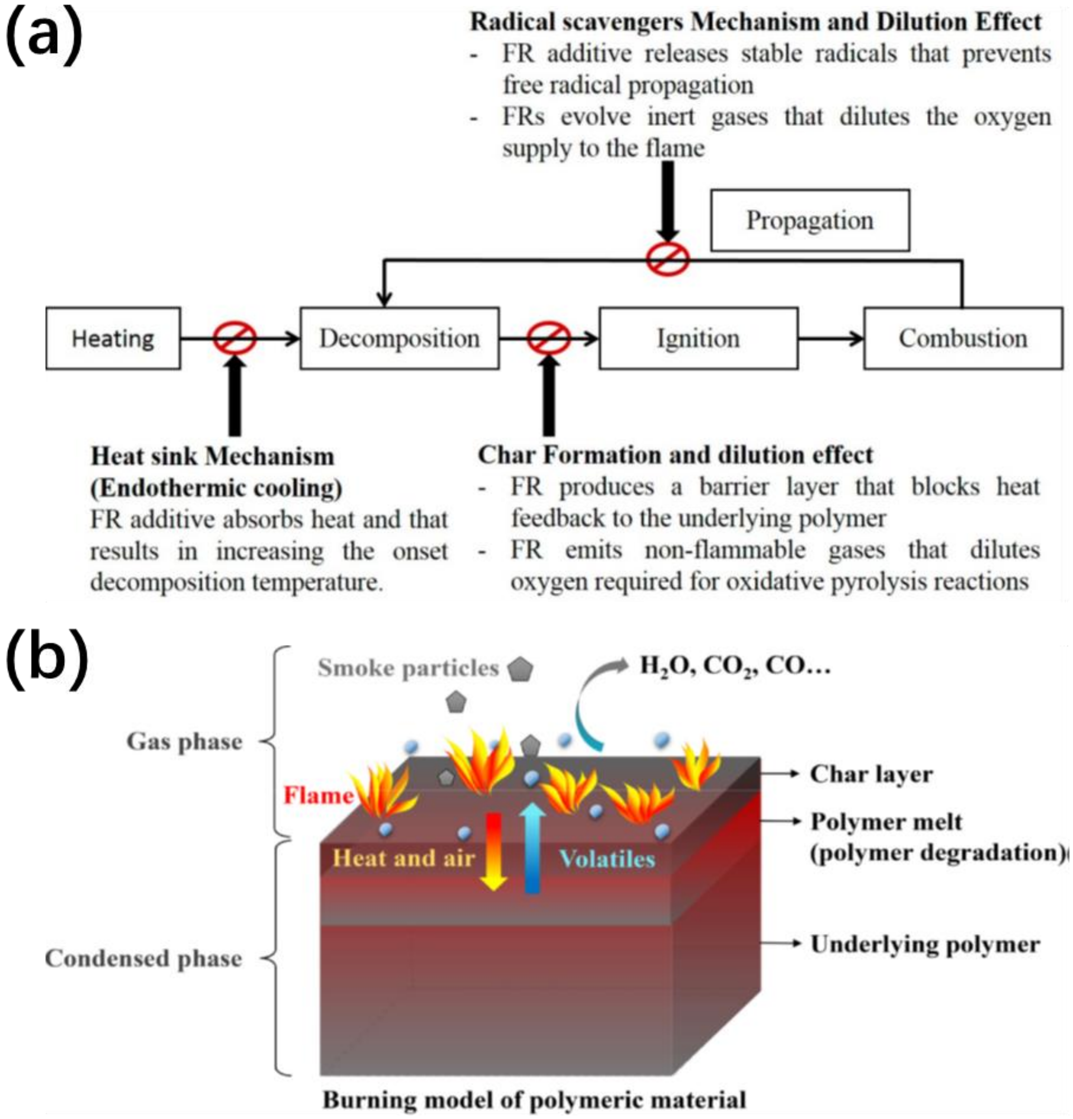


Figure. 1-23 (a) Strategies to stop the recycle of polymer burning [115] (b) Scheme illustration of combustion behaviors for polymer [117]

Figure. 1-23 (b) has provided a scheme illustration of combustion behaviors for polymer. In fact, the combustion of polymer occurs mainly at the interface between the solid and gas phase. Therefore, the FR mechanisms for polymer materials are commonly divided to gas phase and condensed phase mechanisms. The gas phase is the phase at which the burning of flammable volatiles and oxygen occurs, while the decomposition of polymer occurs at condensed phase. In general, the mechanisms of all FR additives can be grouped into five effects: inert gas dilution effect and radical quenching effect in the gas phase, protective char layer effect, endothermic cooling effect and catalyst effect in the condensed phase [117]. The classification of FR mechanisms is shown in Figure. 1-24.

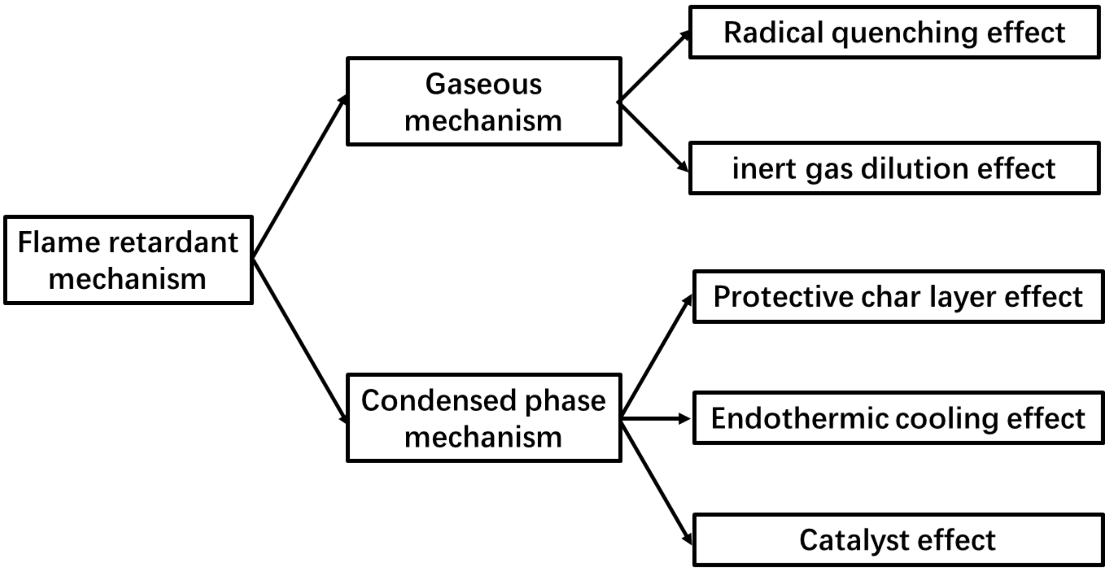


Figure. 1-24 The classification of FR mechanisms

The gas-phase FR mechanism commonly involves two effects: radical quenching effect (or radical scavenger effect) and inert gas dilution effect. The pyrolysis of polymer molecule is a chain reaction containing initiation, growth and termination of polymer chain. The active free radicals generated in the burning of polymer can promote the chain reaction. Therefore, some FR additives represented by halogenated [118] or some organophosphorus compounds [119] can release free radicals which would trap the active radicals and restrain the propagation of chain reaction in polymer pyrolysis, finally inhibit the intensity of combustion [120].

Another gas-phase FR mechanism is the dilution effect of inert gas. This effect is relevant to the inflammable gases such as H_2O, NH_3, CO_2 or N_2 produced from decomposition of polymer or FR additives. The representative examples on the basis of this effect are metal hydroxide (generate H_2O) and nitrogen-based FR additives (generate N_2 or NH_3). These incombustible gases are released into gas phase and reduce the concentration of combustible gases and air, thus decreasing the scale of gas-phased burning.

In terms of the FR mechanisms in condensed phase, there are majorly three correlated effects: protective char layer effect, endothermic cooling effect and catalyst effect. The protective char layer effect (or char barrier effect) is based on FR additives which can promote the carbonization of polymer. The carbonization of polymer can form an insulating char layer on the surface of material which acts as barrier to constrain the substrate and heat transmission between gas and condensed phase. The phosphorus-based (the phosphate group acid generated from FR additives catalyzes the formation of char) and aromatic ring-containing (aromatic rings tend to crosslink and form continuous char layer in combustion) FR additives are typical chemicals related to protective char layer effect [121, 122]. Another representative and relevant FR additive is EG. Normally, dense and less porous carbon layer is considered to be more effective to improve the flame retardancy of substrate. However, polymer modified by EG exhibit distinct char morphology after burning, the residual char are loose and expanded with worm-like structures. The expanded char layer acts as tortuous pathway which can hinder the substance exchange between inner polymer and air [123].

The second condensed phased FR effect is endothermic cooling effect. The decomposition of some FR additives and evaporation of the decomposition products absorb numerous heat. The lost heat decrease the temperature of condensed phase, thus slowing down the pyrolysis of polymer and improving the inflammability of material. Some chemicals with high specific heat capacity also correspond to this effect. The typical FR additive meets this effect is $Al(OH)_3$, which decomposes to aluminum oxide and water in burning of polymer. The decomposition reaction and evaporation of water will absorb a lot of heat.

The last FR mechanisms in condensed phase is called catalyst effect. It is worth mentioning that some metallic elements can play a catalytic role in the combustion of polymer. For example, Zn^{2+} can promote the formation of network of epoxy resin in burning through catalyzing the ring-opening reaction [124]. Cu_2O was reported to catalyze the oxidation of CO to CO_2 through redox reaction owning to the effect of Cu^+ [125].

According to aforementioned information, five effects related to the gaseous or condensed phased FR mechanism are outlined. It is worth noting that a large proportion of the FR additives may involve more than one of these five effects. However, sometimes it is difficult to achieve satisfied inflammability by incorporating single FR additive in material. As a result, another crucial and popular research branch correlated with FR mechanisms of composite is to study the synergistic effect between different FR additives. One or more synergists are mixed into an existed FR material system, and the mixed FR system show much higher FR efficiency than previous system even the total content of FR additives are same. The intumescent FR system composed of acid source, carbonization agent and blowing agent is to take advantage of synergistic FR effect which combines char layer effect and dilution effect to improve the inflammability of material. Numerous combination of FR additives have been proved to show synergistic effect such as phosphorus/nitrogen system [126], phosphorus/nitrogen/silicon system [127], EG and aluminum hypophosphite [128], aluminum hydroxide/red phosphorus/expandable graphite [129], graphene nanosheets and DOPO [130].

In this section, the classification of FR mechanism for polymer is illustrated based on the phase where combustion occurs and the specific physical and chemical mechanisms of FR additives. The action modes of most of the FR additives are ascribed into these five effects. The information about FR mechanism of polymer combustion can provide guidance for the selection of effective FR additives.

1.5.3 Introduction of flame retardant additives

In a composite system, most of polymer matrices are flammable in air. Once being ignited, the polymer matrix will continue to burn and cannot self-extinguish until it burns out. Therefore, different kinds of FR additives are necessary to improve inflammability of composite. The previous section has summarized the FR mechanisms of FR additives and this section will discuss the relationship between types of FR additives with FR mechanisms. In 2006, the approximated total consumption (465,000 tons) of various FR additives in Europe's industry is displayed as Figure. 1-25 [131]. FR materials industry is a sizable market which is valuable to developed. Usually FR additives are classified according to the chemical characteristics and contained elements. The types of FR additives can be grouped into: (1) Metal hydroxides, metal oxides and metal salts FR additives (2) Halogenated FR additives (3) Phosphorus-based FR additives (4) Nitrogen-based FR additives (5) Silicon-based FR additives (6) Boron-based FR additives and (7) Carbon and nanocarbon FR additives.

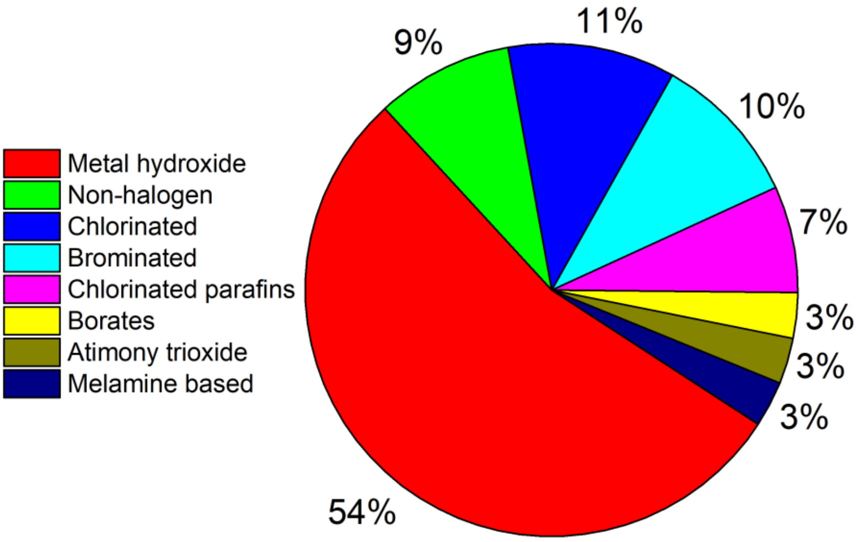


Figure. 1-25 The approximated total consumption of various FR additives in Europe's industry in 2006 [131]

(1) Metal hydroxides, metal oxides and metal salts FR additives

Metal hydroxides (e.g., $Al(OH)_3$ or $Mg(OH)_2$), metal oxides (e.g., Sb_2O_3) and metal salts (e.g., $CaCO_3$ or $MgCO_3$) act as FR additives mainly on the basis of their endothermic decomposition in condensed phase. The H_2O generated from hydroxide and CO_2 generated from carbonate possess dilution effect and the evaporation of the gas removes large quantity of heat from burning. Furthermore, the produced metal oxide can integrate into structure of residual char and increase the protective char layer effect [132]. These FR additives are most widely applied FR fillers for polymer matrices due to the facile mixing process and low cost. However, to achieve promising FR efficiency, the loading of this category of FR additives is commonly higher than 40 wt%, which has negative influence on processibility and mechanical performance for materials [133]. Some of these chemicals such as Sb_2O_3 show catalyst effect on the radical quenching reaction of halogenated FR additive [134].

(2) Halogenated FR additives

Halogenated FR additives can effectively restrain the propagation of fire by free radical scavenging effect by releasing halogen radicals in gas phase. The reaction is shown as following equations:

$RX \rightarrow R\bullet + X\bullet$;

$HX + H\bullet \rightarrow H_2 + X\bullet$;

$HX + OH\bullet \rightarrow H_2O + X\bullet$

(X=Cl or Br)

The halogen radicals generated at high temperature can capture the H• and OH• radicals thus ameliorating the intensity of flame. Only organochloride and organ bromine are suitable to be applied as FR additives. The stability of fluorinated compound is too high while iodine containing compounds have stability and cost problem. However, the generation of hydrogen chloride or hydrogen bromide gases from burning of halogenated FR additives are high toxic, which hinders the application of halogenated FR additives.

(3) Phosphorus-based FR additives

Phosphorus-based FR additives can be roughly divided into inorganic ones (such as APP, metal phosphite) and organic ones (such as melamine, piperazine). Phosphorus groups possess both radical scavenging effect in gaseous phase and protective char layer effect in condensed phase. The scavenging effect of phosphorus group is shown as the equations:

$PO\bullet + OH\bullet \rightarrow HPO\bullet + O\bullet$;

$HPO\bullet + H\bullet \rightarrow PO\bullet + H_2$;

$PO\bullet + H\bullet \rightarrow HPO\bullet$

The PO• and HPO• radicals generated from P=O groups can trap the active radicals in gas phase and interrupt the chain mechanism of burning. Furthermore, phosphate groups function as acid source and catalyze the dehydration reaction of polymer thus promoting the formation of char layer [135]. Phosphorus-based FR additives are most potential alternatives to halogenated FR additives due to their high effectiveness and relatively lower toxicity.

(4) Nitrogen-based FR additives

Nitrogen-based FR additives are popular for smoke suppression and low toxicity application. These FR additives mainly act by releasing inflammable gas like N_2 and NH_3 which correspond to inert gas dilution effect. However, utilizing inert gas dilution effect alone is not sufficient to achieve self-extinguishing material. Therefore, Nitrogen-based FR additives always contain phosphorus element and N-containing groups in FR additives can be considered as synergists to improve the FR effective of P-containing groups (i.e., APP, melamine cyanurate and melamine polyphosphate). For instance, melamine modified polymer possess favorable fire safety performance due to P/N synergistic effect [136].

(5) Silicon-based FR additives

Silicon-based FR additives majorly involve silicon dioxide and silicates. The advantages of silicon-based FR additives are with eco-friendship, low toxicity, promising thermal stability and low price. The FR mechanism of silicon-based FR additives is relevant to the presence of Si-O-Si network in residual surface char layer, the Si-O-Si network improve the integrity of char layer thus preventing the interaction between oxygen and substrate under the char [137]. A crucial silicon-based FR additives are nanoclays, a natural mineral silicates containing magnesium and aluminum, etc. It is also worth mentioning that silane coupling agent is one of the few FR modifiers which can simultaneously improve the fire safety and mechanical performance of the material [127]. However, solely addition of silicon-based FR additives into polymer can only achieve acceptable FR performance at high loading content, as a result silicon-based FR additives are always applied as favorable FR synergists for synergistic FR system.

(6) Boron-based FR additives

Boron-based FR additives represented by zinc borate and boron nitride show similar application and FR mechanism as silicon-based FR additives. The major FR mechanism is ascribed to char barrier effect based on combination of boron-oxide network with structure of char layer. Boron-based FR additives are utilized owning to their outstanding smoke suppression performance and low pollution. However, the boron-containing FR additives are usually adopted as synergists in FR system as well, for example, boric oxide and red phosphorus are combined as a synergistic FR system to improve inflammability of epoxy [138].

(7) Carbon and nanocarbon FR additives

Carbon and nanocarbon FR additives, i.e., EG, carbon nanotube and graphene, are developed as substitutes to conventional FR additives owning to their effects in enhancing inflammability, thermal stability and electric conductivity of polymer. The carbon-based additives are proved to act as synergists combined with phosphorus-based FR additives without sacrificing of mechanical performance of polymer. The primary FR mechanism of carbon-based FR additives are relevant to the formation of insulating char layer which delays the pyrolysis of polymer in condensed phase [139].

Nearly all the FR additives can be divided according above categories and the FR additives in same category will following similar FR mechanisms. The relevant information are summarized as Table. 1-8.

Table. 1-8 Summarized FR additives and their FR mechanisms [103, 115]

FR additives	Major FR mechanism	Remarks
Metal hydroxides, metal oxides and metal salts FR additives	•Endothermal cooling effect •Catalyze effect	High loading content (>40%) is needed thus reducing the mechanical performance of material.
Halogenated FR additives	•Scavenging effect	The additives are most harmful, Toxicity of smoke generated in combustion.
Phosphorus-based FR additives	•Scavenging effect •Char barrier effect	Most of additives have environmental toxic, though not harmful. The FR efficiency is relatively higher than other FR additives.
Nitrogen-based FR additives	•Dilution effect	Usually applied as synergist in P/N FR system.
Silicon-based FR additives	•Char barrier effect	Usually applied as synergist. Smoke suppression.
Boron-based FR additives	•Char barrier effect	Usually applied as synergist. Smoke suppression.
Carbon and nanocarbon FR additives	•Char barrier effect	The FR additives can simultaneously improve FR and mechanical performance of polymer.

Except for aforementioned FR additives, there are some innovative types of FR additives worth mentioning. Firstly, some green FR additives based on natural-sourced feedstock are exploited to satisfy the requirement for green materials, lignin derived [140] or phytic related [141] FR additives are representatives. Secondly, layered double hydroxides containing adjustable metal ions are synthesized as replacement for traditional metal hydroxide, the layered double hydroxides take the advantage of the catalyst effect of different metal ions [142]. Thirdly, some intrinsically FR resin system based on FR modified epoxy monomer or curing agent are developed, the representative examples are DOPO derived FR additives [112]. In addition, sulfur-containing [143] and iron-containing FR additives [144] have been verified to show FR effectiveness. At last, an advanced two-dimensional titanium carbide called “MXene” is exploited to be applied as FR additives in recent studies [145]. These innovative FR additives have provided new possibilities and perspectives for development of FR materials.

To design a fibre reinforced polymer composite with improved flame retardancy, it is necessary to find a balance between the manufacturing of composites and how to achieve FR modification. The introduction of FR modification approaches, FR additives and corresponded FR mechanisms have provided a guide for researches about FR composites. Some literatures about flame retardant fibre reinforced composites also provided numerous information [22, 100, 115, 146].

1.5.4 Flame retardant characterization

In recent years, polymeric composites have gradually taken the place of metallic materials due to light weight requirement. However, the high flammability of polymers have constrained the range of application and FR additives are used to modify polymer to improve the fire safety. Relevant information about FR materials are reviewed in previous section. To evaluate and compared the FR behaviors of different polymer composites, several standards and test methods are established. According to specific applications of FR materials in industry, the FR materials are categorized into different types with corresponded test standards (As Table. 1-9).

Table. 1-9 Applications and standards for FR materials [115]

Application field	Utilization	Standards adopted
Fabrics	Natural fabrics or synthetic fabrics	•ASTM D-1230
Electronic devices	Wires ,cables or smartphones	•International Electrotechnical Commission (IEC) 62441 •UL 746C Guidance
Constructions	Roofs, floors or coatings	•ASTM E-84 in the USA or Single Burning Item (SBI) in the EU •ASTM E-162 for small-scale test to evaluate flame propagation
Transportation	Interiors, panels, coverings or seats	•Federal Motor Vehicle Safety Standard No. 302 evaluates the fire safety for materials used in the interior decorations of automobiles •Federal Aviation Regulations (FAR) 25.853 for aircraft interiors containing vertical burning, heat release (Ohio State University calorimeter) and smoke density tests

From academic perspective, there are majorly five typical tests to comprehensively evaluate the FR performance of a materials: TGA, limit oxygen index (LOI) test, vertical burning (UL-94) test, cone calorimeter test (CCT), chemical structure and morphology of residual char.

TGA data describes the change of sample weight as a function of increasing temperature in given atmosphere (N_2 or air). For FR polymer composites, the weight loss of sample can be attributed to decomposition of the relevant components in composites. The decomposition temperature of each components can be analyzed to study the influence of FR modification on thermal stability of composite. Another important parameter obtained from TGA is the mass of residual char which is correlated with char barrier effect to improve the flame retardancy of composite [147].

In an LOI test, one laminated material sample is vertically fixed in a chamber filled with O_2/N_2 gas mixture, the concentration of O_2 in gas mixture can be adjusted and LOI is the minimum O_2 concentration which keeps the burning of ignited sample for 3 min or burns a length of 5 cm (According to ASTM D-2863 or ISO 4589 standard). The value of LOI is mainly correlated with the spread rate of fire for ignited material. Normally, materials with LOI value less than 21% are thought to be combustible materials. When the LOI of a material is between 21% and 28%, the material can be regarded as slow burning material. For materials with LOI value higher than 28%, the materials is with acceptable flame retardancy [148].

UL-94 test is a vertical burning test to evaluate the ignitability of materials. Depending on the combustion behavior, the FR materials can be divided to three categories: V-0, V-1, or V-2 (According to ISO 1210 standard). The criteria for each category is summarized as Table. 1-10. In a UL-94 test, the material sample is vertically suspended and a flame is applied to the bottom of sample for 10 s, then the flame is removed, the after flame time of material is recorded as t_1. Then the flame is applied to bottom of sample again for 10 s and then removed, the after flame time is recorded as t_2. The test will be repeated for 5 times, the fire safety criteria is determined by the value of t_1 and t_2 for each sample and the summation of t_1+t_2 for 5 samples [149].

Table. 1-10 UL-94 vertical burning standard [149]

UL-96 category	Criteria
V-0	t_1 and t_2 <10 s for each sample Summation of t_1 + t_2<50 for five samples No dripping
V-1	t_1 and t_2 <30 s for each sample Summation of t_1 + t_2 <250 s for five samples No dripping
V-2	t_1 and t_2 <30 s for each sample Summation of t_1 + t_2 <250 s for five samples Dripping allowed

CCT is a bench scale test which provides comprehensive information about the combustion behavior of a material (According to ASTM E-1354 or ISO 5660 standard). This method is established on the basis of detecting the variation of oxygen concentration of combustible sample in a sealed chamber (A determined heat flux is input). The test result of CCT involve many crucial parameters such as time to ignition (TTI), heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR), smoke production rate (SPR), total smoke production (TSP). These parameters can be analyzed to evaluate the fire and smoke behavior of material which is most approximate to real-world fire hazard [150]. However, there are significant differences of combustion behaviors for different polymeric matrices. Therefore some more general parameters are recommended on the basis of CCT results to compared the flame retardancy of different polymer (Table. 1-11).

Table. 1-11 Parameter to evaluate the flame retardancy of materials according to CCT

Parameters	Remarks
FGI=$\frac{PHRR}{T_{PHRR}}$	•Fire growth index (FGI), T$_{PHRR}$ is the time needed for HRR to reach PHRR, this parameter illustrates the rate of flame growth [151]
FPI=$\frac{TTI}{PHRR}$	•Fire performance index (FPI), this parameter illustrates the intensity and range of the flame [152]
FRI=$\frac{(THR*\frac{PHRR}{TTI})_P}{(THR*\frac{PHRR}{TTI})_{FR}}$	•Flame retardancy index (FRI), P and FR represents the pristine material and FR modified material, this parameter illustrates the effectiveness of FR modification and the final FR performance of material. Normally, when the value of FRI is: <1, poor flame retardancy Between 1 and 10, good flame retardancy >10, excellent flame retardancy [153]

The last test related to the evaluation of FR performance of material is chemical structure and morphology of residual char obtained from Raman spectrum and scanning electron microscopy (SEM), respectively. The chemical structure and morphology of residual char are crucial in discussion of FR mechanism of material. Chemical structure from Raman spectrum can denote the degree of graphitization and compactness of residual char [154]. By SEM, the surface morphology of residual char is detected, information such as smoothness and distribution of pores or defects can illustrate the FR mechanism of material especially for protective char layer effect [155].

1.5.5 Research progress about flame retardant natural fibre reinforced polymer composite

After some introduction about significance, FR mechanism, FR additives and relevant characterization of FR composite, this section tend to summarize some recent progress about flame retardant NFRP composites. Table. 1-12 summarizes some papers about the FR modification of NFRP composites. On the basis of the results from these work, the following conclusions can be drawn: (1) For natural fibre with fabric preform, the proper manufacturing for corresponded NFRP composite are compression molding or RTM process. (2) Phosphorus-containing FR additives represented by APP is commonly applied for NFRP composite, and the effective of the APP is acceptable. (3) Few papers specifically discussed the influence of fibre FR modification on the flammability of fibre reinforced composite.

Table. 1-12 Recent process about flame retardant NFRP composites

Materials	FR modification	Flammability[1]	Reference
Hemp fabric+epoxy	APP was mixed with epoxy resin and then the composite was manufactured via RTM process	•The best formula was 65 wt% epoxy (23.1 wt%APP in epoxy)/35 wt% hemp. •The inflammability passed FAR 25..853 standard. •HRR: 121.6→48.6 kW/m^2 •THR: 68→27 MJ/m^2	[156]
Flax fabric+epoxy resin	APP and ATH was mixed with epoxy resin and then the composites were fabricaed by hand lay-up process	•The best formula was epoxy/flax composite with 2 plies if flax fabric (areal density was 550 g/m^2) and 3 mm sample thickness, the weight fraction of APP in epoxy is 30 wt%. •The inflammability was V-0 category. •LOI: 21.3→30.3%	[157]
Sisal fabric+nanoclay+epoxy	Nanoclay was mixed with epoxy resin, sisal fabric was treated by silane coupling agent. The composites were fabricated by compression molding	•The best formula was 69 wt% epoxy/30 wt % sisal fabric /1 wt % nanoclay • The inflammability was V-1 category. •LOI: 20.%→27.0% •THR 141.7→104.3 MJ/m^2	[158]
Flax fibre+ poly(lactic acid) (PLA)	The flax was treated by polydopamine and then modified by iron phosphonate. The flax fibre and PLA were mixed via melt mixing following by compression molding	•The best formula was 70 wt%PLA/30 wt% FR modified flax •The inflammability was V-2 category. •LOI: 20.0→26.1% •HRR: 400→330 kW/m^2	[159]
Ramie fibre+DOPO modified carbon nanotube+PLA	Carbon nanotube was modified by DOPO. The PLA, DOPO modified carbon nanotube and ramie fibre were mixed by twin-screw extruder.	•The best formula was 85 wt% PLA/10 wt% ramie fibre/5 wt% DOPO modified carbon nanotube •The inflammability was V-2 category •LOI: 21.6→26.4%	[160]

Diammonium phosphate modified bamboo fibre+polyurethane (PU)	The bamboo fibre was modified by diammonium phosphate. The PU and FR modified bamboo fibre were mixed by twin-screw extruder and the composite was fabricated by compression molding.	The best formula was 90 wt% PU/8 wt%APP/2 wt% modified bamboo •The inflammability was V-0 category •LOI: 21.4→30.5% •THR: 79→51 MJ/m^2	[161]
Ramie fabric+PLA	Ramie fabric was dip coated by APP solution. PLA was mixed with APP by twin-screw extruder. The composite was fabricated by compression molding.	The best formula was 59.5 wt%PLA/5.2 wt%APP (mixed with PLA)/30 wt% RF/5.3 wt% APP (coating on RF) •The inflammability was V-0 catagory •LOI: 19.1→35.6 %	[162]

1 The best formula was referred to the composite formular with best flame retardancy in corresponded work.

This section has thoroughly reviewed significance of improving fire safety of material, FR modification approaches, different FR mechanisms, classification of FR additives, characterization of FR material and recent progress about flame retardant NFRP composites. These information has provided a direction for design and optimization of flame retardant natural fibre reinforced polymer composite.

1.6 Identifying the research gap

In section 1.1, the information about natural fibres (involving classification, structure, chemical composition, mechanical performance and thermal degradation behavior) are reviewed. The comprehensive performance (light weight application, high specific mechanical strength, damping and sound absorption application, biodegradability, cost-effectiveness) of natural fibres makes them potential substitute to conventional synthetic fibres such as glass fibre or carbon fibre.

In section 1.2, the relevant information about NFRP composite (including factors affected the mechanical properties of composites, mechanical performance and application of NFRP composites) are introduced. This section has provided a comprehensive guidance for determination of various parameters (selection of natural fibres and polymers, treatment for fibres and manufacturing process) in the design of NFRP composite materials. A selection chart is also referred to illustrate the relationship between mechanical performance of NFRP composite and manufacturing parameters such as natural fibre preforms and fabrication process.

Furthermore, except for natural fibre reinforcements, polymer matrices developed from natural-sourced feedstock are another answer of green composite. However, bio-based polymers refer to too many materials so that Section 1.3 is only focused on bio-sourced epoxy resins. The development of composite with bio-sourced epoxy matrix is the focus of this work. In section 1.3, the recent progress of rosin-sourced epoxy resin, itaconic acid derived epoxy resin and some other bio-sourced epoxies are reviewed. However, there is still a gap between the performance of composites based on bio-sourced resin and commercial resin matrix. Some issues in manufacturing process such as high viscosity should also be solved. Also, there are few studies about the performance of fibre reinforced composite with novel bio-sourced epoxy matrix.

In addition, to solve the flammability of both natural fibre and polymer matrix for NFRP composites, the development of FR composite (including significance of employment of FR materials, approaches to achieve flame retardancy, FR mechanisms in condensed and gaseous phases, characterization of flame retardancy for materials) is introduced in section 1.4. Due to poor interface between FR additives and polymer, one of the primary problems of FR materials is how to balance the mechanical properties with fire safety performance of materials. Additionally, the industrialization of FR materials should take the cost-effectiveness and the difficulty of large-scale production into consider.

On the basis of aforementioned information, this work identifies following research gap:

Firstly, numerous researches about green composites are focused on replacing synthetic fibres with natural fibres, while the matrices of composites are still petroleum-based. Therefore, fully green composite based on natural fibre reinforcement and bio-sourced resin matrix may be a potential research topic. The combination of natural fibres with bio-sourced epoxy will cause some problems, for instance, the selection of fibre and matrix, suitable manufacturing process corresponded to properties of fibre and matrix, the optimization of manufacturing parameters, these problems should be considered thoroughly.

Secondly, compared to commercial resins, there are some problems in the development of bio-sourced resins, especially for fibre reinforced composite based on bio-sourced resin system. In the case of fibre reinforced composite with bio-sourced epoxy matrix, some parameters such as high viscosity will make the manufacturing difficult. For example, the high viscosity of rosin-sourced epoxy system makes the resin difficult to be applied in RTM process, which restrains the application range of the resin. Consequently, the optimization of fabrication process is needed to achieve better performance of composite. The difficulty of manufacturing process and large-scale problem should be considered as well.

At last, the development of NFRP composite with favorable flame retardancy is a significant topic as well. Different from incorporating FR additives into pristine polymer, the incorporation of FR additives into fibre reinforced polymer composites is less effective. The exist of inert fibres constrains the generation of integrated insulating char layer, which can cause candle wick effect [163]. Hence simultaneously FR modification to both resin and fibre, instead of solely adding FR additive into matrix, is a solution to improve the fire safety of fibre reinforced composite [115].

In summary, the research gaps are identified as follows:

(1) The development of fully green composite based on natural fibre and bio-sourced epoxy, the current work is mainly relevant to ramie fabric reinforced rosin-

sourced epoxy resin composite. The possibility of replacing traditional petroleum-based fibre reinforced polymer composite with fully green NFRP composite was discussed.

(2) The optimization of fabrication process of fibre reinforced bio-sourced epoxy composite, specifically, this work try to fabricate RF reinforced rosin-sourced epoxy composite via RTM process, which is considered to be difficult due to high viscosity of epoxy system cured by rosin-sourced hardener.

(3) To solve the flammability problem of natural fibre and bio-sourced epoxy polymer, the current work tried to improve the inflammability of NFRP composite. Also, the effect of combination of FR modification to fibre with FR modification to polymer matrix. The role of FR modified fabric in flame retardancy improvement of fibre reinforced composite is the focus of the work.

(4) To furtherly investigate the influence of fibre reinforcement on composite, carbon fibre and glass were chosen as control group of ramie fibre due to their inflammability. Additionally, another aim is to provide the fundamental information about mechanical performance of IABE/GF and IABE/CF composites

The design process of the fully green NFRP composite in current work is shown as Figure. 1-26. The objective of the work was to develop fully green composite composed of natural fibre and bio-sourced resin, RF and rEP resin are chosen as fibre reinforcement and bio-sourced epoxy matrix. Another objective of this work is to investigate the combined effect of fibre FR modification and matrix FR modification. Therefore, RF was modified by OP and rEP were modified by different FR additives (APP, ATH, ZnB or EG) respectively with proper process. According to characteristics of RF and rEP, the manufacturing process and relevant parameters are determined and optimized. During the manufacturing, it was found that the high viscosity of rEP resin system influenced the processibility of the resin, and the resin was not suitable for RTM process. To cope with the high viscosity problem, an ex-situ LCM process was investigated. At last, the fabricated composite samples are characterized to investigate their mechanical and inflammability performance. In addition, this work also involved itaconic acid based epoxy composites reinforced by GF and CF, it was a pre-experiment for future work about IABE composite.

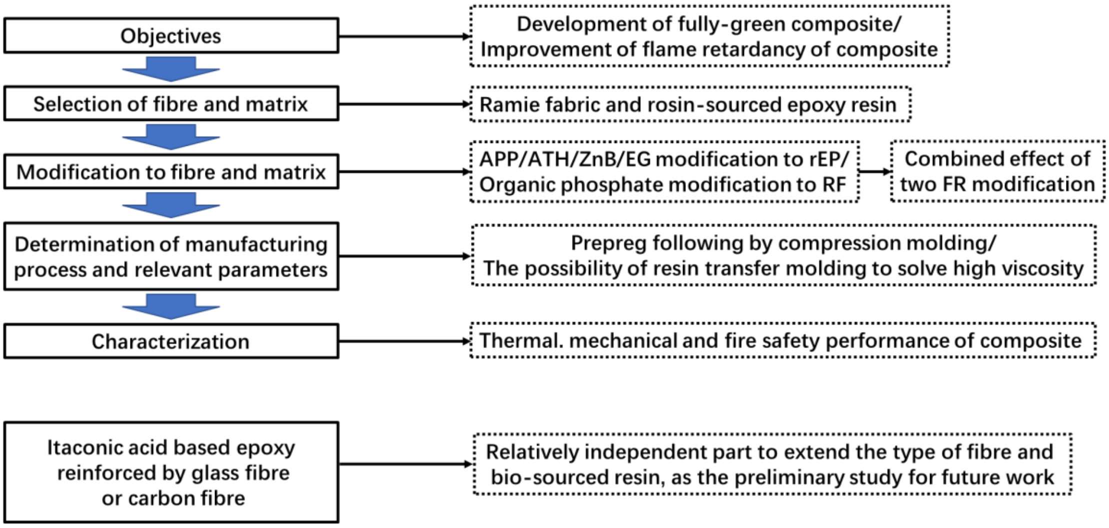


Figure. 1-26 The design process of the fully green NFRP composite in current work

Chapter 2 Study on Flammability And Mechanical Properties of A Fully-Green Composite

2.1 Introduction

In chapter 1, the significance and advantages of development and application of natural fibres and bio-sourced epoxy resins were reviewed. Also, to match the requirement of materials in the actual engineering, natural fibre reinforced polymer (NFRP) composites possess greater range of applications and more application scenarios than solely using natural fibres. Furthermore, by employment of bio-sourced resin as matrix of NFRP composite, the content of green component in composite can be furtherly increased to achieve fully-green natural fibre reinforced bio-sourced epoxy composite. In this chapter, a bio-sourced epoxy resin system composed of traditional epoxy monomer and rosin derived curing agent was applied as matrix [164], the resin was designated as rosin-sourced epoxy (rEP) resin. Ramie fabric (RF) was chosen as natural-sourced reinforcement, the RF was white plain-woven fabric with relatively stable parameters such as areal density, yarn diameter or fibre type.

After the selection of fabric reinforcement and polymer matrix, the next step is to determine a proper manufacturing process. Normally, in the cases of combination of fabric and epoxy resin which need high temperature for curing, viable manufacturing process are resin transfer molding (RTM) and compression molding process [81]. In practice, the rEP resin was found to with high viscosity, which was difficult to achieve acceptable infiltration in RTM process. Therefore, compression molding was applied to prepare the composite and the vacuum bag was applied to ensure the even pressure in manufacturing.

In addition, after review of recent progress about flame retardant (FR) composite in chapter 1, especially for FR fibre reinforced composite, the effect of whether the fibre was FR modified or not on the flame retardancy of composite was not investigated in detail. To improve the fire safety of composite, ammonium polyphosphate (APP) was mixed into the rEP system. An organic phosphate (OP) FR additive was used to modify RF. By employment of original resin and FR modified resin as matrix, original fabric and FR modified fabric as reinforcement, four groups of fully-green FR composites were fabricated, the mechanical and FR properties of the composites were evaluated. The influence and combined effect between FR modified matrix and FR modified fabric were evaluated. The work was a preliminary study to explore sustainable composite combined green reinforcement with green matrix, also the combined effect between FR treated fabric and FR treated resin was investigated.

2.2 Materials & Methods

2.2.1 Materials

Plain ramie fabric (RF) was purchased from Huangshengdongting Co., Ltd (Hunan, China, with specification shown in Table. 2-1). Rosin-sourced resin (rEP, type AGMP-5600) and APP modified bio-sourced resin (APP@rEP, type AGMP-5601, which was prepared by mixing rEP with APP via a hot mixing process, the weight fraction of APP was about 20%) were provided by AVIC Composite Corporation Ltd (Beijing, China) [164]. A water soluble and commercial fire retardant additive organic phosphate was purchased from Hete Company (Shanghai, China). Citric acid and sodium hydroxide were provided by Tianjin Polytechnic University (Tianjin, China). Acetone was purchased from Sinopharm Chemical Reagent Co., Ltd. The deionized water was self-produced in the lab.

Table. 2-1 Specification for original ramie fabric

Yarn number/S		Yarn density/Thread/2.5 cm		Width (cm)	Areal density (g/m^2)	Thickness (mm)
Warp	Weft	Warp density	Weft density			
21	21	52	58	160	123	0.3

2.2.2 The flame retardant modification for ramie fabric and rEP

The organic phosphate modified ramie fabric (OP@RF) was prepared by dip-coating method. Firstly, the original RF was rinsed with 2% NaOH solution for 2 h to remove dust and chemical agents on the fabric. Then the organic phosphate FR additive and citric acid were dissolved in deionized water, the concentration of FR additive and citric acid were 400 g/L and 25 g/L, respectively. The ramie fabric was immersed into FR additive solution, after the padding and drying process (160 °C/3 min), the OP@RF was prepared.

According to the formula:

$$w = \frac{m_{OP@RF} - m_{RF}}{m_{RF}} * 100\% \quad (1)$$

Where w is the weight gain of fabric after the FR dip-coating process, $m_{\mathrm{OP@RF}}$ is the average weight of RF after FR modification, m_{RF} is the original average weight of RF. The areal density of RF was 123 g/m^2. after FR treatment, the areal density of OP@RF was increased to 162 g/m^2, so the weight gain of OP on RF was 31.7%.

Whereas for the rEP matrix, the original rEP is provided by Aviation Composite Co., Ltd, the specific information about the rosin-sourced resin can be found in relevant work [90]. The APP modified rEP (APP@rEP) was prepared by hot mixing APP powder into pristine rEP. The rEP was melted at 90 °C in a three-roller grinding machine firstly, then 20 wt% of APP powder was stepwise added into the melted rEP, after one hour blending, the APP@rEP mixture was rapidly collected before cooling.

2.2.3 Fabrication of resin/fabric prepregs

The composition of composite prepregs was shown in Figure. 2-1. By combination of RF, OP@RF with rEP, APP@rEP, four constitutions of resin/fabric prepregs labelled with rEP/RF, APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF were fabricated.

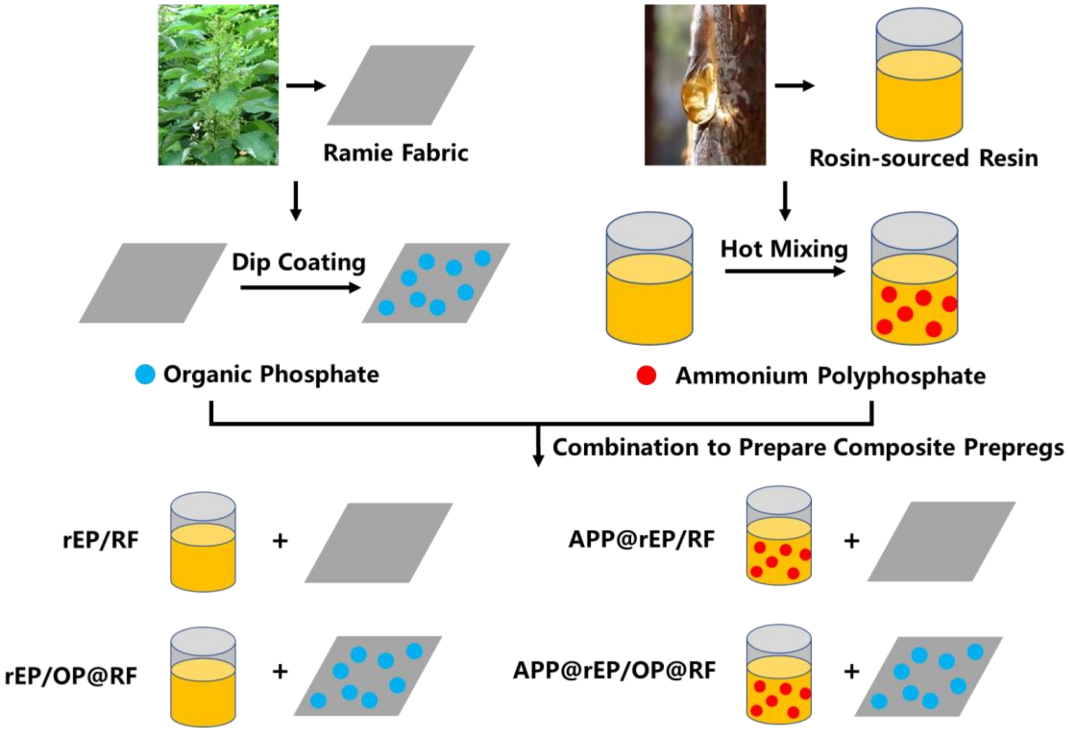


Figure. 2-1 Four constitutions of composite prepregs

To prepare resin/fabric prepregs, the rosin-sourced epoxy was dissolved in acetone at the ratio of 1:2, then the mixed solution was painted onto the RF (with the release film under the fabric) by hairbrush. The ratio of resin/acetone solution to fabric was 4:1 by weight. The painted fabric was then put into the vacuum oven at 60 ℃ for 1h drying. APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF prepregs were prepared by similar process.

2.2.4 Manufacturing of composites

The composite samples were fabricated by vacuum bag assisted compression molding method as exhibited in Figure. 2-2. Two steel molds were applied in fabrication, the molds were cleaned by acetone and pre-coated by releasing agent. 10 plies of 300*300 mm^2 rEP/RF prepregs were stacked on the mold. Several metal dams with 2 mm thickness were placed between two molds to control the final thickness of composite sample. The releasing films were used on the top and bottom of prepregs to ensure the separation of sample from mold. A breather ply was positioned on mold to absorb resin squeezed out during compression molding. The vacuum bag with sealing tape and vacuum outlet linked to vacuum pump was prepared to provide an even pressure during the melting of resin in the pre-curing process (90℃/30 min). After pre-curing, the temperature was raised to 160℃, meanwhile the pressure was increased to 4 MPa by the hydraulic compression machine for the post-curing process, after three hours the composite laminate was fabricated, the compression molding parameters for the whole process were displayed as Figure. 2-3. APP@rEP, rEP/OP@RF and APP@rEP/OP@RF composites were manufactured via same process.

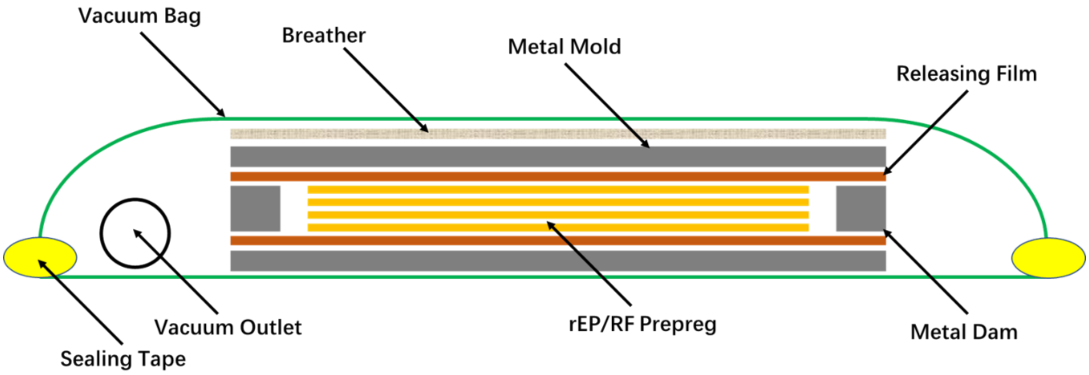


Figure. 2-2 Sketch diagram of vacuum bag assisted compression molding process

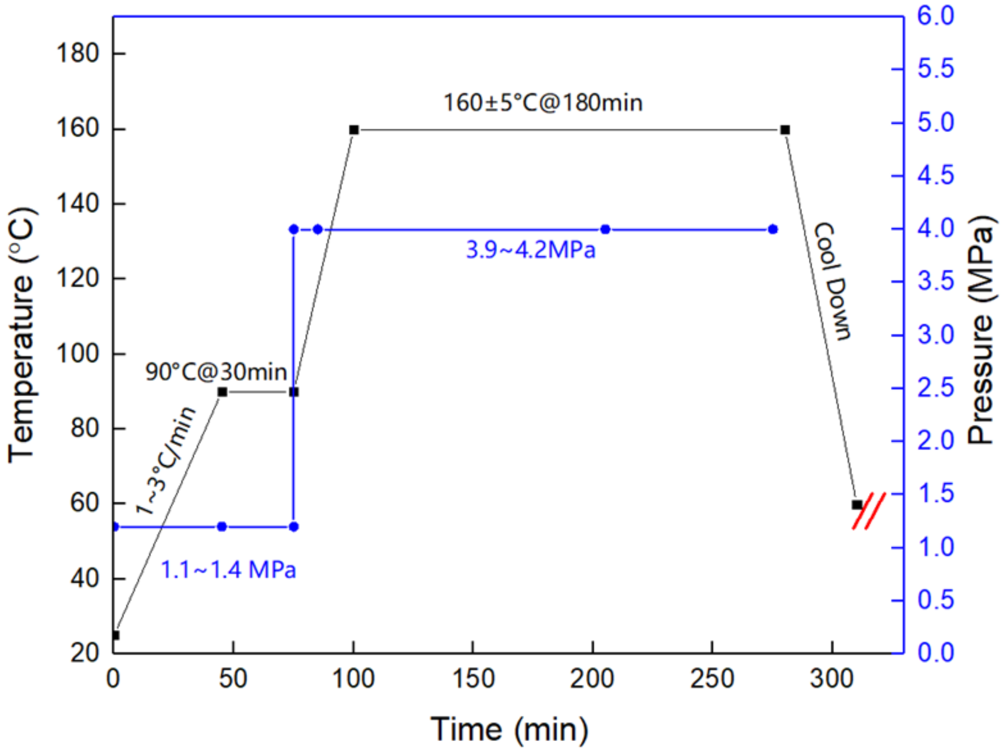


Figure. 2-3 Experiment parameters for compression molding

To investigate the flame retardant properties of rEP and APP@rEP without RF reinforcement. The rEP and APP@rEP samples were fabricated by melting casting method: the resin was heated to 90 ℃ to form the resin liquid with high viscosity, then the melted resin was poured into a mold for the curing process (the temperature and time parameters were same as compression molding for composite in Figure. 2-3, but there was no pressure).

The value of resin content in prepreg was higher than final resin content in composite, a steel mold was applied in the compression molding process to control the thickness of the sample so that excessive resin on prepregs would be squeezed out during fabrication.

The volume fraction of RF is calculated by:

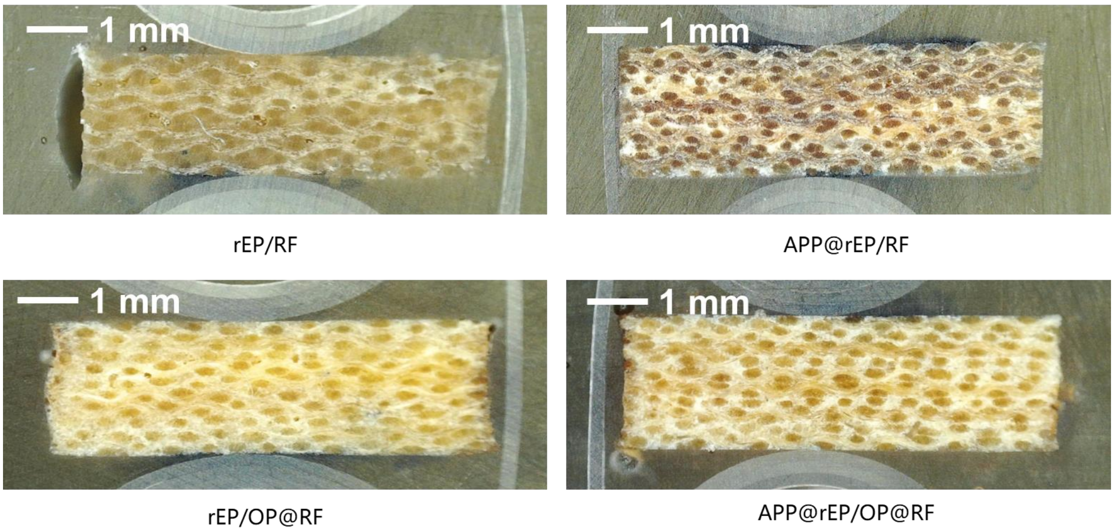
$$V_{RF} = A_{RF} * N * S/(\rho_{RF} * h * S) \quad (2)$$

Where V_{RF} is the volume fraction of RF, A_{RF} is the areal density of RF, N is the number of prepreg plies, S is the area of the sample, ρ_{RF} is the density of RF and the value is 1.50 g/cm^3, h is the thickness of sample. The volume fraction of OP (V_{OP}) on RF is calculated by:

$$V_{OP} = V_{RF} * \rho_{RF} * W/\rho_{OP} \quad (3)$$

Where W is weight gain percent of FR additive on RF as aforementioned, ρ_{OP} is the density of OP on fabric and the value is 1.36 g/cm^3. For rEP/RF and APP@rEP/RF composites, the value of V_{OP} is 0.

The images of the cross-section for composites were exhibited as Figure. 2-4. It can be observed that there was not visible void or defect in composite.



rEP/RF

APP@rEP/RF

rEP/OP@RF

APP@rEP/OP@RF

Figure. 2-4 The digital images of cross-section for composites

If the porosity or defect of composite was not considered, the volume content of rEP or APP@rEP is:

$$V_R = 100\% - V_{RF} - V_{OP} \quad (4)$$

Where V_R is volume fraction of rEP or APP@rEP.

The composite composition was calculated and denoted in Table. 2.

Table. 2-2 Composition of four groups of composites

Composite	rEP	APP	RF	OP	Thickness (mm)
	By volume (%)				
rEP/RF	57.6	0	42.4	0	1.81
APP@rEP/RF	51.3	8.1	40.6	0	1.89
rEP/OP@RF	43.2	0	42.1	14.7	1.82
APP@rEP/OP@RF	40.3	6.4	39.5	13.8	1.95

2.3 Characterization

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra was applied on Cary 660+620 spectrometer (Agilent, USA), the frequency range was from 4000 to 500 cm-1 with 32 scans.

The thermal degradation test of samples were performed on a thermogravimetric analysis (TGA) Q600 instrument (TA instrument Co. Ltd, New Castle, DE, USA). Samples were heated from room temperature to 800℃ with a heating rate of 10 ℃/min, the gas-flow was 20 mL/min and the atmosphere was N_2 while the sample weight was about 15~20 mg.

The dynamic mechanical analysis (DMA) of composites were characterized on Perkin Elmer DMA8000 equipment (Perkin-Elmer Corporation, USA). The sample size was 40*10*2 mm^3, test mode was single cantilever mode, the frequency was set to 1Hz during test and the temperature range was 30-180 ℃ with a heating rate of 3 ℃/min.

The tensile, flexural and compressive properties for composites were measured on an electronic universal testing machine (MTS Systems Corporation, Shenzhen, China). Tensile test was performed based on ASTM D-3039 standard, the sample size was 250*15*2 mm^3 and the crosshead speed was 1 mm/min, The span between two clamps was 150 mm without end tab. Flexural properties were measured according to ASTM D-790-03 standard, the speed of crosshead was 1 mm/min and sample dimension was 84×12.5×2 mm^3 with 64 mm span. Compressive test was based on ASTM D-6641 standard. The dimension of sample, crosshead speed and span of compressive test were 140*12*2 mm^3, 1.3 mm/min and 13 mm, respectively.

The 12 s vertical burning (flame penetration) test was carried out on a burner (TESTech Instrument Technologies Co., Ltd, Suzhou, Jiangsu, China) with exposed specimen dimension of 305×75×2 mm^3 according to the FAR 25.853 standard, the flame height was 38 mm.

The limiting oxygen index (LOI) value of composites were evaluated by oxygen index meter (TESTech Instrument Technologies Co., Ltd, Jiangsu, China) according to ISO-4569 standard with the sample size of 80*10*2 mm^3.

Cone colorimeter test was conducted with a Type FTT-0064 cone calorimeter meter (UK) according to ASTM E-1345 standard, the size of sample was 100*100*1 mm^3, the heat flux was set to 35 kW/m^2.

The morphology of residual char after cone colorimeter test was characterized using Mustcam HDMI Microscope (Mustech Electroincs Co., Ltd, Shenzhen, China).

2.4 Results and Discussion

2.4.1 FTIR analysis of RF and OP@RF

The FTIR spectra of pristine RF and OP modified RF were displayed in Figure. 2-5. Both of spectra had the characteristic absorption peaks corresponded to typical cellulose, including O-H stretching (3370 cm^{-1}), C-H stretching (2900 cm^{-1}), C-H bending (1430 cm^{-1}), C-O-C stretching (1160 cm^{-1}) and C=O stretching vibration (1060 cm^{-1}) [165]. Compared with pristine RF, The OP@RF had two new characteristic absorption peaks at 1237 and 823 cm^{-1}, which were ascribed to vibration of P-O-C and P=O bond [166], indicating that OP was coated on the RF surface. The P-O-C bond was probably related to reaction between cellulose and phosphate group of OP [162].

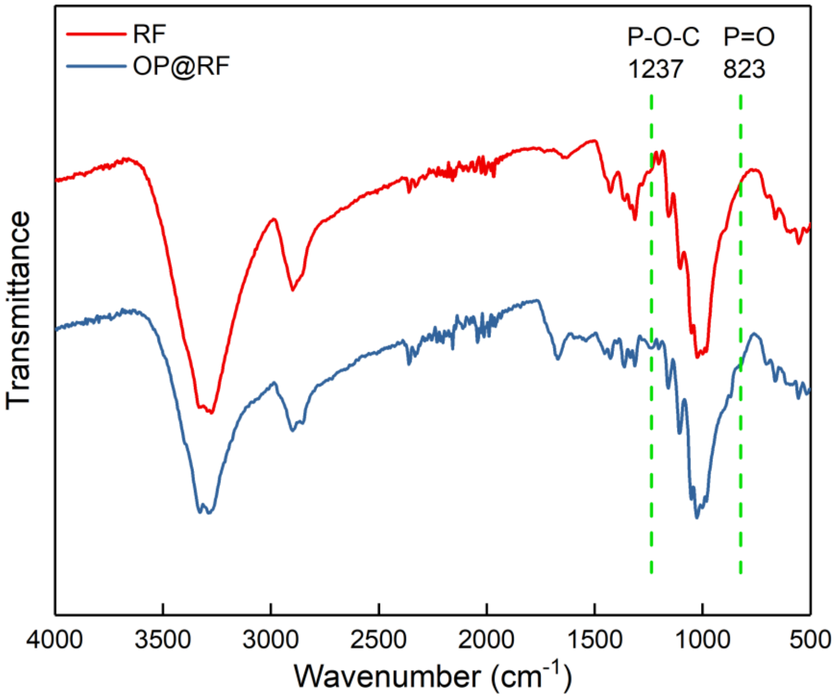


Figure. 2-5 FTIR spectra of RF and OP@RF

2.4.2 Thermal stability of resin matrix and fabric

The thermal decomposition behavior of RF and rEP with or without FR treatment was summed in Figure. 2-6. With respect to resin matrix, there was one-step thermal degradation for both rEP and APP@rEP, the incorporation of APP slightly reduced the thermal stability of resin, meanwhile the mass of char residue at 800 °C was increased by 12.1% compared with that of rEP. The increased char mass was attributed to the crosslinked phosphate ester generated from the reaction between APP and the hydroxyl group of rEP [167]. Regarding the fabric reinforcement, both RF and OP@RF underwent one-step thermal degradation. The thermal degradation temperature of OP@RF at maximum loss rate was about 290 °C, around 70 °C lower than that of the original RF, which implied that the introduction of OP on fabric promoted the thermal degradation of ramie fibre. The char residue of OP@RF was also higher than that of original RF, which proved that the FR treatment facilitated the char formation of RF. The decreased thermal stability and increased char residue of fabric were relevant to the low decomposition temperature of FR additives as well as the dehydration reaction of phosphate-containing OP and the cellulose hydroxyl group of natural fabric [162].

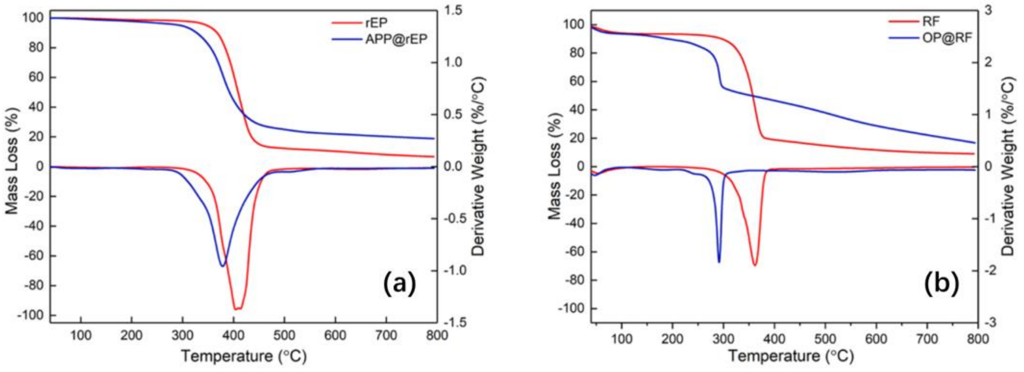


Figure. 2-6 TG and DTG curves of (a) rEP, APP@rEP and (b) RF, OP@RF in N_2 atmosphere

2.4.3 Thermal stability of composites

The TGA and DTG curves for four groups of composites were plotted in Figure. 2-7, while the detailed results were listed in Table. 2-3. $T_{5\%}$ was defined as the temperature at when the mass loss of composites reached 5%, and the $T_{5\%}$ can be used to reveal the beginning of composites thermal decomposition. The $T_{5\%}$ value for rEP/RF, APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF composites were 291.1 ℃, 231.5 ℃, 227.2 ℃ and 208.1 ℃, respectively. Obviously, either the addition of APP in resin or OP on RF decreased the thermal stability of the composites. All the composites exhibited two-step degradation, T_{max1} and T_{max2} were defined as temperature with maximum weight loss rate for two peaks. Compared the data with Figure. 2-6, it can be inferred that the first decomposition peak was referred to the degradation of fabric and the second peak was related to the decomposition of rosin-sourced resin. It was indicated that the incorporation of APP in epoxy resin or OP on fabric decreased the T_{max1} and T_{max2} value of composites. The reduction of thermal decomposition temperature of composites containing FR additives was due to the effect of phosphorus derivatives during combustion. The phosphorus derivatives such as phosphorus acid acted as acid source and promoted the carbonization of composites, which was proved by the increase of char yield at 800 ℃ [168]. It was indicated that the mass of residual char of rEP/RF was higher than those of rEP or RF alone, the increased char residue was relevant to the catalytic effect of phosphoric acid group and carbonization effect of lignin from RF [140].

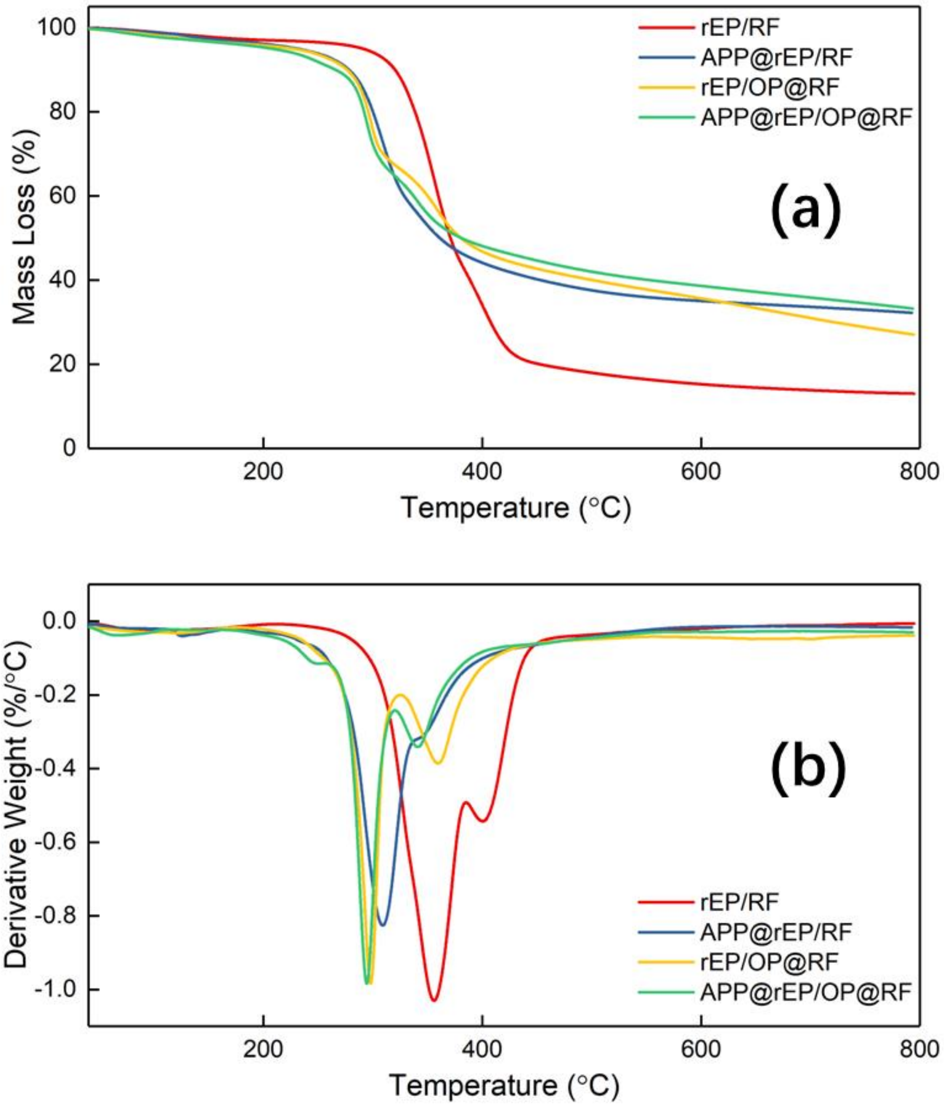


Figure. 2-7 (a) TGA and (b) DTG curves for four groups of composites in N_2 atmosphere

Table. 2-3 Thermal degradation results of four groups of composites

Composite	**$T_{5\%}$ (℃)**	**T_{max1} (℃)**	**T_{max2} (℃)**	**Char at 800℃ (%)**
rEP/RF	291.1	355.9	400.3	13.1
APP@rEP/RF	231.5	309.1	346.6	32.3
rEP/OP@RF	227.2	298.1	359.8	27.1
APP@rEP/OP@RF	208.1	294.1	341.1	33.3

2.4.4 Dynamic mechanical analysis results of composites

The influence of resin FR treatment and fabric FR treatment on the composite viscoelastic behavior was investigated by DMA. The storage modulus and loss factor as a function of temperature for composites were plotted as Figure. 2-8. For APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF composites, as the temperature increased, the storage modulus of composites decreased to the lower limit of the testing range for single cantilever mode and the tests were terminated at 109, 133 and 83 ℃, respectively (denoted by red remarks in the Figure. 2-8). Meanwhile, the glass transition temperature of rEP/RF composite was 176 ℃, it can be inferred that both FR treatment to resin and fabric decreased the glass transition temperature of composites. The incorporation of APP in rEP decreased the glass transition of resin matrix due to weak interaction between APP and rEP, also the APP reduced the cross-linking density of rEP curing system [169]. Whereas for the OP@RF, the continuous OP coating on RF surface deteriorated the interface between resin matrix and fabric, the weak interface carried a less stress thus reduced the glass transition of composite [162]. Compared with rEP/RF composite, the storage modulus of APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF composites exhibited rapid reduction at a relatively lower temperature, the reduction of storage modulus and glass transition temperature was relative to the change of molecule chain mobility. More chain slippage occurred for the interface between resin matrix and FR additives, while more chain stretch occurred for original resin due to the crosslinked structure of the epoxy resin system.

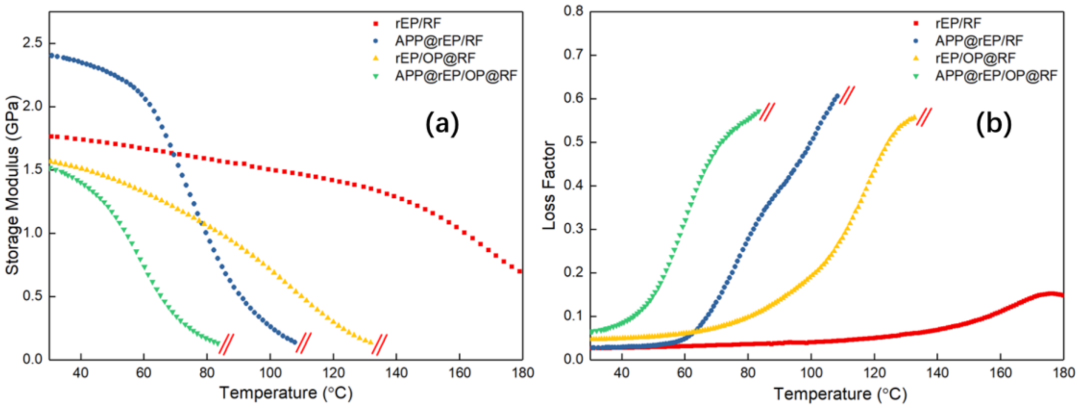


Figure. 2-8 Dynamic mechanical analysis results: (a) storage modulus (b) loss factor of four groups of composites

2.4.5 Mechanical properties of composites

The mechanical properties include tensile properties, flexural properties and compressive properties for composites were displayed in Figure. 2-9, Figure. 2-10 and Figure. 2-11, respectively. The specific data was summarized as Table. 2-4. On the whole, the incorporation of both two FR additives reduced the mechanical strength and modulus of the composites. The reduced mechanical properties were possibly due to two reasons: firstly, according to TGA results, OP reacted with fabric at around 300℃, the phosphate ester group promoted the dehydration reaction of cellulose and influenced the strength of ramie fibre [170], another reason was that OP coating on fabric weaken the interaction between matrix and ramie fabric [161].

It can be observed that the tensile, flexural, compressive modulus of APP@rEP/RF composite was higher than those of rEP/RF composite, which implied the incorporation of APP in resin increased the stiffness of the resin system. The increased modulus of APP@rEP/RF composite was relevant to high stiffness of APP particles, which hindered the polymeric mechanical deformation [162, 171]. Meanwhile, the mechanical strength of APP@rEP/RF composite was lower than those of rEP/RF composite, which implied lower crosslinking density or incompatibility caused by addition of APP [172]. However, as for rEP/OP@RF and APP@rEP/OP@RF composites, both strength and modulus of composites were lower than those of rEP/RF composites. The decreased mechanical performance was related to unfavorable interface between fabric surface and resin due to the introduction of OP and APP. The dispersion of FR additives in composite also influenced the mechanical performance of the material. The continuous OP coating on RF surface showed a passive effect on the mechanical strength of composites.

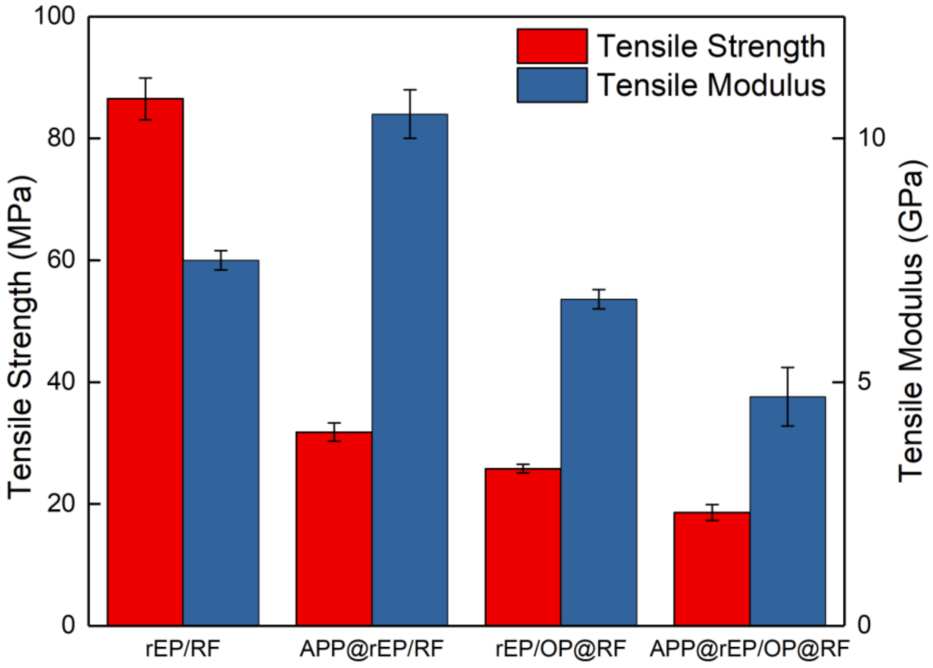


Figure. 2-9 Tensile properties of four groups of composites

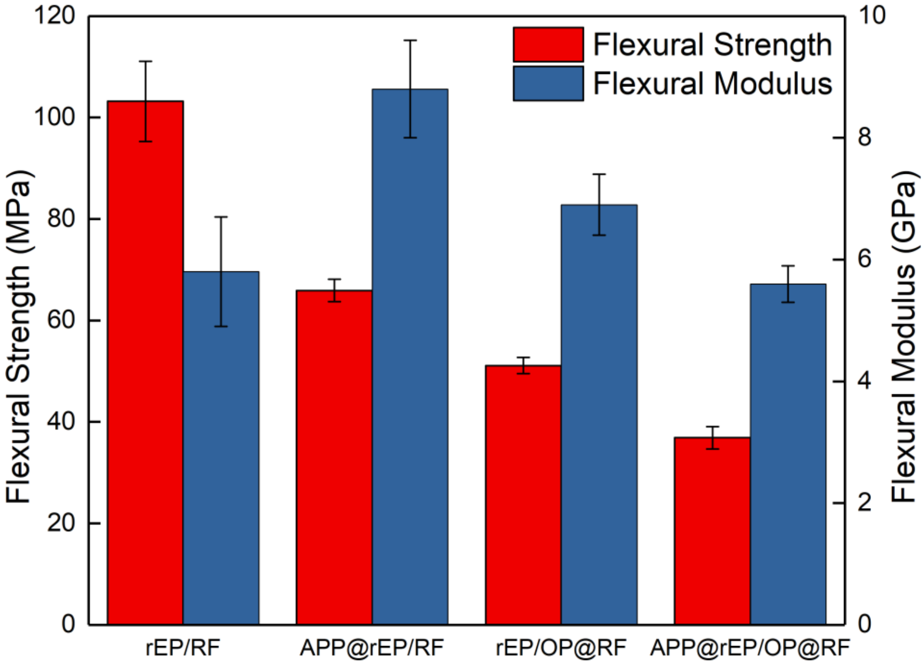


Figure. 2-10 Flexural properties of four groups of composites

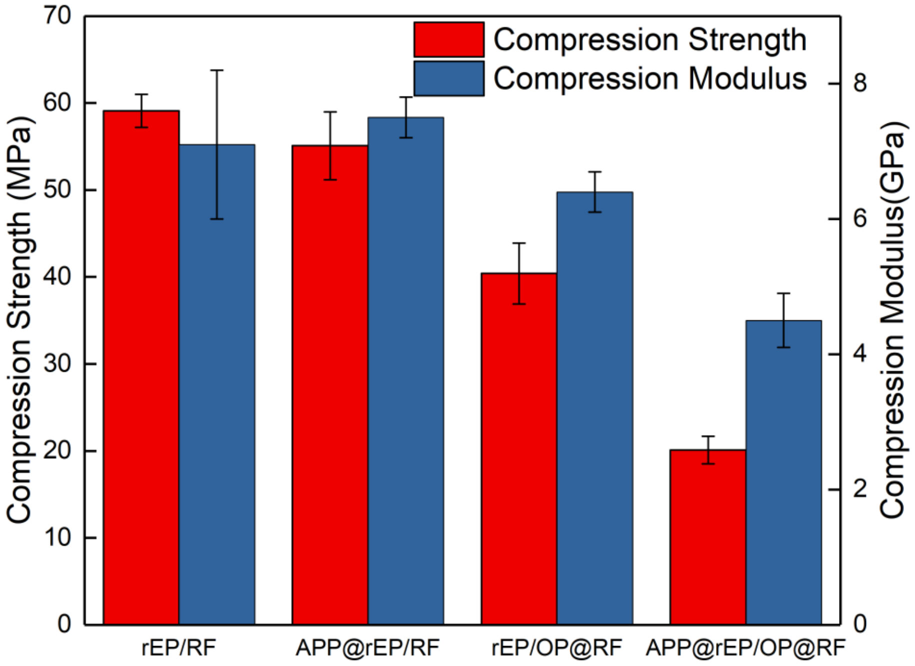


Figure. 2-11 Compression properties of four groups of composites

Table. 2-4 Mechanical properties of composites

Composites	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Compressive Strength (MPa)	Compressive Modulus (GPa)
rEP/RF	86.5±3.4	7.5±0.2	103.2±7.9	5.8±0.9	59.1±1.9	7.1±1.1
APP@rEP/RF	31.8±0.5	10.5±0.2	65.9±2.2	8.8±0.8	55.1±3.9	7.5±0.3
rEP/OP@RF	25.8±0.7	6.7±0.2	51.1±1.6	6.9±0.5	40.4±3.5	6.4±0.3
APP@rEP/ OP@RF	18.6±1.3	4.7±0.3	36.9±2.2	5.6±0.3	20.1±1.6	4.5±0.4

2.4.6 Vertical burning and LOI test

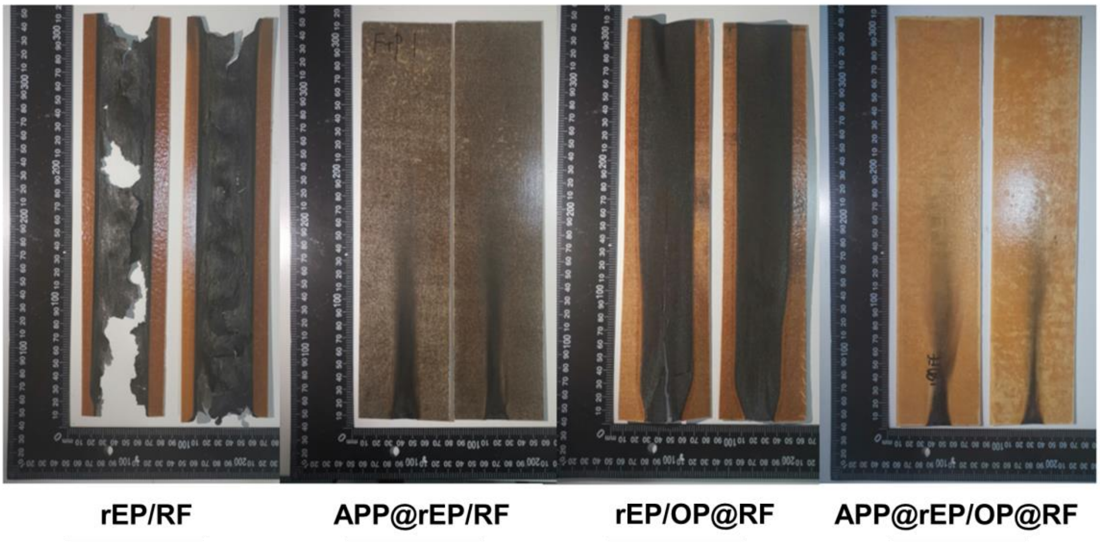


Figure. 2-12 Images of four groups composite after vertical burning test

Table. 2-5 Results of LOI and vertical burning tests of rEP, APP@rEP, RF, OP@RF and four groups of composites

Samples	LOI (%)	Burn length (mm)	Burn time (s)	Drip (Yes or No)
rEP	21.4	305 (All burn)	>180	Yes
APP@rEP	22.8	120	33	No
RF	19.8	305 (All burn)	45	No
OP@RF	40.0	90	<1	No
rEP/RF	25.0	305 (All burn)	153	No
APP@rEP/RF	29.6	140	8	No
rEP/OP@RF	28.8	305 (All burn)	78	No
APP@rEP/OP@RF	33.2	120	<1	No

The LOI and vertical burning tests for rEP, APP@rEP, RF, OP@RF and four groups of composites were carried out to investigate the flammability of composites, the results were summarized in Table. 2-5. The images of composite samples after vertical combustion were displayed in Figure. 2-12.

In the vertical burning test, rEP and RF showed complete combustion due to the intrinsically high flammability of epoxy resin and natural fibre. It was worth noting that the rEP sample showed serious dripping behavior during burning while rEP/RF exhibited un-dripping property. This phenomenon could be ascribed to the influence of lignin in natural fibre because lignin acted as a charring agent in the combustion process and reduced the generation of melt drip [173]. In terms of fabric reinforced resin composites, there was no dripping behavior for all composite samples during combustion. The rEP/RF and rEP/OP@RF were all burnt out and showed no self-extinguish effect. Compared the rEP/RF with rEP/OP@RF samples after burning, some continuous char structure remained for rEP/OP@RF sample and the continuous burning time of rEP/OP@RF was much lower than rEP/RF, the increased char generation and decreased burning time of rEP/OP@RF composite verified the char effect of FR treatment to RF. However, the rEP/OP@RF composite did not possess self-extinguishing property. The FR treatment to RF alone was not enough to change the flammability of resin-rich area. APP@rEP/RF and APP@rEP/OP@RF composites exhibited favorable auto-extinguished property, the burn length were 140 and 120 mm, respectively. The burn time of APP@rEP/OP@RF composite was less than 1 second, which was much lower than the other composites, which verified the excellent inflammability of APP@rEP/OP@RF composite.

With regard to LOI results, the addition of APP into rEP improved LOI value from 21.4% for rEP to 22.8% for APP@rEP. At the same time, OP@RF composite obtained 40.0% in comparison with 19.8% of RF, which implied the effectiveness of the OP FR additive. Typically, the composite with LOI value higher than 28% can be identified as materials with promising inflammability. APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF composites possessed increased LOI value of 29.6%, 28.8% and 33.2% respectively compared with 25.0% of rEP/RF. The LOI value of APP@rEP/OP@RF was increased by 8.2% compared to that of rEP/RF, which proved that the combination of two FR treatments manifested a combined effect and effectively improved the inflammability of composite.

2.4.7 Cone calorimeter test of composites

The cone calorimeter test is an effective lab-scale method to evaluate the real-world fire safety behavior of composite. The curves of heat release rate (HRR), total heat release (THR) and sample mass variation as a function of time during the test were profiled in Figure. 2-13, some key results include peak heat release rate (PHRR) and time to ignition (TTI) were listed in Table. 2-6. The TTI of rEP/RF, APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF composite were 35, 33, 24 and 40 s, respectively. TTI of APP@rEP/RF composite was 2 s lower versus rEP+RF composite while TTI of rEP/OP@RF composite was 11 s lower than rEP/RF composite, the decrease of TTI corresponded with thermal degradation results in TGA test due to the influence of FR additives. In terms of APP@rEP/OP@RF composite, the TTI was prolonged by 5 s compared with rEP/RF composite, which implied the improved inflammability as well as the combined effect of APP@rEP with OP@RF.

The PHRR value of APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF composites were decreased by 60%, 60% and 79% respectively in contrast to the rEP/RF composite. While there were separately 30%, 47% and 57% reduction of HRR value for APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF composites vs. rEP/RF composite. The THR value for APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF composites were also dropped from 29.2 MJ/m^2 for rEP/RF composite to 22.5, 17.5 and 14.2 MJ/m^2, respectively. The significantly reduced PHRR, HRR and THR value of composites verified that both rEP treatment and RF treatment could effectively reduce the heat releasing during the burning and improve the fire safety of composites. Though the rEP/OP@RF composite still showed ignitability in the vertical burning test, it could be observed that the heat releasing of rEP/OP@RF composite was significantly declined versus rEP/RF composite. The sample mass curve as a function of time was relevant to the char formation for composites, the residual char mass of APP@rEP/OP@RF was 31.2%, much higher than that of rEP/RF composite, the thicker char layer acted as a barrier to protect the rEP matrix and restrained the propagation of fire [167].

The combination of two FR treatments showed significantly effectiveness to reduce heat generation during combustion, which implied combined effect of two FR additives. The increased residual char value was attributed to the char effect of the phosphorus-containing group of APP and OP. The P-containing group can generate small particle derivatives such as phosphoric acid, which promotes char formation in the solid phase by dehydration reaction with the hydroxyl group in matrix or fabric[174, 175].

Table. 2-6 Cone calorimeter test results of four groups of composites

Composite	TTI (s)	PHRR (kW/m^2)	HRR(kW/m^2)	THR(MJ/m^2)	Char(%)
rEP/RF	35	862	151	29.2	1.7
APP@rEP/RF	33	345	106	22.5	15.1
rEP/OP@RF	24	342	80	17.5	10.8
APP@rEP/OP@RF	40	178	65	14.2	31.2

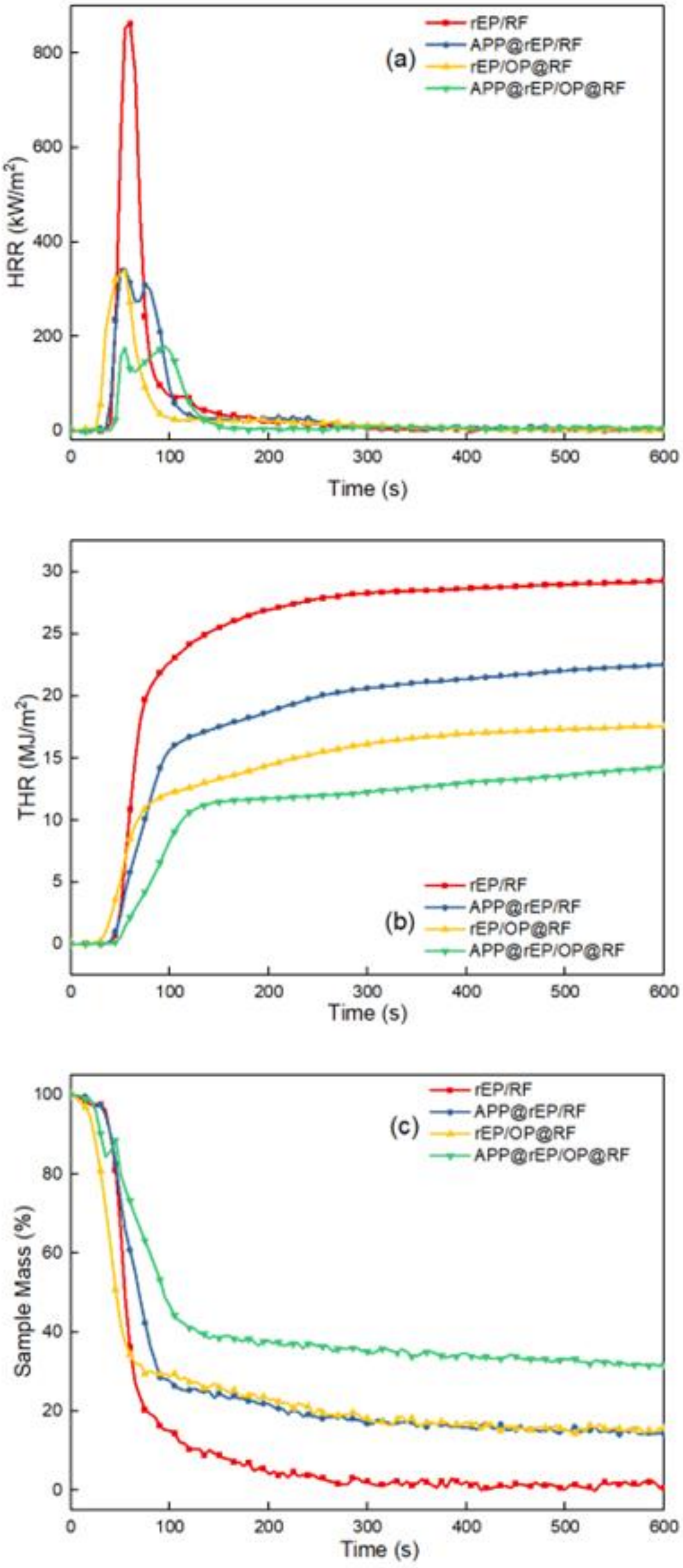

(a)
rEP/RF
APP@rEP/RF
rEP/OP@RF
APP@rEP/OP@RF
HRR (kW/m²)
0
200
400
600
800
Time (s)
0
100
200
300
400
500
600
(b)
THR (MJ/m²)
0
5
10
15
20
25
30
(c)
Sample Mass (%)
0
20
40
60
80
100

Figure. 2-13 Data from cone calorimeter test of four groups of composites: (a) HRR result (b) THR result (c) Sample mass result

2.4.8 Char residue structure

The digital images of composite samples before and after combustion were exhibited in Figure. 2-14 and the microscope images of residual char after burning were shown as Figure. 2-15. As for rEP/RF composite, the flammability of constituents resulted in minimal retaining char in comparison to the other three groups, the residual char was fragile white powder with a network-like structure similar to RF, the different color of residual char of rEP/RF was caused by fully decomposition and pyrolysis of the resin and there was no dense and solid char formed after combustion [176]. The residual char of APP@rEP/RF composite exhibited mineral-like and continuous char structure with some crack while rEP/OP@RF composite obtained residual char with carbonized network structure like fabric. The increased residual char mass verified the char formation effect of OP and APP FR additives. As for APP@rEP/OP@RF composite, the morphology of char seemed to be the combination of APP@rEP/RF and APP@rEP/OP@RF structures. The charring surface was more compact and smoother, which implied a more effective protective char layer effect [177].

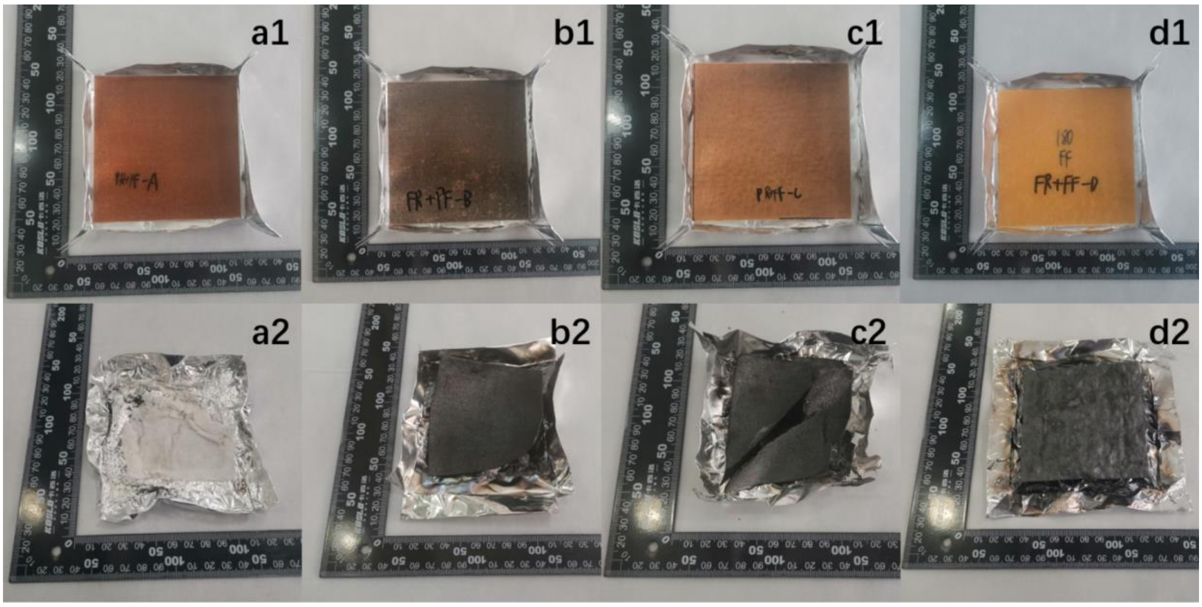


Figure. 2-14 Digital images of composite samples and residue char after combustion, composite samples: (a1) rEP/RF (b1) APP@rEP/RF (c1) rEP/OP@RF (d1) APP@rEP/OP@RF; Residual char: (a2) rEP/RF (b2) APP@rEP/RF (c2) rEP/OP@RF (d2) APP@rEP/OP@RF

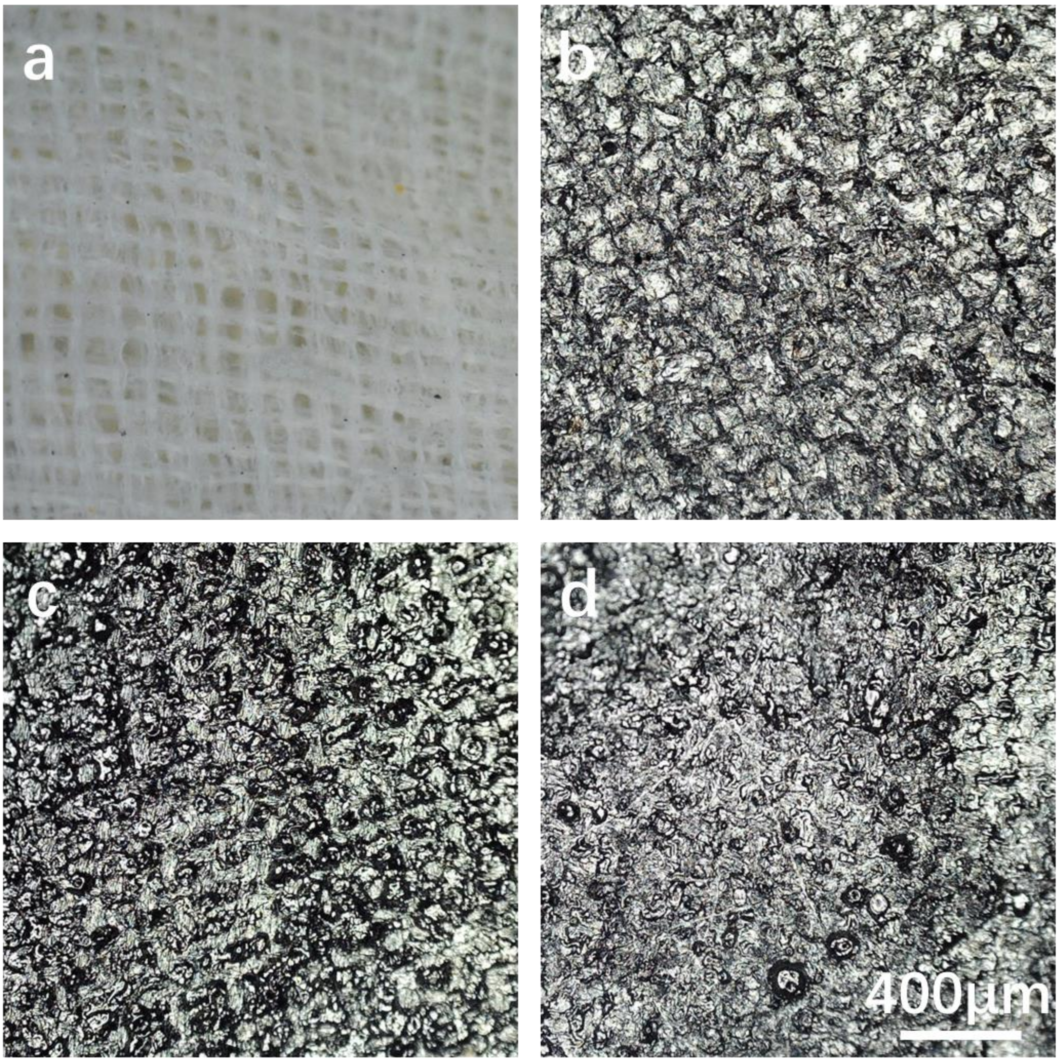


Figure. 2-15 The microscope images of composites collected after cone calorimeter test: (a) rEP/RF (b) APP@rEP/RF (c) rEP/OP@RF (d) APP@rEP/OP@RF

2.5 Fire retardant mechanism

The flame retardant mechanism of OP@RF and APP@rEP was displayed as Figure. 2-16. In terms of composite with APP@rEP matrix, APP in resin possessed three FR mechanisms: (1) APP generated PO• and HPO• radicals in gas phase during combustion, which captured high active H• and OH• radicals thus acting a scavenging effect to reduce the fire intensity during combustion. (2) The pyrolysis of

APP released inert gas such as H_2O and NH_3, which had a dilution effect and reduced the concentration of combustible compounds in the gas phase. (3) Phosphorus-containing group promoted polyaromatic reaction of rosin-sourced resin and formed protective char layer which hindered the heat and substrate interchange in condensed phase [135, 178]. Regarding OP@RF reinforced composite, rEP/OP@RF and APP@rEP/OP@RF, OP coated ramie fibre thermally decomposed before resin due to the dehydration reaction between phosphoric-containing group and cellulose. The TGA results also proved the earlier decomposition of OP@RF compared with rEP matrix. The dehydrated fabric showed partial carbonization that possessed char effect, thus improving inflammability of composite. Furthermore, the carbonized RF formed a supporting network framework for residual char, which restrained chains movement and release of volatile segment [160].

A tentative explanation for the FR mechanism for composites was displayed in Figure. 2-17. For rEP/RF composite, because both rEP and RF were highly flammable materials, the composites underwent drastic combustion once being ignited and little char was remained. As for APP@rEP/RF composite, the APP could effectively improve the inflammability of rEP matrix and formed protective char layer on composite burning surface. In case of rEP/OP@RF composite, OP catalyzed the dehydration and carbonatation of cellulose of RF and formed char layer on fabric surface, but the resin-rich area was still flammable and rEP/OP@RF composite did not pass vertical burning test, proved that only fabric treatment was not enough to achieved acceptable flame retardancy. For APP@rEP/OP@RF composite, the APP@rEP matrix and OP@RF reinforcement achieved a dual effect in burning: OP on RF led to the earlier decomposition of fabric than resin matrix, the dehydration reaction between OP and fabric promoted the formation of layered char structure. Then the resin-rich area between the carbonaceous fabric decomposed, and the incorporation of APP reduced the flammability of the resin due to the aforementioned mechanism. The inflammability and decreased heat releasing in cone calorimeter test for APP@rEP/OP@RF composite was excellent.

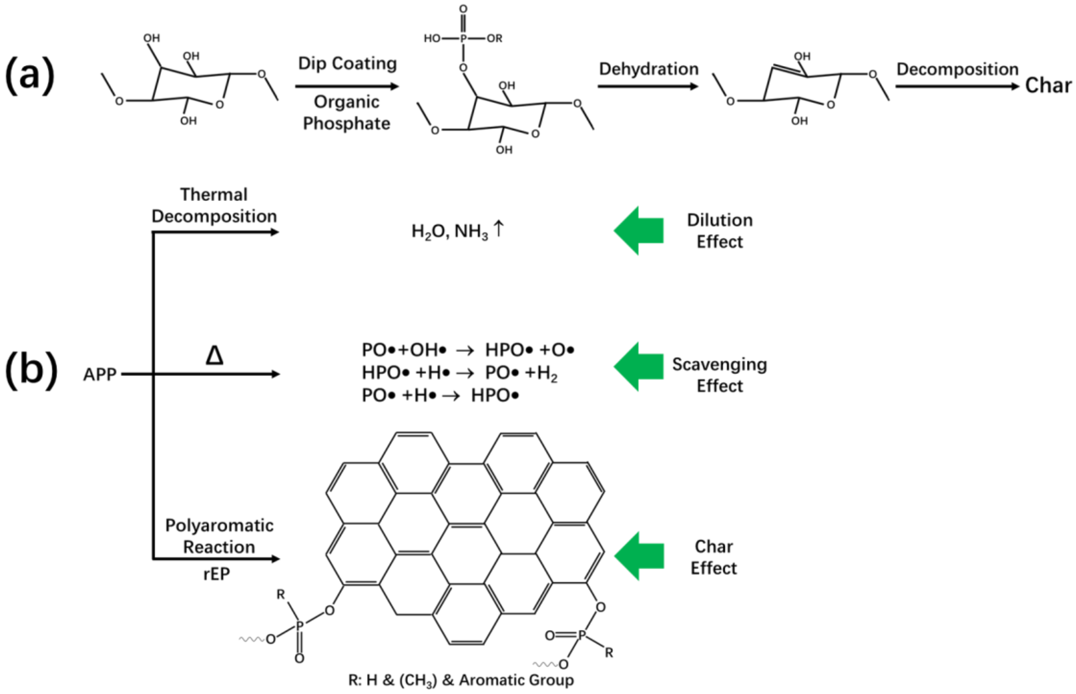


Figure. 2-16 Possible thermal degradation mechanism for (a) OP@RF (b) APP@rEP [162, 172]

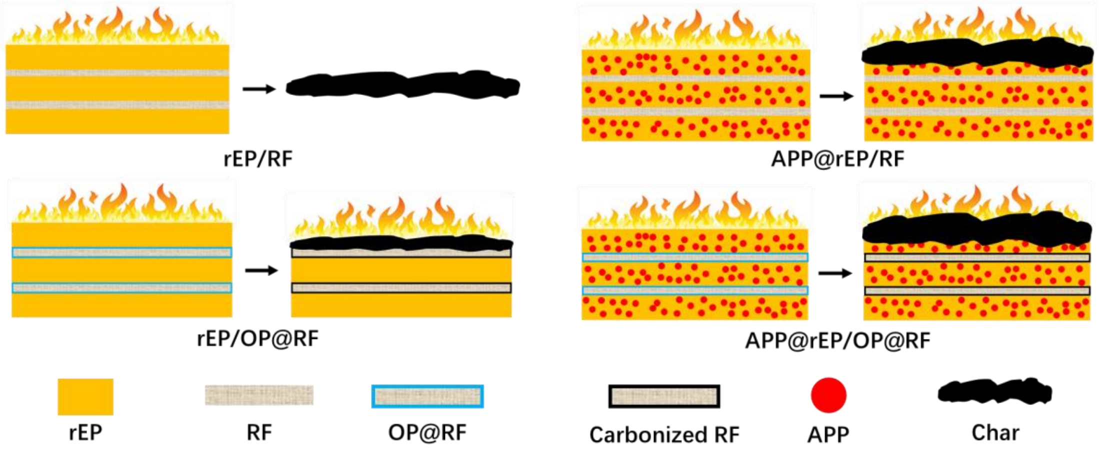


Figure. 2-17 Schematic diagram of flame retardant mode of composites

2.6 Conclusion

The increasing concern about the environment has facilitated the development and application of natural-sourced composites in recent years. To develop green composite as well as improve the fire safety performance of composite, in this work, RF reinforced rosin-sourced epoxy resin composites were fabricated by prepreg preparation then followed by vacuum bag assisted compression molding process. To solve the high flammability of RF and rEP, the fabric and resin were treated by OP and APP respectively. By the combination of rEP/APP@rEP with RF/OP@RF, the influence of two FR treatments on composite performance was evaluated. The prepared composite contributes a new perspective for fully-green material.

In the vertical burning test, in contrast to the high flammability of rEP/RF composite, APP@rEP/RF and APP@rEP/OP@RF composites achieved high inflammability. As for the LOI test, the LOI value of APP@rEP/OP@RF composite reached 33.2%, much higher than 25.0%, 29.6% and 28.8% of rEP/RF, APP@rEP/RF, rEP/OP@RF composites, respectively. In terms of the cone calorimeter test, in comparison with the rEP/RF composite, the PHRR and HRR of APP@rEP/RF, rEP/OP@RF, APP@rEP/OP@RF composites were reduced by 60%, 60%, 79% and 30%, 47%, 57% respectively. The significantly improved fire safety performance verified the combined effect that simultaneously treated fabric reinforcement and resin matrix with OP or APP respectively.

However, TGA and DMA results indicated that the addition of APP into rEP, as well as OP on RF, reduced the thermal stability of the composites. Regarding the mechanical performance of composites, the tensile, flexural and compressive properties were reduced by FR treatments for matrix and fabric. The hydrophilicity of P-containing FR additives, the weak interaction between resin matrix and OP@RF, the dehydration reaction between OP and hydroxyl group on ramie at high temperature limited the mechanical performance of the composite.

The balance between fire safety and mechanical performance of the composite is a crucial problem for flame retardant materials. This preliminary study has drawn some significant conclusions: Firstly, the combination of fabric FR treatment with resin FR treatment showed the dual effect to furtherly improve the fire safety performance of the composite. Secondly, the weak compatibility between hydrophilic FR additives with resin matrix and catalytic effect of P-containing agent on ramie dehydration reduced the mechanical behavior of composite. In future work, it is significant to search for FR additives with higher compatibility and thermal stability.

Chapter 3. Influence of Different Flame Retardant Additives on Ramie Fibre Reinforced Rosin-sourced Epoxy Composite

3.1 Introduction

In chapter 2, the fully-green rEP/RF composites were fabricated by compression molding process. To improve the flame retardancy of the composite, the RF was modified by OP while the rEP was modified by APP, and the mechanical and FR properties of rEP/RF, APP@rEP/RF, rEP/OP@RF and APP@rEP/OP@RF composites were characterized. It can be found that both FR modification to RF and FR modification to rEP improve the flame retardancy of the composite, and APP@rEP/OP@RF showed excellent inflammability, which implied the combined effect of two FR modification.

On the basis of work in chapter 2, this chapter aimed to furtherly investigate the combined effect of FR modified fabric with FR modified matrix in fibre reinforced composite system. In this work, the OP@RF was still applied as reinforcement, while different FR additives were applied to modify the rEP as alternative to APP in chapter 2. Except investigating the influence of FR additive and searching for novel FR additive, the combined effects between FR additives are crucial branch for fire safety composite. On the whole, the flame retardant mechanism can be roughly divided into four categories: (1) Endothermic reaction, the pyrolysis reaction of some FR additives are endothermic which can absorb large amount of heat in combustion, aluminum trihydride (ATH) [129] is a representative one. (2) Radical scavenger effect, the halogenated FR additive releases halogen radical which can capture active radical such as •OH or •H during burning process thus reduce the fire intensity [104]. (3) Dilution effect, the combustion of FR additives such as ammonium polyphosphate release inert gas such as H_2O or NH_3 which could dilute the oxygen concentration in fire propagation. (4) Char effect, some FR additives such as phosphorus-containing compound can catalyze the generation of protective char layer, the char layer can hinder the transfer of substance and oxygen during the burning [115]. The combination of more than one FR additives with different FR mechanism may lead to extra improvement to fire safety performance of material, this effect is called combined effect. Numerous works are established to study the FR combined effect, a great deal FR additives couples are proved to show combined effect, for instance, zinc borate (ZnB) and APP [179], expandable graphite (EG) and hypophosphite [128], ATH and EG [129], ZnB and magnesium hydroxide [180]. In this work, four conventional FR additives (APP, ATH, ZnB and EG) were chosen to investigate their combined effect with OP@RF.

Based on the aforementioned information, this work applied RF as reinforcement and rosin-sourced epoxy resin as matrix to fabricate natural fabric reinforced bio-sourced epoxy composite. To improve the FR performance of composite and study combined effect between FR additives, RF was treated by OP whereas rEP resin was modified by four different types of FR additives, APP, ATH, ZnB and EG, respectively.

3.2 Materials & Methods

3.2.1 Materials

Ramie fabric was bought from Huangshengdongting Co., Ltd (Hunan, China), the areal density of RF is 132 g/m^2. The FR modified RF was provided by Tiangong University, a commercial and water soluble FR additive (organic phosphate, the chemical structure is confidential) was applied to modify the RF via dip coating process and the weight gain of OP on fabric was 32%, the OP treated RF was designated as OP@RF. Rosin-sourced resin (type AGMP-3600, the curing temperature is at 130 ℃, relevant information of the resin can be referred to another work [90]) was provided by Aviation Composite Co., Ltd (Beijing, China). Flame retardant additives including APP (type HT-208), ATH (type HT-205) and ZnB (type HT-207) were purchased from Taixing New Material Co. Ltd., (Shandong, China).

Flame retardant expandable graphite (type EG-150, 150 meshes) was provided by Qingdao Yanhai Carbon Materials Co. Ltd., (Shandong, China).

3.2.2 Preparation of rEP/RF prepreg

Owning to the high viscosity of rEP system, the processibility of the resin is not ideal and it was difficult to achieve homogeneous dispersion of FR additives in rEP resin. To cope with high viscosity of rEP resin system, a solution mixing method followed by hand lay-up process was applied to prepare rEP/RF prepreg.

As for solution mixing method, acetone was employed to dissolve the rEP resin. The rEP was weighed and added into a glass beaker, appropriate amount of acetone was added to the beaker. Seal the beaker with plastic wrap and after some sonication and stirring, the rEP/acetone solution was prepared. The APP, ATH, ZnB and EG powder were grinded and dried in a vacuum oven for 80 °C/6h. The FR additives were respectively slowly added into the previous rEP/acetone solution and stirred 30 minutes to attain uniform suspension. The ratio of FR additive: rEP: acetone was 15:85:200 by weight so that solid content of resin solution was 33.3%.

In the case of hand lay-up process, OP@RF was cut to 300*300 mm^2 size, about 35.1 g FR resin solution was evenly painted on each OP@RF by hairbrush. After painting, the infiltrated fabric was put into fume hood at room temperature for 24 h, then dried in vacuum oven for 60℃/1h to remove residual acetone and the rEP/RF prepregs were prepared. According to the types of FR additives, six groups of prepregs were prepared via similar process and designated as rEP/RF (control group), rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF prepregs.

3.2.3 Fabrication process of FR composite by vacuum bag assisted hot-press process

The composite samples were fabricated by hot-press molding assisted by vacuum bag process, the arrange of vacuum bag was showed as Figure. 3-1. Ten plies of 300*300 mm^2 rEP/RF prepregs were stacked on the bottom mold (350*350 mm^2), several stop blocks with 2 mm were placed next the boundary of prepregs to control the final thickness of composite samples. The fabrication parameters of composite curing process was displayed as Figure. 3-2. Before manufacturing, the laminated prepregs were degassed at room temperature. In first stage, the prepregs were pre-cured for 90℃/30 min with vacuum of pump and then followed by 130 ℃/2 h curing process with 4 MPa pressure by hot-press machine. In the last stage, the sample was cooled to room temperature with 4 MPa pressure to avoid deformation of samples. The rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites were fabricated by same process with corresponded prepregs.

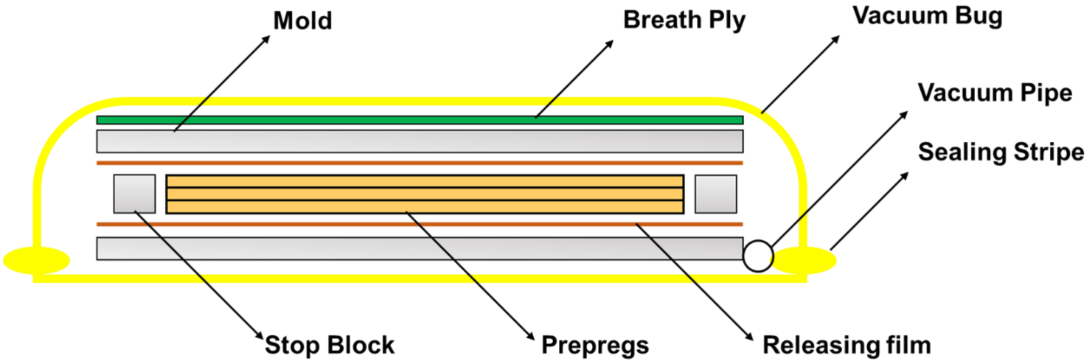


Figure. 3-1 Sketch map of vacuum bag for fabrication process

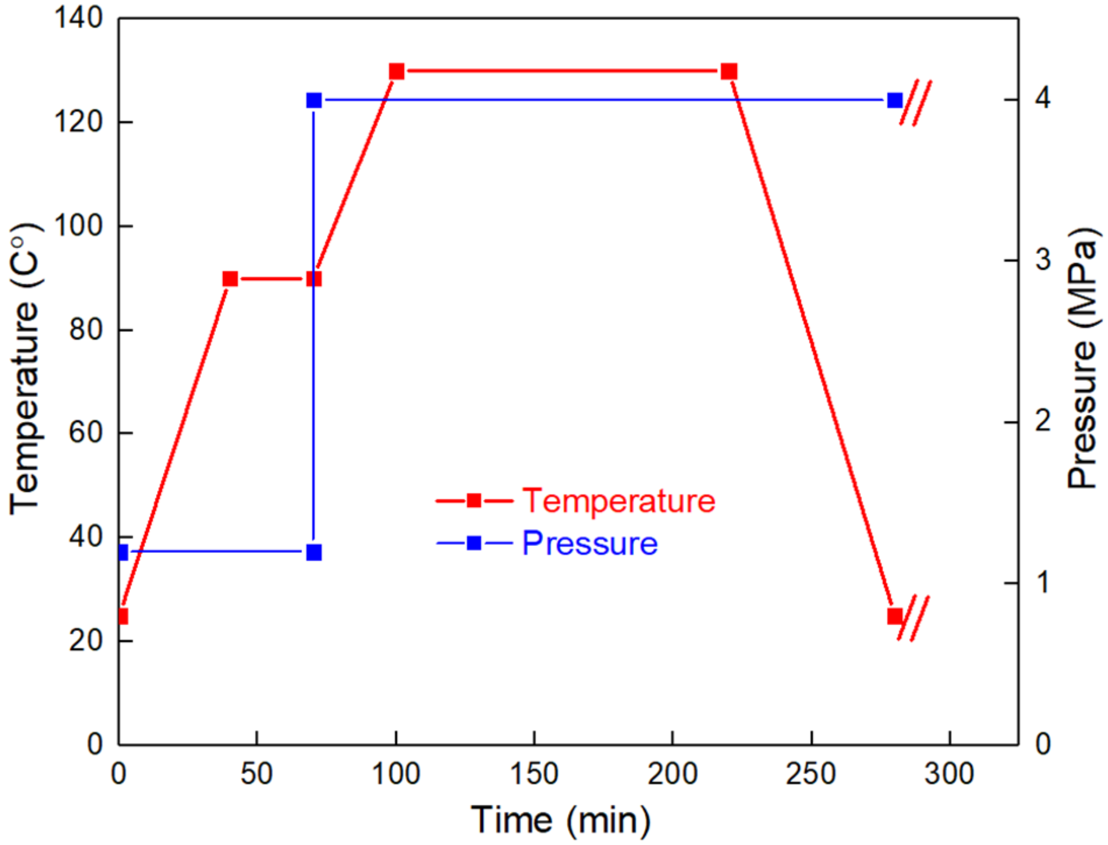


Figure. 3-2 Curing parameters for rosin-sourced epoxy resin system composite

Supposed that there is no defect or void in composite, the composite constituents can be calculated by:

$$V_{RF} = \frac{n * A_{RF} * S}{\rho_{RF}} * \frac{1}{S * h} * 100\% \ (1)$$

$$V_{OP} = V_{RF} * \frac{\rho_{RF}}{\rho_{OP}} * w_{OP@RF} \ (2)$$

$$V_{rEP} = \frac{\frac{1-w_{FRa}}{\rho_{rEP}}}{\frac{1-w_{FRa}}{\rho_{rEP}} + \frac{w_{FRa}}{\rho_{FRa}}} (1 - V_{RF} - V_{OP}) \ (3)$$

$$V_{FRa} = \frac{\frac{w_{FRa}}{\rho_{FRa}}}{\frac{1-w_{FRa}}{\rho_{rEP}} + \frac{w_{FRa}}{\rho_{FRa}}} (1 - V_{RF} - V_{OP}) \ (4)$$

Where V_{RF}, V_{OP}, V_{rEP} and V_{FRa} are the volume fraction of RF, OP, rEP and FR additives (APP, ATH, ZnB or EG mixed with rEP) in composites, respectively. ρ_{RF}, ρ_{OP}, ρ_{rEP}, ρ_{FRa} are the density of RF, OP, rEP and FR additives (ρ_{APP}=1.9, ρ_{ATH}=2.42, ρ_{ZnB}=2.44 and ρ_{EG}=2.4 g/cm^3), respectively. A_{RF} is areal density of pristine RF and the value is 132 g/m^2. $w_{OP@RF}$ is the weight gain of OP on the RF and the value is 32%. w_{FRa} is the weight fraction of FR additives dispersed in rEP resin and the value is 15%. n is the number of stacked prepregs and here n=10. S is the area of sample, h is the sample thickness. The specific formulations for control, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites were calculated and listed in Table. 3-1.

Table. 3-1 Formula for control, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites

Composite	**rEP**	**FR additives**[1]	**RF**	**OP**	**Thickness (mm)**
	By volume (%)				
Control[2]	61.7	0	38.3	0	2.01
rEP/OP@RF	48.3	0	38.3	13.4	2.01
APP@rEP/OP@RF	44.4	4.9	37.6	13.1	2.05
ATH@rEP/OP@RF	46.2	4.0	36.9	12.9	2.09
ZnB@rEP/OP@RF	46.9	4.1	36.3	12.7	2.12
EG@rEP/OP@RF	47.1	4.6	35.8	12.5	2.15

1 Each FR additives in rEP is with a weight fraction of 15%, the density of APP, ATH, ZnB and EG are 1.9, 2.42, 2.44 and 2.4 g/cm^3, respectively.

2 Composite composed of pristine rEP and RF (rEP/RF) was designated as control group.

3.3 Characterization

Thermogravimetry analysis (TGA) was conducted by TGA Q600 instrument (TA instrument Co. Ltd, DE, USA) to investigate the thermal stability of the composite samples. The heating rate was 10 ℃/min, temperature range was 30-800 ℃, the atmosphere was nitrogen with a flow rate of 50 mL/min, about 15~20 mg of sample was tested for each test.

The flexural properties of samples were tested by an electronic universal testing machine (MTS Systems Corporation, Shenzhen, China) according to ASTM D-790-03 standard, the crosshead speed, sample dimension and span were 1 mm/min, 84*12.5*2 mm^3 and 32 mm, respectively. The tensile tests were carried out using same machine as flexural test based on ASTM D-3039 standard, the sample size was 250*15*2 mm^3 and the crosshead speed was 1 mm/min. The span during test was 150 mm due to there were 50 mm long end tabs adhered to two ends of samples. Five samples were tested for each formulation of composite.

The UL-94 vertical burning test was carried up using chamber burner instrument (TESTech Instrument Technologies Co., Ltd, Jiangsu, China) based on ISO-1210:1992 standard. The sample size was 130*13*2 mm^3, the ignition time was 10 s while the flame height was 20 mm.

The limiting oxygen index (LOI) test was performed on an instrument (TESTech Instrument Technologies Co., Ltd, Jiangsu, China) with a sample dimension of 80*10*2 mm^3. The applied standard was ISO-4582-2:1999.

Cone calorimeter test (CCT) was measured with cone calorimeter 6810 (Suzhou Vouch Testing Technology Co. Ltd., Jiangsu, China) according to ISO-5660 standard, the sample size was 100*100*2 mm^3, the heat flux was set to 50 kW/m^2.

The surface morphology images of the residual char after cone calorimeter test were observed on scanning electron microscope (SEM) (ZEISS IGMA/VF, Oberkochen, Germany).

3.4 Results and Discussion

3.4.1 Thermal stability of composites

Figure. 3-3 showed the TG and DTG curves of all composites as a function of temperature from 30 °C to 800 °C, the relevant data was summarized in Table. 3-2. The $T_{5\%}$ was the temperature at which the loss wight of sample was 5% and the value of $T_{5\%}$ can denote the onset decomposition temperature of sample. T_{max1} and T_{max2} were corresponded to the temperature with maximum degradation rate, T_{max1} was relevant to decomposition of OP@RF [181] whereas T_{max2} matched the decomposition of rEP resin [182]. The value of char at 800 °C implied the degree of carbonization of the composites after thermal decomposition.

Compared the control group with other composites reinforced by OP@RF, it can be found that the incorporation of OP onto RF significantly reduce $T_{5\%}$, T_{max1} and T_{max2} of the composites, which implied the decrease of thermal stability. Meanwhile, the mass weight of residual char at 800 ℃ for control group was much lower than that of rEP/OP@RF, the OP modification on RF effectively promoted the char formation of composites, this result was correlated with the dehydration reaction between OP and cellulose [162].

Compared rEP/OP@RF composite with other groups based on rEP modified by different FR additives, it can be observed that the addition of APP and EG decreased onset temperature ($T_{5\%}$) of composite while ATH and ZnB slightly increased the initial decomposition temperature. The decreased $T_{5\%}$ value of APP@rEP/OP@RF and EG@rEP/OP@RF composites were caused by low decomposition temperature of APP and EG. In terms of the variation of T_{max1}, the incorporation of ATH, ZnB and EG exhibited nearly no influence on decomposition behavior of OP@RF while the encompassing of APP decreased 28 ℃ of T_{max1}. This result implied that cellulose fibre would react with APP due to unstable P-O and P=O groups from decomposition of APP [181]. Whereas for T_{max2}, APP@rEP/OP@RF and EG@rEP/OP@RF composites showed reduced maximum degradation temperature. The T_{max2} value of ZnB@rEP/OP@RF composite was 17 ℃ higher than that of rEP/OP@RF composite due to water released by ZnB decomposition [179], the thermal stability of ATH@rEP/OP@RF composite was slightly increased compared with rEP/OP@RF composite for same reason. In terms of mass of residual char at 800 ℃, the incorporation of all FR additives led to higher mass residues than that of rEP/OP@RF composite, the FR modification to rEP showed moderate influence on char formation of composite. On the whole, for composite system composed of OP@RF and rEP modified by FR additives, the addition of APP and EG reduced thermal stability while ATH and ZnB improved thermal stability.

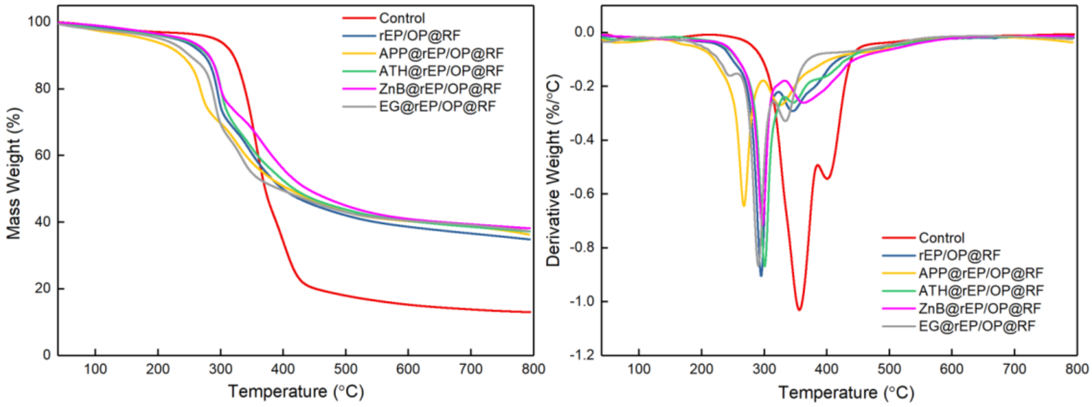


Figure. 3-3 (a) TG and (b) DTG curves of control, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites in N_2 atmosphere

Table. 3-2 TGA results of control, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites

Composite	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Char at 800°C (%)
Control	291.1	355.9	399.5	13.1
rEP/OP@RF	228.5	294.8	345.4	34.9
APP@rEP/OP@RF	179.8	267.3	325.4	36.3
ATH@rEP/OP@RF	234.4	300.5	346.1	37.2
ZnB@rEP/OP@RF	241.5	296.8	362.2	38.2
EG@rEP/OP@RF	204.9	290.2	333.5	37.4

3.4.2 Mechanical properties of composites

The results of flexural and tensile tests for all composites were shown as Figure. 3-4 and Figure. 3-5. Compared the mechanical performance of control group with other groups with OP@RF, the flexural and tensile properties of control groups were obviously higher than those of composites reinforced by OP@RF. The decreased mechanical performance was attributed to incompatibility between OP coating on fabric and rEP matrix due to the hydrophilicity of OP [183].

Except for control group, the flexural strength of APP@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites were reduced by 19.3%, 11.8% and 28.1% respectively compared with rEP/OP@RF composite meanwhile the flexural modulus also showed 9.8%, 29.5% and 41.0% decrease. In the case of ATH@rEP/OP@RF composite, the flexural strength and modulus was increased by 11.8% and 23.0% respectively in comparison to rEP/OP@RF composite, this result was due to the influence of metal hydroxide on load transfer and acceptable interface with matrix [184]. As for tensile performance, the tensile strength and modulus exhibited similar trends to flexural results. Compared with 39.2 MPa of rEP/OP@RF composite, APP@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites possessed lower tensile strength of 34.4, 37.1 and 26.8 MPa respectively while ATH@rEP/OP@RF composite had a higher tensile strength of 49.3 MPa. The slightly decreased flexural and tensile properties for composites based on OP@RF were relevant to dispersion and compatibility problems of FR additives with rEP matrix [185-187]. It can be speculated that the influence of OP modification on RF is more significant than the influence of mixing FR additives into resin matrix on mechanical performance of composites.

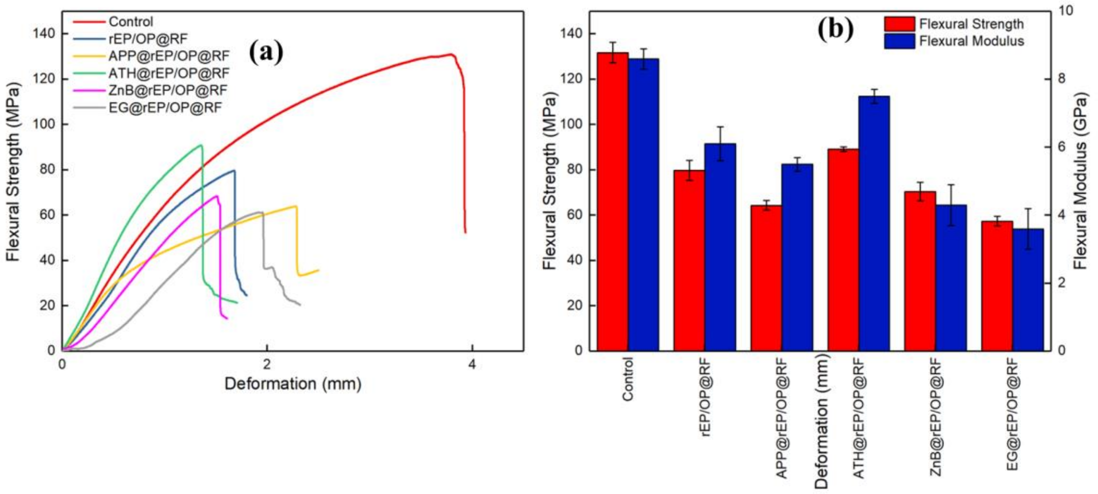


Figure. 3-4 (a) Flexural strength vs. deformation curves and (b) Flexural strength and modulus of control, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites

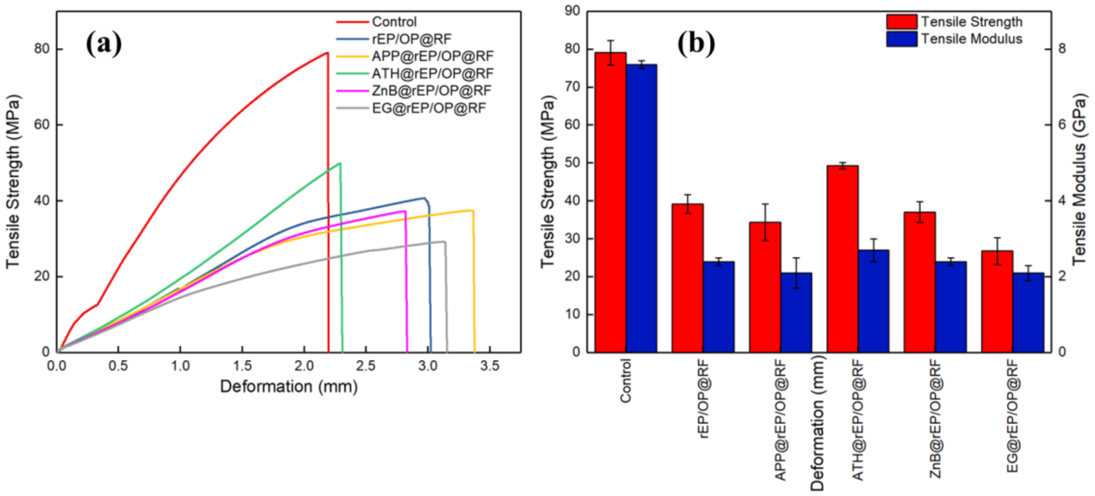


Figure. 3-5 (a) Tensile strength vs. deformation curves and (b) Tensile strength and modulus of control, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites

3.4.3 UL-94 and LOI tests of composites

The results of UL-94 vertical burning and LOI tests were summarized in Table. 3-3. In comparison to other composites reinforced by OP@RF, the control group possessed lower LOI value of 24.8% and no rating inflammability in UL-94 test, only for control group, there was melt drip of rEP during the combustion of sample as well. It can be inferred that single employment of OP@RF was not enough to achieve ideal flame retardancy for composite, but was effective to decrease generation of melt drip of polymer.

Compared the results of composites with OP@RF with each other, it was denoted that the addition of APP, ATH, ZnB and EGR all could increase the LOI value of composites with different extent. Normally, when LOI value of a material is between 21% to 28%, the material is defined as “slow burning”, whereas a material with LOI higher than 28% can be considered as “self-extinguishing”, which means the ignited material will extinguish itself after removing flame source [188]. The addition of ATH and ZnB increased the composite LOI value from 27.2% of rEP/OP@RF composite to 29.6% and 29.8% respectively, the moderate increase was caused by endothermic reaction of ATH and ZnB during burning [128, 179]. The LOI value for APP@rEP/OP@RF and EG@rEP/OP@RF composites were 35.0% and 41.5%, 7.8% and 14.3% higher than the LOI of rEP/OP@RF composite, which proved efficiency of APP and EG to improve the flame retardancy of composites.

UL-94 vertical burning test was used to evaluate the flammability and flame propagation speed of a material after being ignited. According to test standard, the samples were fixed in vertical position and ignited from bottom for two times (if the sample was self-extinguished after first time ignition), the duration of time after removing the ignitor was recorded as t_1 and t_2. All five groups of samples did not generate melt drip during the combustion. The flammability of rEP/OP@RF, ATH@rEP/OP@RF and ZnB@rEP/OP@RF composites were nearly same, all three groups of samples showed self-extinguishing in first time ignition but were burnt out in secondary ignition, this phenomenon probably could be explained by the different thermal stability of fabric and resin, FR fabric was carbonized to quench the combustion in first time ignition but resin rich area was still flammable and burnt out in secondary ignition. The APP@rEP/OP@RF and EG@rEP/OP@RF composites showed immediately self-quenching after removing the flame source, corresponding to V-0 category. The results from UL-94 and LOI tests proved that APP and EG were more effective FR additives than ATH and ZnB at same loading content.

On the basis of previous discussion, it can be conjectured that the FR modification to epoxy matrix was more effective than FR modification to fabric, though these two modifications showed combined effect to improve the fire safety performance of composite.

Table. 3-3 UL-94 vertical burning and LOI test results of control, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites

Composite	LOI (%)	UL-94			
		Burn length (mm)	t1/t2 (s)	Drip	Category
Control	24.8	Burn out	-/-	Yes	No rating
rEP/OP@RF	27.2	Burn out	3/-	No	No rating
APP@rEP/OP@RF	35.0	50	1/1	No	V-0
ATH@rEP/OP@RF	29.6	Burn out	3/-	No	No rating
ZnB@rEP/OP@RF	29.8	Burn out	2/-	No	No rating
EG@rEP/OP@RF	41.5	30	1/1	No	V-0

Denote: “-” means the sample was all burnt in test

3.4.4 Cone calorimeter test of composites

Cone calorimeter test, which is a lab-scale test applied to evaluate the fire safety performance of a material in real-world, was carried and the heat release rate (HRR), total heat release (THR), total some production (TSP) and residual mass weight versus time curves for composites were plotted as Figure. 3-6. More data include time to ignition (TTI) and peak heat release rate (PHRR) was summarized as Table. 3-4. Compared control group with rEP/OP@RF composite, the introduction of OP on fabric decreased TTI from 38 to 34 s, PHRR from 499.9 to 488.4 kW/m^2, HRR from 251.8 to 180.8 kW/m^2, THR from 64.3 to 42.4 MJ/m^2, TSP from 8.2 to 5.4 m^2 while increased residual mass from 8.9 to 14,1%. The introduction of FR modified RF effectively reduced the heat release and smoke generation of composite during burning, through the TTI and PHRR value kept nearly same, which implied the ignitability was not improved by OP@RF.

Except for the control group, The TTI of APP@rEP/OP@RF and EG@rEP/OP@RF composites were respectively 23 s and 14 s, decreased by 11 and

20 s compared to 34 s of rEP/OP@RF composite, the decreased TTI was attributed to the low decomposition temperature of APP and EG. The incorporation of ATH and ZnB slightly increased the TTI of composites. The results of TTI were corresponded to the results from TGA. The HRR, PHRR and THR of APP@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites were reduced by different extents compared with rEP/OP@RF composite. It was noteworthy that the PHRR, HRR and THR of EG@rEP/OP@RF composite was 71.4%, 46.6% and 18.9% lower than those of rEP/OP@RF composite. There were 42.7%, 21.1% and 16.7% reduction of PHRR, HRR and THR repectively for APP@rEP/OP@RF composite in comparison to rEP/OP@RF composite. In terms of TSP, EG@rEP/OP@RF composite displayed significantly lower TSP than rEP/OP@RF composite (reduced from 5.4 to 2.7 m^2). The residual char mass of APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF were 26.7%, 22.8%, 28.0 and 24.9% respectively, much higher than 14.1% of rEP/OP@RF composite. The increased char formation could restrain the heat and flammable substance transfer between gas and condensed phase in polymer combustion thus improving FR performance of materials [167]. However, the heat and smoke release did not significantly decline by addition of ATH into rEP resin, this result was ascribed to the lower weight content (15%) of ATH, some other work has observed similar result [129]. The combination of APP@rEP or EG@rEP with OP@RF visibly improved fire safety of composite, especially for composite incorporated with EG. The combined effect of simultaneous FR modification to both resin and matrix on improving inflammability of composite was verified.

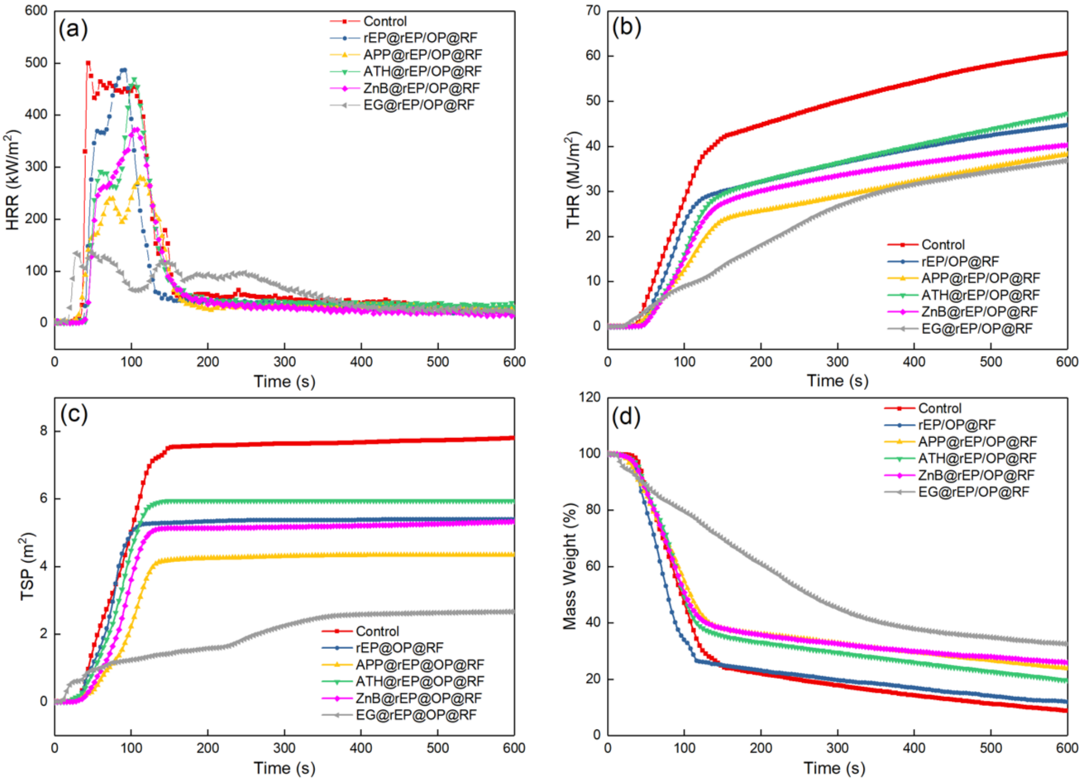


Figure. 3-6 The curves of (a) HRR (b)THR (c) TSP (d) Mass weight as a function of time of control, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites

Table. 3-4 Cone calorimeter data of control, rEP/OP@RF, APP@rEP/OP@RF, ATH@rEP/OP@RF, ZnB@rEP/OP@RF and EG@rEP/OP@RF composites

Composite	TTI (s)	PHRR (kW/m²)	HRR (kW/m²)	THR (MJ/m²)	TSP (m²)	Mass (%)
Control	38	499.9	251.8	64.3	8.2	8.9
rEP/OP@RF	34	488.4	180.8	42.4	5.4	14.1
APP@rEP/OP@RF	23	279.7	142.6	35.3	4.3	26.7
ATH@rEP/OP@RF	37	469.5	182.6	43.8	5.9	22.8
ZnB@rEP/OP@RF	35	374.6	169.9	38.4	5.3	28.0
EG@rEP/OP@RF	14	139.3	96.6	34.4	2.7	34.9

3.4.5 Char residue morphology

The digital images of residual char for all composites after CCT test were displayed as Figure. 3-7. The residual char of control group was with minimal thickness and possessed non-integral structure. The char for rEP/OP@RF composites was sheet-like char layer with visible cracks. The other four groups of residual char had higher of char yield, indistinct layers could be observed from the side view which corresponded to different layers of OP@RF. For ATH@rEP/OP@RF and ZnB@rEP/OP@RF composites, some white particles were observed on the char surface, the particles probably were corelated with product generated by ATH and ZnB after combustion. EG@rEP/OP@RF composite showed an expanded and loose residual char due to the strongly thermal expansion of EG during combustion.

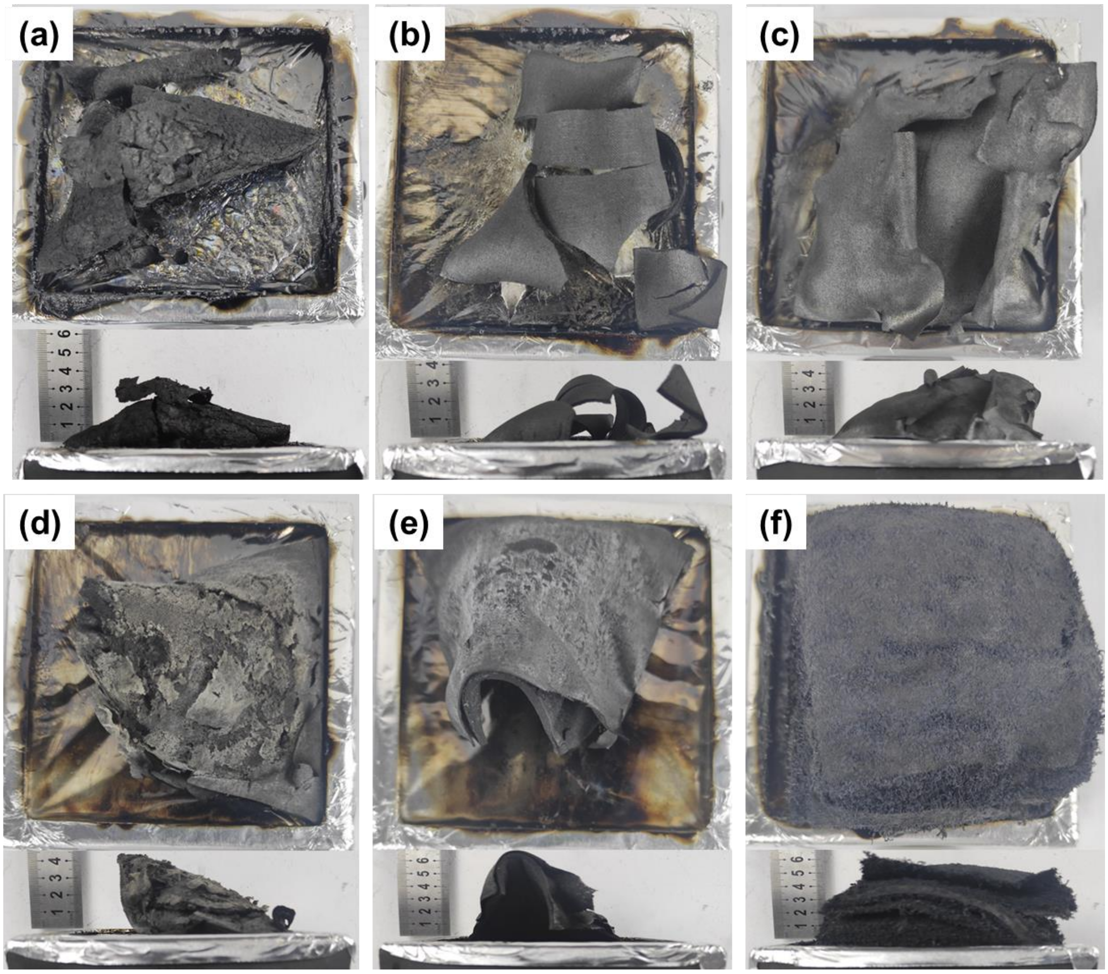


Figure. 3-7 The digital images of residual char of (a) control (b) rEP/OP@RF, (c) APP@rEP/OP@RF, (d) ATH@rEP/OP@RF, (e) ZnB@rEP/OP@RF and (f) EG@rEP/OP@RF composites after CCT test

SEM was applied to furtherly study the detailed microstructure of char residue. As shown in Figure. 3-8, it can be observed some holes on the surface of control and rEP/OP@RF group. Except for control and EG@rEP/OP@RF composite, the indistinct outline of carbonized fibre network was observed for other composites, which verified the carbonization effect of OP to RF. rEP/OP@RF composite possessed loose and porous char structure, which could not effectively restrain the flammable mass and energy exchange in combustion. In contrast to rEP/OP@RF composite, the char structure of APP@rEP/OP@RF was smoother and more compact with less pores on surface, the change of char structure verified the catalytic effect of APP on promoting the formation of char based on the generating of P-containing compound [189]. Regarding ATH@rEP/OP@RF and ZnB@rEP/OP@RF composites, it can be observed that some particles generated on char surface, which meant a portion of the ATH or ZnB did not integrate to char structure. An insulating and “worm-like” char layer generated from EG formed on the surface of EG@rEP/OP@RF composite after burning. The compact char of APP@rEP/OP@RF composite and insulating “worm-like” char of EG@rEP/OP@RF composite possessed protective char effect to improve FR performance of composites [190].

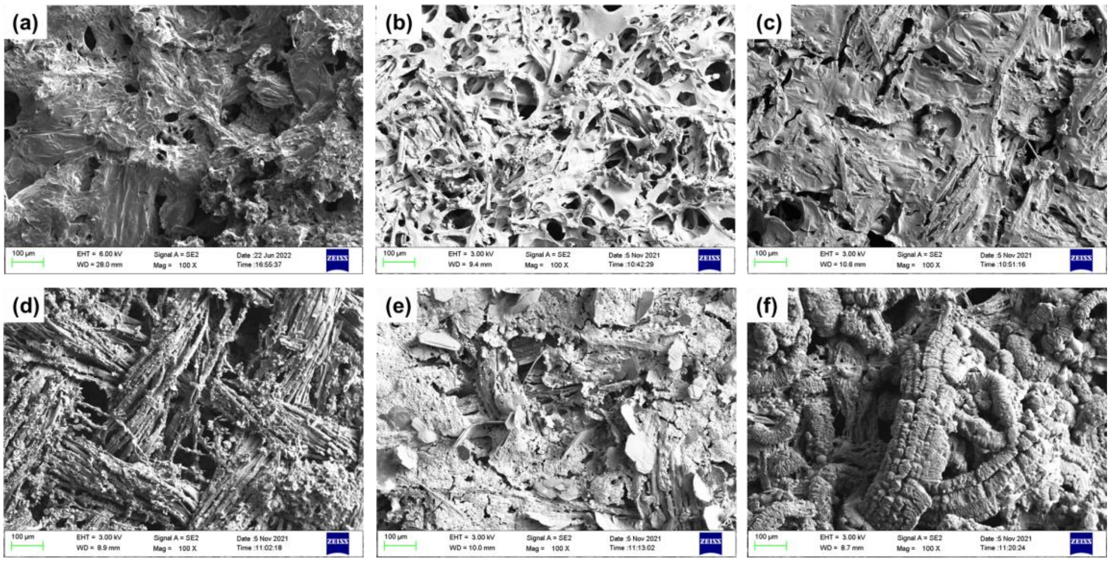


Figure. 3-8 SEM images of residual char of (a) control (b) rEP/OP@RF, (c) APP@rEP/OP@RF, (d) ATH@rEP/OP@RF, (e) ZnB@rEP/OP@RF and (f) EG@rEP/OP@RF composites after CCT

3.5 Flame retardant mechanism

To discuss FR mechanism of composites, at first the FR mechanism of each FR additives should be considered separately. For OP@RF reinforcement, the main FR mechanism was relevant to catalytic effect of OP to RF. The phosphate group can generate phosphoric acid or polyphosphoric acid in thermal decomposition, and the acidic group will promote the dehydration of cellulose and form protective char layer. The generated char layer acts as barrier to impede the transfer of flammable volatile and oxygen thus reduce the combustion intensity (As shown in Figure. 3-9) [191].

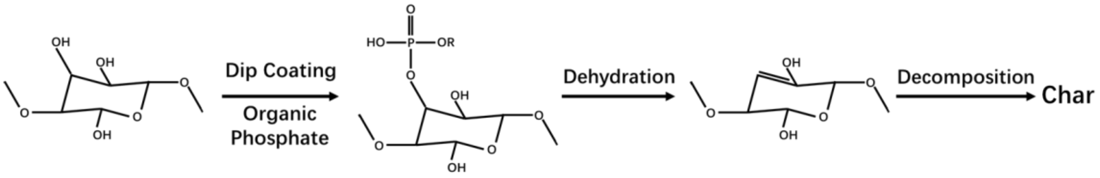


Figure. 3-9 The FR mechanism of OP@RF

However, according to results from UL-94 vertical burning and CCT test of control and rEP/OP@RF composites, OP@RF alone was not enough to achieve acceptable fire safety performance. The resin rich area in composite was still flammable. Accordingly, it was necessary to modify rEP with FR additives to furtherly improve the FR performance of composites.

For APP@rEP/OP@RF composite, the FR agent APP would decompose at about 267 ℃ (T_{max2} in TGA test, which is relevant to decomposition of APP@rEP) and yield ammonia and polyphosphoric acid (Equation (5)), ammonia plays a role in dilution effect while polyphosphoric acid promotes polymer carbonization and shows char barrier effect [179, 190]. Furthermore, in burning, APP generates P• and PO• radicals which can capture highly active radicals to reduce fire hazard [128].

$$n(NH_4PO_3) \rightarrow nNH_3 + [HPO_3]_n \quad (5)$$

Regarding ATH and ZnB FR additives, the endothermic decomposition (As Equation (6) and Equation (7) showed) of additives could reduce the heat releasing during combustion, the H_2O generated in dehydration reaction has dilution effect which reduces the concentration of flammable volatiles, the thermal stability of metal or boron oxide products also shows positive effect on inflammability of composite [129, 192].

$$2Al(OH)_3 \rightarrow 2Al_2O_3 + 3H_2O \quad (6)$$

$$2ZnO \cdot 3B_2O_3 \cdot 3H_2O \rightarrow 2ZnO \cdot 3B_2O_3 + 3H_2O \quad (7)$$

In the case of EG, high temperature leads to intense thermal expansion of EG and forms “worm-like” char layer on composite surface, the thick and fluffy char forms tortuous pathway char structure which has excellent char barrier effect [193].

With regard to fibre reinforced polymer composites, the primary area where combustion occurs was the upper surface of the material sample, which was also the resin rich region. Some FR effects in gaseous or condensed phase such as protective char layer effect [194] or endothermic cooling effect also occurred in this region. Therefore, the high flammability of resin rich region was inevitable when the resin was not modified by FR additives. However, the FR modification to RF was also necessary due to candle-wick effect of fabric [163].

Based on the flammability test results, the APP@rEP/OP@RF and EG@rEP/OP@RF composites achieved excellent inflammability which verified the effectiveness of combining FR modified RF with FR modified rEP. On one hand, the increased total content of FR additives played significant roles, on the other hand, the incorporation of FR additive into rEP resin increased the inflammability of resin-rich area, the combined effect of two FR modifications furtherly improved fare safety performance. However, ATH@rEP/OP@RF and EG@rEP/OP@RF composites did not possess acceptable anti-flammability due to relatively lower content of ATH or ZnB. The fire performance of materials in this work were comparable to composites with similar loading ratio of FR agents in other works [157, 179, 181, 195].

3.6 Conclusion

In this work, the fully green composites composed of rEP and rEP resin matrix were fabricated via hand lay-up prepreg followed hot-press process. The matrix and reinforcement of composite was both bio-sourced, which corresponded to demand for sustainable and green composite. To improve the fire safety of the composites, RF was treated by OP, meanwhile four different FR additives (APP, ATH, ZnB and EG) were respectively mixed with the rEP resin. The combined effect of OP@RF with rEP modified by different FR additives on fire safety and mechanical performance of composites were investigated.

According to TGA results, the introduction of OP@RF decreased thermal stability of composites. Compared with rEP/OP@RF composite, the thermal stability of composites were slightly increased by addition of ATH or ZnB while the incorporation of APP or EG decreased the thermal stability.

In tests correlated with flammability, APP@rEP/OP@RF and EG@rEP/OP@RF composites both achieved V-0 anti-flammability category in UL-94 vertical burning test and possessed relatively high LOI value of 35.0% and 41.5%. There were 71.4% and 42.7% of PHRR reduction, 46.6% and 21.1% of HRR reduction, 18.9% and 16.7%

of THR reduction for APP@rEP/OP@RF and EG@rEP/OP@RF in comparison to rEP/OP@RF composite in CCT test. The FR efficiency of APP and EG were higher than ATH and ZnB. The FR performance results verified the combined effect of OP@RF with rEP modified by different FR additives. It is noteworthy that the FR efficiency of FR modification to resin is higher than that of OP modification to fabric, which was because that combustion occurred primary at resin-rich region on the upper surface of composite.

However, the introduction of OP on RF visibly reduced the mechanical performance of the composites. The OP modification was not suitable for natural fibre due to the exist of phosphorus-containing group.

Chapter 4 A Conceptional Approach of Resin-Transfer-Molding to Rosin-Sourced Epoxy Matrix Green Composites

4.1 Introduction

In chapter 2 and chapter 3, the rEP/RF composites were manufactured by prepreg making following by vacuum bag assisted compression molding process. In the case of NFRP composite, the optimization of cost issues is more crucial than composite reinforced by synthetic fibres because the NFRP materials are extensively used in relatively cheap scenarios. However, during the practice of manufacturing in chapter 2 and chapter 3, it was found that the viscosity of rosin-sourced epoxy system was high and it was difficult to achieve good infiltration of matrix. Therefore, epoxy resin with high viscosity was thought to be not suitable for RTM process. By developing the RTM technique for rEP/RF composites, the rEP/RF composites can be fabricated with more types of geometric shape and lower cost.

In this chapter, by pre-loading rosin-sourced hardener on RF, the rEP composite reinforced by RF or CF were successfully fabricated by RTM process, and the mechanical performance of composites fabricated via prepreg/compression process and RTM process were compared. In the early stage of experimental design, the pre-loading of rosin-sourced hardener in this chapter was as control group for a novel bio-sourced hardener derived from daidzein, which was proved to show intrinsically flame retardant property. The expected result was that the daidzein hardener could solve the incompatibility problem between phosphate and ramie fabric while providing flame retardant improvement. However, the results were not ideal, though the interfacial problem was improved, the composite with pre-loaded flame retardant hardener did not achieve acceptable fire safety performance, consequently that part of work correlated with daidzein based hardener was not included in the thesis. Some background of relative information was as following.

Epoxies can be induced to cross-link with many different curing agents. Acid anhydrides are typically used for applications in filament winding and the cross-linked epoxy composites show generally high glass transition temperature, high modulus and tensile elongation, low moisture absorption, low thermal shrink, and ease in molding [196].

Recently, rosin acid has received increasing attention as a bio-sourced form of re-newable feedstock in thermosetting polymer science. From rosin acid, an anhydride-type epoxy curing agent was synthesized as maleopimaric acid (RAM) [197]. By using RAM to cure a two-component resin consisting of an E51-type epoxy and a solid phenolic epoxy, a bio-sourced epoxy matrix resin has been developed for prepreg preparation with a bio-content of about 30% [90]. As reported, the formulated resin system behaves well in film manufacturing and subsequent pre-pregging, leading to production of "green composites" for autoclave molding. Compared with its 100% petroleum-sourced prepreg composite counterparts, the rosin-sourced green composite presents generally higher application performance [198]. Considering the increased use of polymer-based composites in aerospace industry and its eco-friendly and green needs, the rosin-sourced green composites has drawn a great deal interest from aerospace industry with the potential as quasi-structural aircraft interior parts [85, 87].

However, the typical anhydride-curing epoxies, rosin-sourced epoxy cannot be used conveniently in liquid composite molding (LCM) at all, due to its intrinsically high viscosity. Among the various composites manufacturing processes, LCM has been recognized as a cost-effective and promising technology [199] due mainly to elimination of the costly pre-pregging stage. LCM summarizes a variety of process technologies such as resin transfer molding (RTM), reaction injection molding (RIM), and vacuum-assisted resin injection (VARI) that use thermoset resins and continuous fabric reinforcements to produce fibre reinforced composites. Unlike processing of prepreg materials in autoclaves, that is generally very time consuming and expensive, LCM allows a relatively fast and high-quality production of advanced composites.

In a typical RTM process, the textile preform is placed in a closed mold; a liquid polymer with very low viscosity as the matrix resin is then either injected under pressure or drawn into the mold due to vacuum, to infiltrate and wet the fibre mat preform. The process is accompanied with a complex flow mechanism that combines macro and micro infiltration of the dry fibre preform [200]. It is obvious that the lower the resin viscosity is, the better the infiltration quality will be. The time needed for infiltration and wetting varies from a few seconds for smaller parts up to hours for very large parts such as rotor blades used for wind energy plants. The processing time for the infiltration is limited by the ultimate rise in resin viscosity as cross-linking commences. In other words, the pot life of the resin determines how much time is available for impregnation.

In this study, a preform-based LCM technique [201], named ex-situ LCM, is introduced which can be applied to liquid composite molding using thermoset matrix resins of high viscosity, and allow very long flow and infiltration process time. Two rosin-sourced epoxy matrix resin systems were developed, one for ex-situ LCM and another as prepreg material for autoclave molding. The viscosity behavior of the two resins and the associated process conditions were then compared. Carbon fibre composite laminates manufactured respectively by ex-situ LCM and autoclave using the two green epoxies were subsequently tested in terms of mechanical properties and glass transition temperature. In parallel, “greener” composites were also developed that exploited ramie fibres as reinforcement and the rosin-sourced epoxies as matrix. The ramie fibre composites were manufactured by ex-situ LCM and compression molding, respectively. We will later demonstrate that the ex-situ LCM processed composite laminate had seemingly similar properties to the autoclaved, or compression molded controls.

As introduced, LCM is widely used for manufacturing composite parts as an affordable process technology. Any LCM process generally consists of two functional process steps, namely the impregnation of the fibrous reinforcing preform in the mold with a low viscosity liquid, and simultaneously wetting and removing of dissolved gases and moisture entrapped in the media, and then, the heat induced crosslinking reaction to solidify the resin. Fast filling requires that the resin viscosity be as low as possible, and this low viscosity should be maintained as long as is practicable. In practice, successful infiltration requires a processing viscosity in the range of 1–100 mPa·s.

However, the low viscosity cannot be a constant and the gel point of the liquid epoxy will be determined by the mechanism of the hardener and its stoichiometry. Chemical conversion is already underway in the resin flow and infiltration stage, although its rate may be suppressed by temperature control compared to the curing phase. Consequently, the viscosity increases slowly as soon as impregnation commences, and any such changes will influence the processing time for the flow and infiltration. The case of anhydride-curing epoxies is more challenging because of their inherently high starting viscosities and in practice impregnation may be difficult at fibre volume fractions beyond 50%, as with aerospace structural applications.

Resin viscosity depends on the chemical-physical characteristics of the polymer formulation, i.e., the pre-mixed reactive polymer compound. The viscosity increases generally over time because of both temperature variations and as consequence of chemical reactions that commence as soon as the reactive components are mixed. To tackle the process dilemma, a proprietary LCM technology is developed [201]. Instead of pre-compounding the reactive components to prepare a liquid resin, the solid curing agent is first preloaded on the reinforcing preform. Only the nonreactive liquid resin with intrinsically low viscosity is used for flow and infiltration. By carefully controlling the temperature, only the physical process of resin flow, infiltration and wetting occurs in the first stage with almost no chemical reaction. Then, after the mold is filled and the preform saturated, crosslinking is triggered by increasing the temperature. Thus, the two reactive components combine only after the resin saturates the preform. Diffusion and dissolution precede the crosslinking reaction, with viscosity build-up and eventual solidification. The preform-based LCM technique is designated as ex-situ LCM in the study.

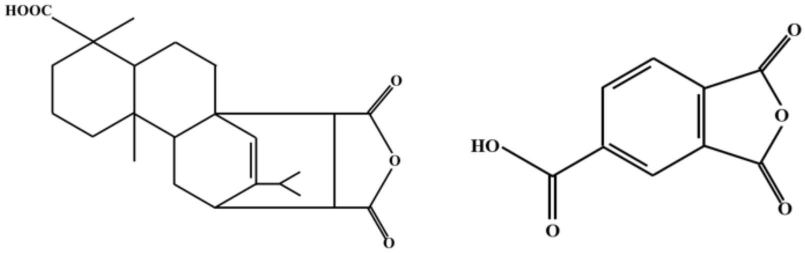
There are two process benefits of ex-situ LCM. The first one is that the resins with high viscosity (or room temperature solid) hardeners can be processed via LCM. The second is that the impregnating resin is essential nonreactive and so can maintain minimum viscosity during filling. The ex-situ LCM process we investigated in this study extends the range of resin and curing agent which can be used as composite matrix in relative field such as aerospace engineering, especially for resin system with high viscosity or short gelation time. As a concept-proof study, some preliminary results of the novel technique will be presented, compared with those of the conventional molding techniques.

4.2 Materials and Methods

4.2.1 Materials

Two epoxy systems were used in the study for the ex-situ LCM and autoclave processes, respectively (Table. 4-1). In both cases, a rosin-sourced anhydride, i.e., maleopimaric acid (RAM, white powder, > 98%, acid number = 133 mg of KOH•g^{-1}) was used as a green curing agent.

To study the flow behavior in comparison with RAM, benzenetricarboxylic anhydride (TMA, white flake, melting point of 164–166 °C) was chosen as a control. The molecular structure of the two curing agents, RAM and TMA is shown in Figure 4-1, respectively. The RAM compound was initially developed by Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences [202]. In the present study, it was dried at 120 °C for 2 hours in an oven before use.



RAM TMA

Figure. 4-1 Chemical structures of the anhydride curing agents used in the study

RDF–160, an E51-type bisphenol F based epoxy with an epoxide equivalent weight of 180–185 g eq^{-1} was used to formulate the RTM resin system, because its viscosity at 25 °C is less than 1500 mPa•s and is thus suitable for liquid composite molding. The prepreg matrix resin was formulated with a two-component epoxy system consisting of another E51-type liquid epoxy, i.e., 2,2-bis [4-(glycidyloxy)phenyl]propane with an epoxide equivalent weight of 171–175 g eq^{-1} and a solid phenolic epoxy resin with an epoxide equivalent weight of 200–238 g eq^{-1}. BC-120, a Lewis acid, is a room temperature latent, elevated temperature and confidential catalyst agent. If mixed with liquid epoxies, a clear homogeneous resin is formed with a shelf lifetime of about one year at room temperature. The catalyst was hence used to formulate the RTM resin system, whereas a two-amino imidazole salt complex, IMA (white powder) was used in the prepreg matrix formulation as accelerator. Except for RAM, all the other chemicals mentioned above were commercially available products.

Table. 4-1 Bio-sourced epoxy system studied

	Main composition	**Curing temperature**	**Curing method**
***Ex-situ* LCM resin**	RAM, RDF-160, BC-120	160 °C	*Ex-situ* LCM
Prepreg resin	RAM, two-component epoxy, IMA	130 °C	Autoclave or compression

A carbon fibre (CF) plain fabric CF3011 obtained from GuangWei Composite Material Co., Ltd (Weihai, China) was used to produce laminate composites. It is a Chinese T300-grade CF material. The specification of CF3011 is shown in Table. 4-2.

Table. 4-2 Specification of carbon fibre fabrics CF3011 used

		Specification
Weave structure		plain
Weight per unit area, g/m^2		193 ± 10
Threads per unit length, number/cm	warp	4.9 ± 0.2
	weft	4.8 ± 0.2
Tensile strength at break, N/25mm	warp	≥ 1700
	weft	≥ 1700

Ramie fabric was also used as natural reinforcing material as specified in Table. 4-3. It was obtained from Huangshengdongting Co., Ltd (Hunan, China).

Table. 4-3 Ramie fibre cloth used as natural reinforcing material

		Standard value	**RP 140**	**RT 140**
Width of the cloth, mm		1000 ± 10	995	1004
Areal density, g/m^2		140 ± 5	145	144
Water content, %		≤ 5.5	3.4	2.3
Tensile force at break, N	warp	≥ 650	685	1010
	weft	≥ 670	793	811

4.2.2 Ex-situ LCM process and sample preparation

As introduced, common LCM process uses a liquid formulated resin pre-compounded with the hardener; its chemical reaction occurs in-situ, whereas in the ex-situ LCM process, one of the reactive components is firstly surface-loaded on the reinforcing fibre preform. Only after the low-viscosity liquid resin saturates the preform, the reactive components come into contact. In principle, as the process temperature is relatively low, the solubility and subsequent diffusion of the distributed hardener could be inhibited, resulting in an expanded processing time window. Only after full saturation is completed, the chemical reaction will be then thermally initiated. Thus, the crosslinking reaction occurs ex-situ in an ex-situ LCM process.

Following the procedure, a calculated dose of the solid rosin-anhydride RAM hardener, was firstly dissolved in acetone. The CF preform was then immersed in the solution for 30 seconds. After the solvent was completely volatilized, the preform was vacuum dried at 60 °C for 1 hour to produce a CF preform pre-loaded with the hardener. As calculated, the RAM mass ratio was approximately 20.4%.

The pre-treated CF preform was placed in a closed mold (Figure. 4-2). The epoxy liquid without hardener was then poured into a tank and degassed for 30−60 min. The liquid resin was then pumped into the closed mold to saturate the preform. Finally, the CF composite was cured according to the process procedure and parameters shown in Figure. 4-3. The volume fraction of CF in ex-situ LCM molded composite was 50% and 55%.

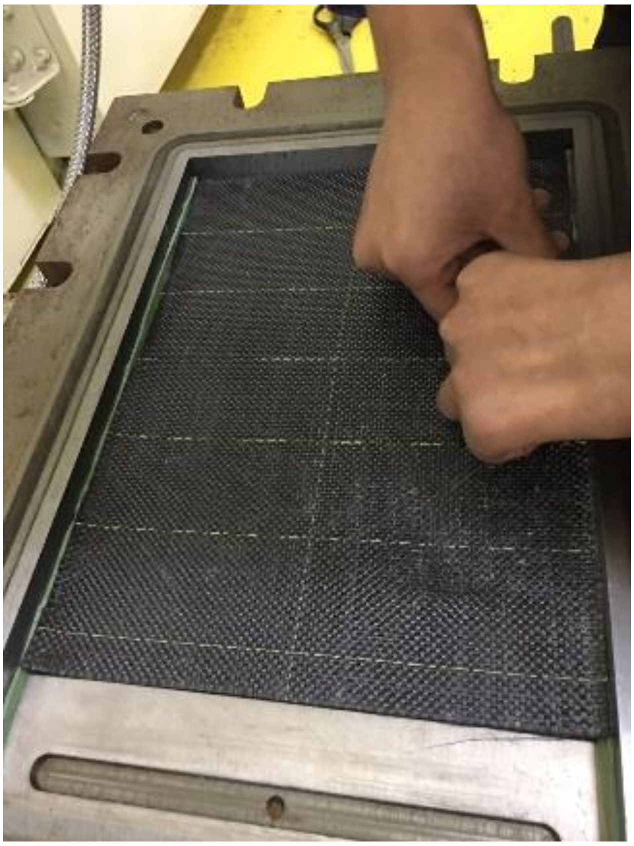


Figure. 4-2 Lay-up process of pre-loaded carbon fibre (CF) preform in resin transfer molding (RTM) mold

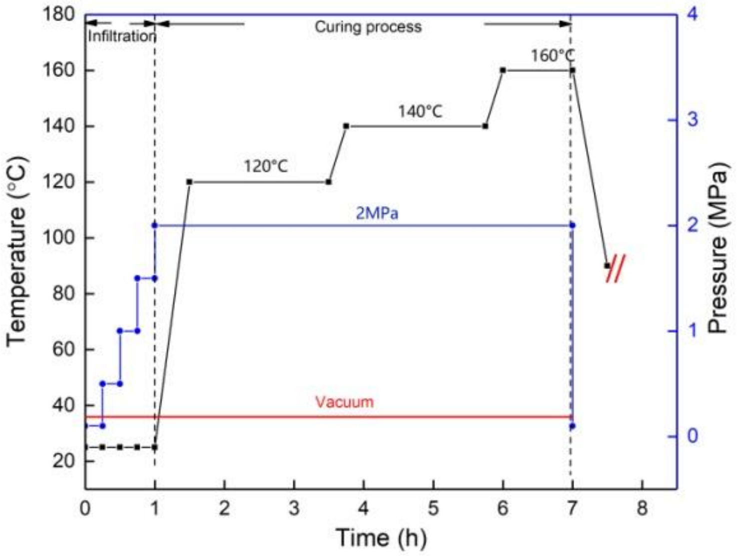


Figure. 4-3 Process parameters and conditions for ex-situ liquid composite molding (LCM).

Ramie cloth preforms were similarly surface-loaded with RAM and resin-transfer-molded and finally cured. As demonstrated in Figure 4-4, the final RF composite sample manufactured using ex-situ LCM process shows a normal appearance. The test samples were then cut from the laminate for test purpose. The volume fraction of ramie fabric in ex-situ LCM molded composite was about 41%.

Figure. 4-4 Ramie fibre reinforced green composites manufactured by ex-situ LCM.

4.2.3 Prepreg reference samples reinforced with CF and RF

Control samples of rosin-anhydride cured CF composite samples were manufactured by prepreg/autoclave method. The volume fraction of CF in the resulted composites was about 57%. In parallel, the ramie fibre control samples were produced, by prepreg/compression molding. The volume fraction of ramie fabric in compression molded composite was about 42%. The parameters of both autoclave process and compression molding are shown in Figure. 4-5.

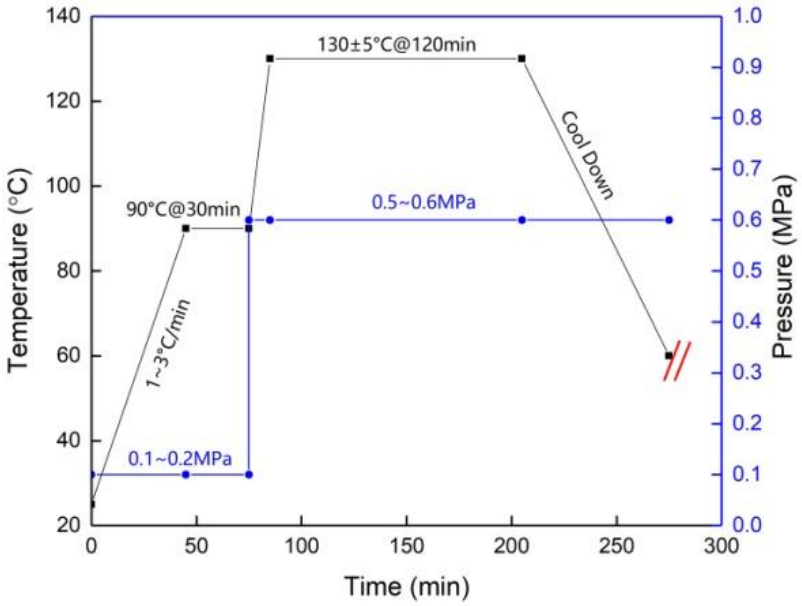


Figure. 4-5 Autoclave and compression molding parameters for resin epoxy CF or RF laminates.

4.3. Characterization

The apparent viscosity was performed on a cone plate viscometer (CAP2000+, Brookfield, Middleborough, MA, USA) with 6th rotation spider at a rotation rate of 300 rpm and a shear rate of 1000 S^{-1}. The viscosity of resin was tested at 80 ℃, 100 ℃

and 120 °C, respectively.

All samples were non-destructively tested by C-scan using a PAC UPK-T36 ultrasonic scanner (USA) prior to further mechanical tests.

A universal testing machine (Instron 3365 testing machine, Instron, Norwood, MA, USA) was utilized to measure the mechanical property of the cured samples. The tensile strength test was conducted according to ASTM D3039. The three-point flexural test was performed according to ASTM D790. The short beam interlaminar shear strength was done according to ASTM D3244. A minimum of five samples were used in each test and their average values are reported below.

Dynamic mechanical analysis (DMA242E, NETZSCH Instruments, Selb, German) was used to study the thermos-dynamic mechanical properties of composite sample and pure cured resin sample. The pure resin samples were fabricated by casting melted resin into the mold, after vacuum deformation at 90 °C for 30 min in vacuum oven, and then cured following the same curing procedure of ex-situ LCM samples. The rectangular samples cutting by size of 50.0 mm × 10.0 mm × 2.0 mm were placed on a three-point bending clamp. The analysis was performed by the three-point bending mode at an oscillation frequency of 2 Hz, an oscillation amplitude of 10 μm and a heating rate of 3 °C/min. The samples were heated from 30 °C to 300 °C.

4.4 Results and Discussion

4.4.1 Viscosity of the ex-situ LCM and prepreg resin

The viscosity behavior of three epoxy systems was assessed over a range of temperatures up to 160 °C, namely E51:RAM:BC120 (red), E51:TMA:BC120 (blue) and E51:BC120 (green), where the colors refer to the plots in Figures. 4-6 and 4-7.

In addition to the RAM (green) hardener and TMA, E51:BC120 was additionally chosen as a baseline without hardener. The viscosity-time curves of the 3 model systems are shown in Figure 4-6 for 3 constant temperatures. It is obvious that, at 80 °C, the viscosity curve of E51:TMA:BC120 increases the fastest, followed by that of E51:RAM:BC120, whilst the viscosity of E51:BC120 at lowest level is almost a constant for the duration of the trial (around 8 hours).

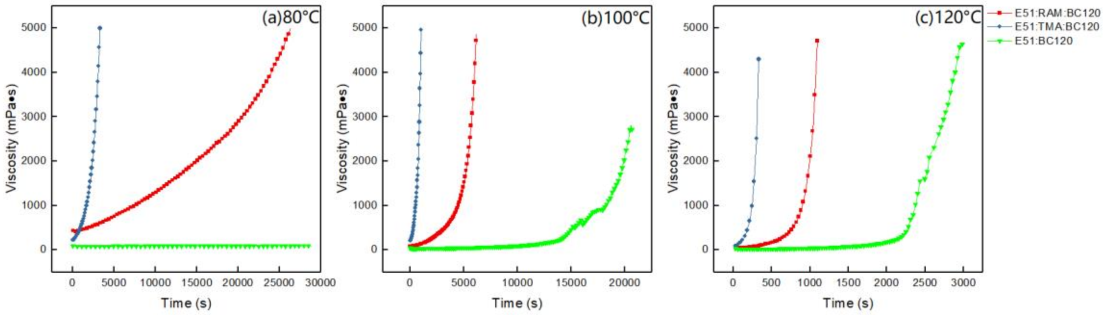


Figure. 4-6 The viscosity-time curves for three experimental systems at (a) 80 °C, (b) 100 °C, (c) 120 °C

The viscosity-time curves of the 3 models at 80 °C, 100 °C and 120 °C are also shown in Figure. 4-6. Under all conditions, the RAM-cured system showed a longer induction period and lower viscosity than that of the TMA, indicating the potential for a wider processing window.

Figure. 4-7 shows viscosity-temperature curves for the 3 epoxy systems at a heating rate of 30 °C /min. Taking viscosities of 100 mPa•s as the upper limit for RTM, it is clear that, below 60 °C, neither E51:RAM:BC120 and E51:TMA:BC120, nor E51:BC120 meets the viscosity requirement, although the last combination shows the lowest viscosity of about 200 mPa•s. However, between 80 °C and 120 °C, the viscosities of all the systems are lower than 100 mPa•s which provide a good processing window for RTM.

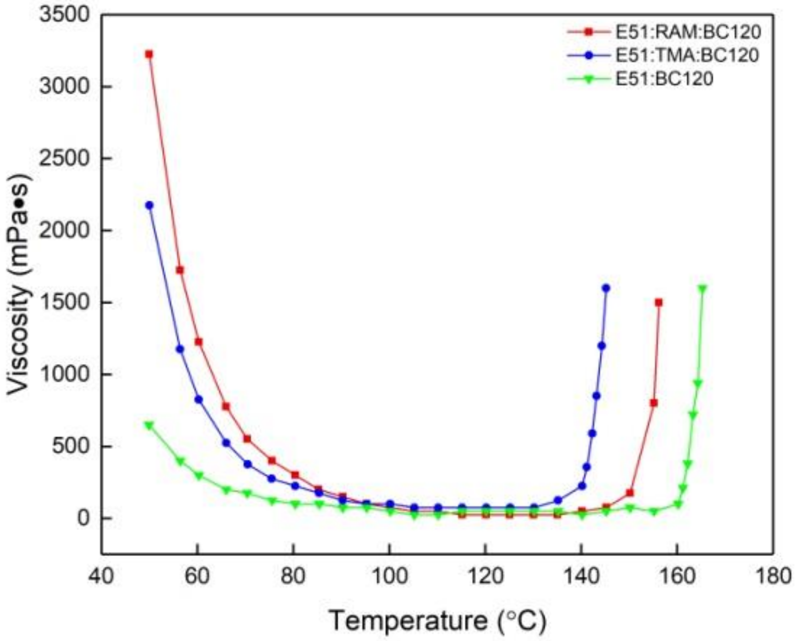


Figure. 4-7 Viscosity-temperature curves for the 3 model systems in comparison

The viscosity of the epoxy for prepreg fabrication was also studied. As mentioned in Table. 4-1, this was a two-component system consisting of E51 with a solid phenolic epoxy, cured with RAM. Figure. 4-8 shows the viscosity curve as a function of temperature. Increasing the temperature from 50 °C to 85 °C, the viscosity first decreased rapidly, and flattened before reaching a turning point the induction temperature of 116 °C. However, the viscosity at no point met the processability requirement for LCM.

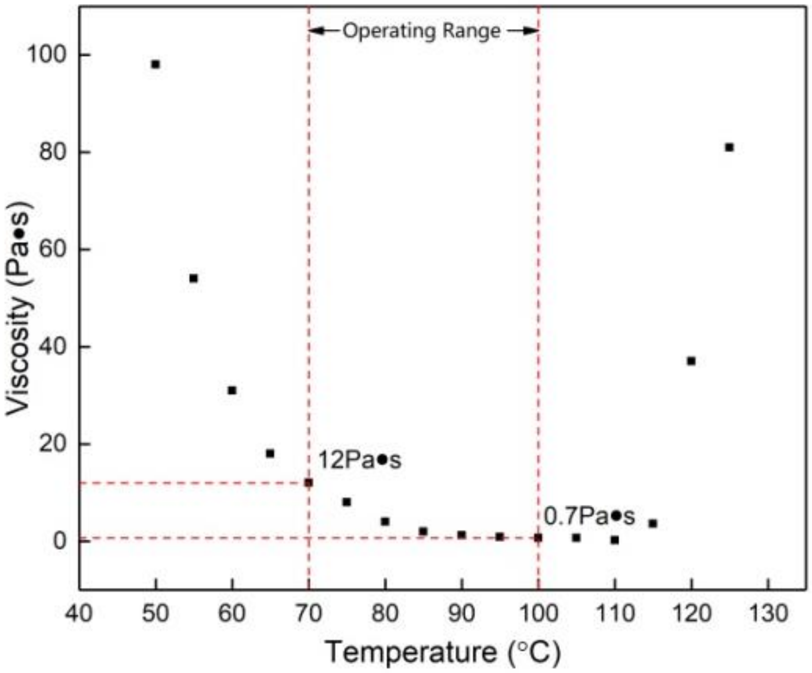


Figure. 4-8 The viscosity-temperature curve of the rosin-sourced prepreg epoxy system.

The rheological tests revealed that by extracting the solid RAM, the main curing agent from the formulated RTM resin system, the remaining liquid epoxy would maintain a suitably low viscosity to permit the successful impregnation of even very large structures [203].

4.4.2 CF composite sample quality evaluated by C-scan

All CF samples manufactured were C-scanned to investigate the distribution of potentially dry areas prior to mechanical test. Figure. 4-9 shows the scan results for the CF laminates produced by ex-situ LCM using the rosin-sourced green matrix resin. There appeared to be no noticeable defect in the samples, and slightly increasing the fibre volume fraction from 50% to 55% did not appear to affect the outcome significantly.

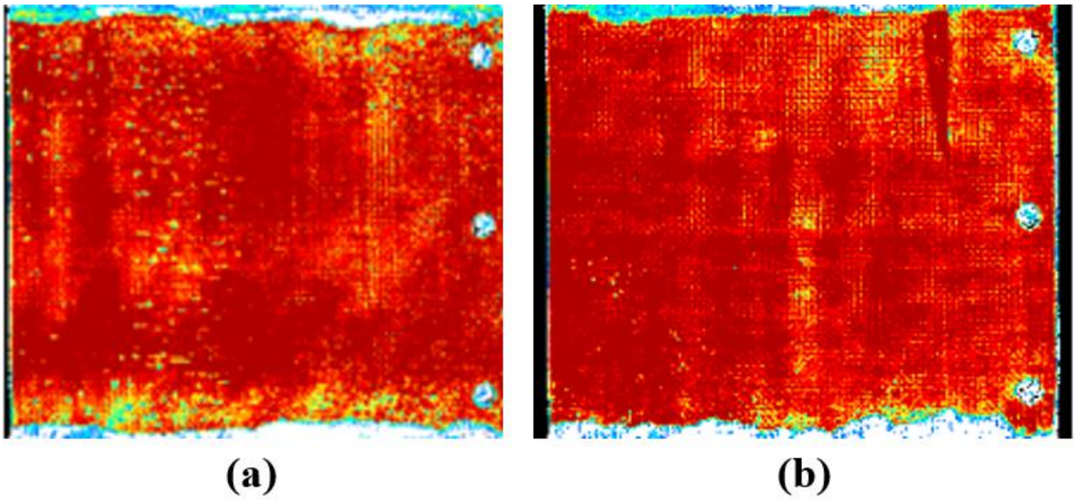


Figure. 4-9 C-scan result of CF laminates with fibre volume content (a) 50%, (b) 55%.

4.4.3 Thermal-Mechanical property

Glass transition behavior of the epoxy cast samples with and without rosin-sourced curing agent RAM was tested by DMA, as well as that of the CF reinforced composite samples manufactured by ex-situ LCM. Figures. 4-10 and 4-11 show typical results. The T_g of the sample cured with RAM, i.e., E51:RAM:BC120, was approximately 170 °C, i.e., 33 °C higher than that of the sample without curing agent, E51:BC120. The glass transition temperature of the CF composites using the matrix resin of E51:RAM:BC120 increased with fibre volume fraction, from 177 °C to 187 °C over the V_f range 0.5−0.55.

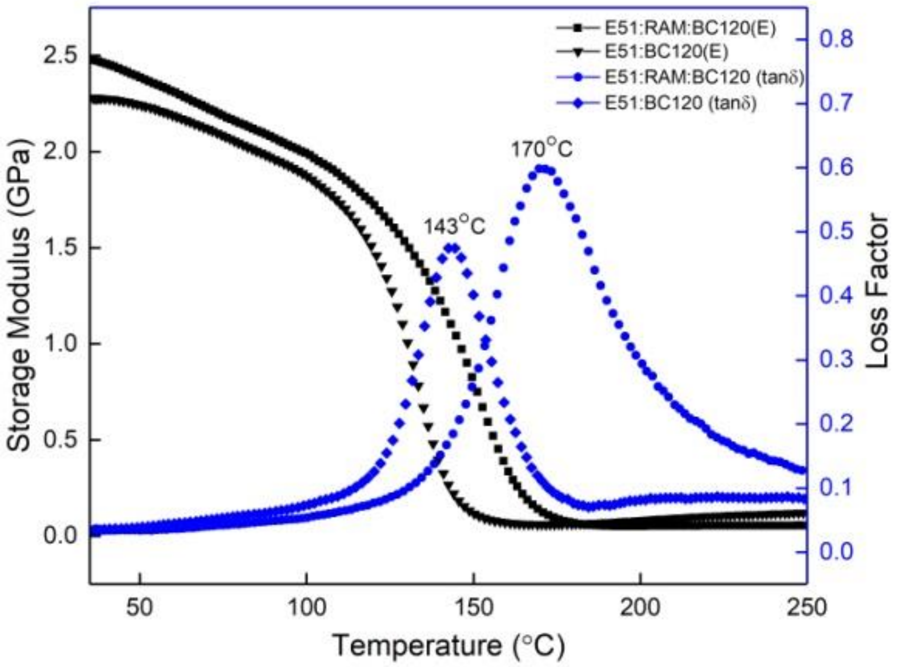


Figure. 4-10 DMA curves for resin cast samples with or without the hardener

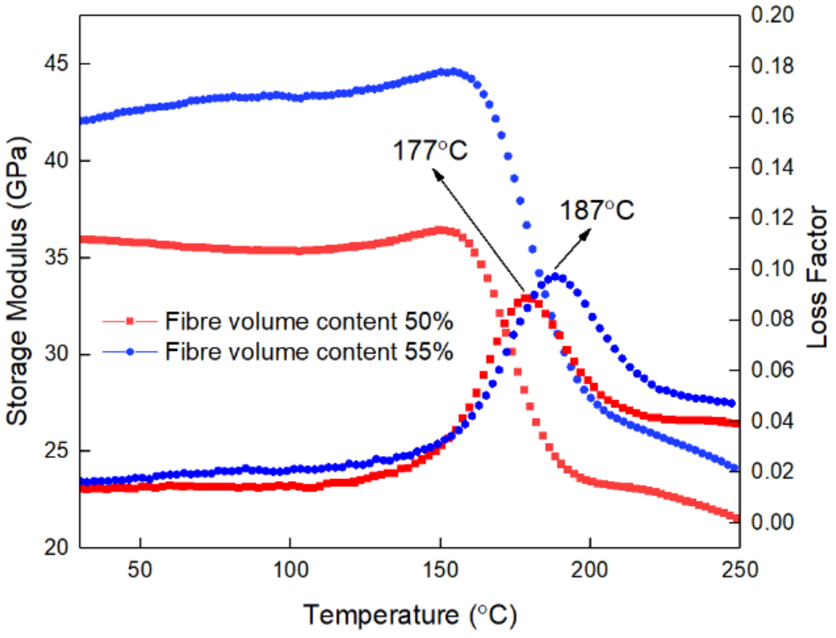


Figure. 4-11 DMA curves for laminates with different CF volume fractions

As shown in Figure. 4-12, the glass transition behavior was also studied for the autoclave-molded green prepreg composite sample, i.e., RAM cured two-component epoxy system of an E51 and a solid phenolic epoxy. A T_g of approximately 182 ℃ can be confirmed, which is quantitatively comparable to those of the samples manufactured by ex-situ LCM, Figure. 4-11.

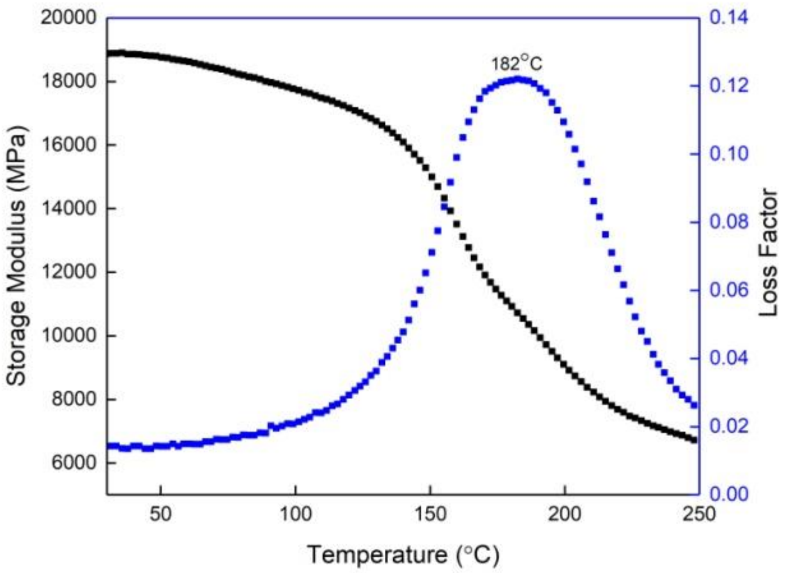


Figure 4-12. DMA curves for rosin-sourced epoxy prepreg laminates with 57% CF volume fraction, manufactured by autoclave.

The C-scan result, together with T_g data of the CF samples manufactured by ex-situ LCM suggests that the CF preform was fully infiltrated and wetted by the liquid epoxy, and the two reactive components have diffused and dissolved with each other, with a homogenous degree of conversion across the laminate.

4.4.4 Mechanical properties of CF composites

CF volume fraction dependent mechanical properties were studied for the composite samples manufactured by ex-situ LCM. Table. 4 lists the flexural properties and interlaminar shear strength (ILSS). As the CF volume fraction increased from 50% to 55%, the flexural properties increased whereas the ILSS decreased.

Table. 4-4 Typical mechanical properties of CF composites produced by ex-situ LCM and autoclave in comparison

CF vol %	Flexural strength, MPa	Flexural modulus, GPa	ILSS, MPa	Manufacturing method
50	734 ± 68	48.8 ± 1.0	49.0 ± 2.1	*Ex-situ* LCM
55	772 ± 69	57.5 ± 1.1	45.6 ± 2.0	
57	883 ± 77	56.8 ± 1.1	55.7 ± 2.2	Prepreg autoclave-molded

For comparison purpose, the flexural and ILSS properties were also tested on the CF reinforced green prepreg composite samples produced by autoclave-molding. The test result is also listed in Table. 44. It is common and usual that the mechanical properties of the laminated CF composites produced by autoclave are generally higher than those of the RTM composites [204].

4.4.5 Mechanical properties of Ramie fibre composites

Similarly, tensile and flexural mechanical properties of the RF composite samples manufactured by ex-situ LCM were tested and reported in Table. 45, as well as those of the compression-molded prepreg material. The fluctuation in the data came likely from the inaccuracy in control of the process parameters due to the preliminary study.

Table. 4-5 Typical mechanical properties of RF composites produced by ex-situ LCM and compression in comparison

Manufacturing method	Tensile strength, MPa	Tensile modulus, GPa	Flexural strength, MPa	Flexural modulus, GPa
***Ex-situ* LCM**	91.0 ± 8.0	9.1 ± 0.1	165.8 ± 4.7	7.3 ± 0.3
Prepreg/Compression molding	86.5 ± 3.4	6.5 ± 0.2	133.0 ± 5.4	8.5 ± 0.3

From the results reported above, it is believed that the ex-situ LCM technique is not only applicable to many other high viscosity resins but can also be used for the production of very large composite part demanding very long resin pot life.

4.5 Conclusion

A novel process concept, i.e., ex-situ LCM for liquid molding using high viscosity matrix resins was first proposed. In the study, it was a rosin-sourced green epoxy that had an inherent high viscosity, thus was conventionally not able to be used for RTM. Rheological study revealed that the liquid resin without the solid anhydride-curing agent could maintain the low viscosity and high flow ability for a very long time. It was demonstrated that, by means of the ex-situ LCM technique, the high-viscosity green epoxy could be used for RTM.

Consider the growing requirement for polymer composite in aerospace industry, the development of this ex-situ LCM process provides new perspective for composite manufacturing which allows to process high viscosity epoxy systems at a cheaper and less time-consuming fabrication technologies and to obtain homogeneous laminates with comparable mechanical properties. It also extends the potential resin system with high intrinsically viscosity or short gelation time in aerospace industry, can be applied as composite matrix by ex-situ LCM technology.

The comparative study from the DMA, C-scan, and mechanical tests yielded important information about composite quality and properties between the samples manufactured by ex-situ LCM and autoclave or compression molding. Both carbon and ramie fibre composite samples were manufactured, studied and compared. For the 55 vol% CF composites fabricated by ex-situ LCM, the flexural strength and ILSS were 72 MPa and 45.6 MPa, respectively, as compared with the 57 vol% compression molded CF samples, which has a flexural strength of 83 MPa and ILSS of 55.7 MPa. However, the flexural modulus of samples fabricated by two process were at similar level. Regarding the RF composites, the tensile strength and flexural strength of ex-situ LCM molded samples were 91.0 MPa and 165.8 MPa, respectively. These properties were marginally higher than those of prepreg/compression molded composite. The preliminary experiment shows that the resulting material quality and mechanical properties were generally comparable with those manufactured by prepreg/autoclave, or prepreg/compression molding.

Chapter 5. Study on Mechanical Performance of Itaconic Acid Based Epoxy Composite Reinforced by Glass or Carbon Fabric

5.1 Introduction

In chapter 2 to chapter 4, the work mainly focused on development and FR modification of fully-green composite based on natural fibre with rosin-sourced epoxy matrix. However, the results from chapter 2 and chapter 3 showed that the modification of phosphate organic to ramie fibre caused decreased mechanical performance of rEP/RF composites. Additionally, chapter 2 and chapter 3 have proved that the FR modification to resin matrix is more effective than FR modification to ramie fibre reinforcement for improvement of fire safety performance for fibre reinforced polymer composite. Therefore, the influence of FR modification to fibre as well as the selection of fibre reinforcement on flame retardant performance of composites are still worth to be investigated.

To furtherly investigate the influence of selection of fibres, glass fibre and carbon fibre are potential substitute of ramie fibre due to their high inflammability. In a previous work [87], the mechanical performance of rEP/GF and rEP/CF composites were tested and compared with mechanical performance of commercial epoxy composite reinforced by same GF and CF.

Meanwhile, considering the high viscosity problem of rosin-sourced epoxy resin mentioned in chapter 4, it is significant to develop novel bio-sourced epoxy resin with better processibility. Chapter 5 was a relatively independent chapter in the thesis which was carried out as a complement to this previous work and pre-experiment for future work relevant to fibre reinforced composite based on itaconic acid based epoxy (IABE) matrix. IABE was another novel bio-sourced epoxy system developed by the collaborators of our research group, and the properties of fibre reinforced composite based on IABE matrix has not been investigated before. The utilization of IABE resin in fibre reinforced epoxy composite is also an important branch of a new project in our team. Therefore, the current chapter fabricated IABE/GF and IABE/CF composites via prepreg/compression process, the mechanical properties of fibre reinforced composites based on rEP matrix and IABE matrix were compared. Some research background correlated with the development of IABE resin was as following.

During the last decade, the exploration of chemical building blocks based on sustainable and natural feedstocks have attracted attention from researchers due to environmental concern. Numerous studies were carried out to attempt the possibility of replacing conventional petroleum-based building blocks with bio-based ones. The development of bio-sourced resins is a crucial branch among the studies which can reduce the dependency on petroleum-based material [205].

In this context, itaconic acid (also called methylene succinic acid), is usually synthesized by the fermentation reaction of carbohydrates include digestible starch or glycogen. As a potential substitute for petrochemicals in materials industry, itaconic acid has been recommended by U.S. Department of Energy as 12 top value added bio-based platform chemicals [206]. With the development of synthesis technology, the global yield of itaconic acid is about 80,000 tons per year and the estimated cost is about 2 US dollars per kilogram [207]. Owning to the high potential of this chemical, the production capacity is forecasted to increase by 5.5% annually from 2016 to 2023 [205].

The chemical structure of itaconic acid is shown in Figure. 5-1. It contains two carboxylic acid groups and an α,β-unsaturated double bond, which enables it to be a possible precursor for a myriad resin system.

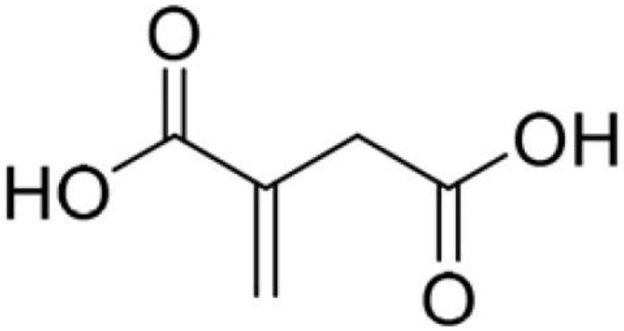


Figure. 5-1 Chemical structure of itaconic acid [208]

Some studies have explored the epoxy system based on itaconic acid. Songqi Ma et al. [209] has synthesized a trifunctional epoxy monomer based on dehydrobromination reaction between itaconic acid and allyl bromide followed by epoxidation reaction, the synthesis route is depicted in Figure. 5-2. The epoxide value and viscosity (at 25 ℃) of trifunctional epoxy monomer are 1.16 and 0.92 Pa•s respectively, which provides acceptable processibility of resin in fabrication process. The flexural strength and modulus of epoxy based on itaconic acid based epoxy are comparable to those of epoxy based on petroleum-based monomer.

In order to improve flame retardancy of epoxy resin, 9, 10- dihydro-9, 10-oxa-10-phosphaphenanthrene 10-oxide (DOPO) is reacted with α,β-unsaturated double bond of itaconic acid, then the DOPO modified chemical is furtherly modified to synthesis epoxy monomer via similar route as previous work [209]. The synthetic route DOPO modified epoxy monomer is denoted in Figure. 5-3 [210].

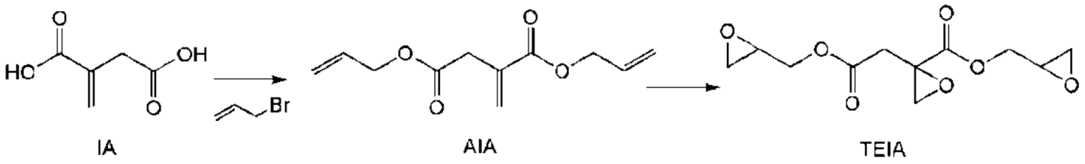


Figure. 5-2 Synthetic route of trifunctional epoxy monomer based on itaconic acid [209]

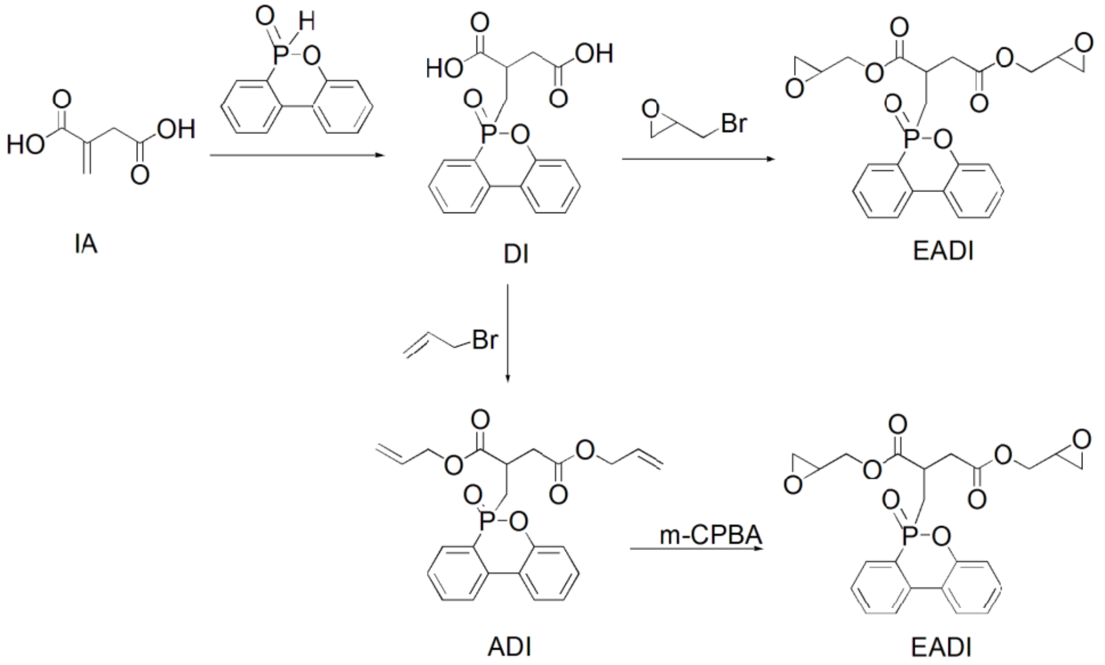


Figure. 5-3 Synthetic route of DOPO modified itaconic acid based epoxy resin [210]

To explore the application of itaconic acid derivatives in fibre reinforced composite field, in this work, an itaconic acid based epoxy resin system was chosen as matrix, the synthetic process of IABE resin was denoted as Figure. 5-4 [92]. Glass fabric (GF) and carbon fabric (CF) were chosen as reinforcements. The IABE/GF and IABE/CF composites were fabricated by vacuum bag assisted compression molding process and mechanical performance of composites was characterized. The aim of this chapter is to provide a new perspective for fibre reinforced polymer composites based on bio-sourced epoxy matrix, it is a preliminary study to exploit possible substitutes for fibre type as well as the bio-sourced epoxy type.

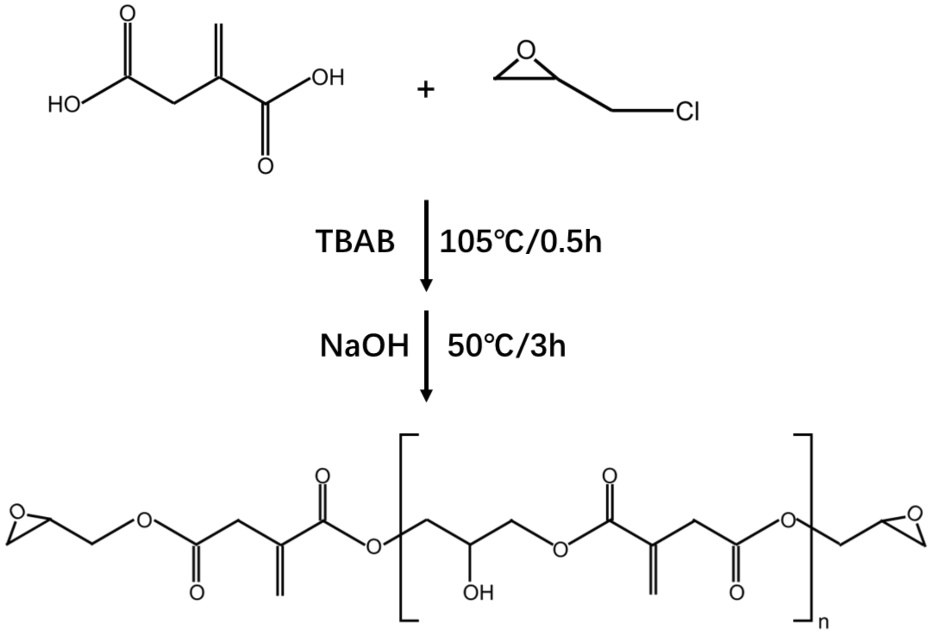


Figure. 5-4 Synthetic process of itaconic acid based epoxy resin system [92]

5.2 Materials & Methods

5.2.1 Materials

IABE/GF and IABE/CF prepregs were provided by Ningbo Nike New Material Co., ltd. (Ningbo China). The prepregs were fabricated by hot-melt prepreg process and corelated information of two prepregs were listed in Table. 5-1. The GF is high strength alkali-free glass fabric while the type of CF was 6kT300.

Table. 5-1 Speculation of IABE/GF and IABE/CF prepregs

Prepregs	**Type**	**Areal density of prepreg (g/m^2)**	**Areal density of fabric (g/m^2)**
IABE/GF	NIC3200/G300	654	300
IABE/CF	NIC3200/C300	565	300

5.2.2 Sample fabrication

The composite samples were fabricated by compression molding assisted by vacuum bag process, the arrange of vacuum bag was showed as Figure. 5-5. Eight plies of 300*300 mm^2 IABE/GF or IABE/CF prepregs were stacked on the bottom mold (350*350 mm^2), several stop blocks with 2 mm were placed next the boundary of prepregs to control the final thickness of composite samples. The fabrication parameters of composite curing process were displayed as Figure. 5-6. Before manufacturing, the laminated prepregs were degassed at room temperature. In first stage, the prepregs were pre-cured for 90℃/40 min with vacuum of pump and then followed by 100 ℃/1 h, 110 ℃/1 h and 130 ℃/1 h curing process with 4 MPa pressure respectively by compression machine (to avoid explosive polymerization of IABE). In the last stage, the sample was cooled to room temperature with 4 MPa pressure to avoid deformation of samples.

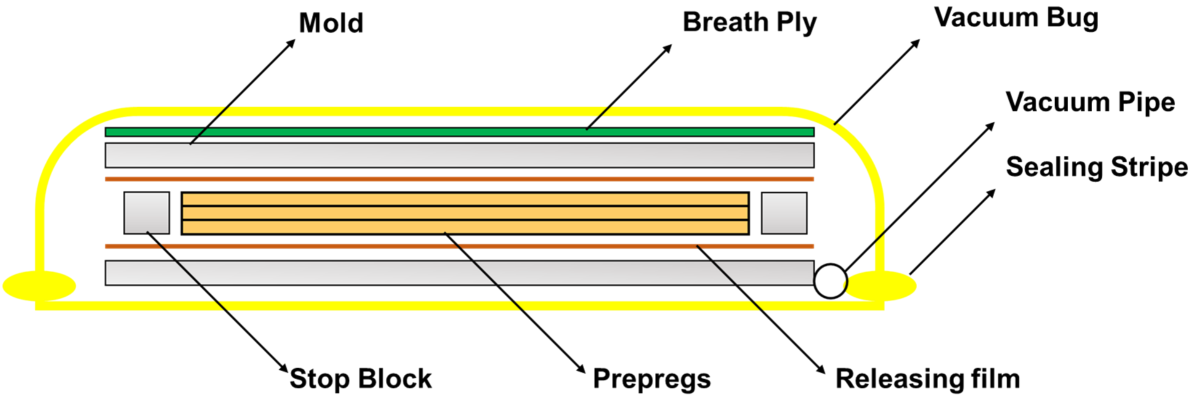


Figure. 5-5 Sketch map of vacuum bag for fabrication process

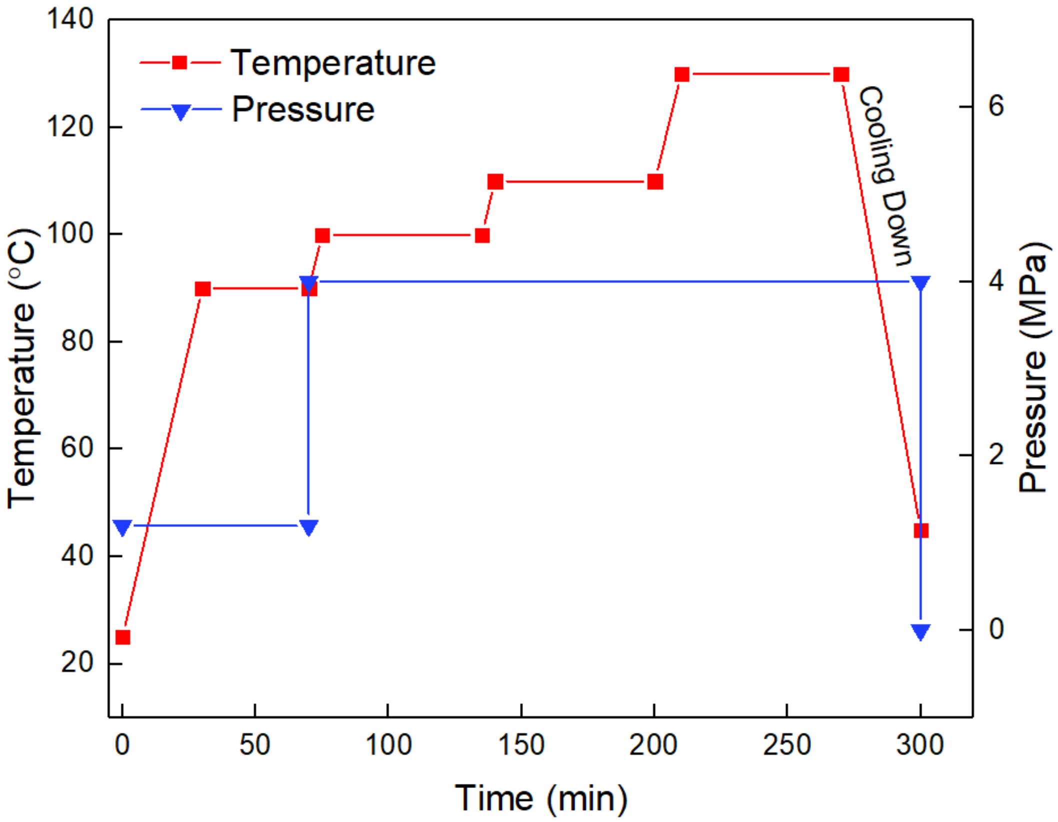


Figure. 5-6 Process parameters for the curing of IABE/GF and IABE/CF prepregs in compression molding

Supposed that there is no defect or void in composite, the volume fraction of fibre in composite can be calculated by:

$$V_{fabric} = \frac{n * A_{Fabric} * S}{\rho_{Fabric}} * \frac{1}{S * h}$$

Where V_{Fabric} is the volume fraction of GF or CF in composites respectively, n is the number of plies, A_{Fabirc} is the areal density of GF or CF, which are both 300 g/m^2. ρ_{Fabric} is the density of GF or CF, here were 2.54 g/cm^3 and 1.8 g/cm^3 respectively. h is the thickness of the composite sample. The formula of IABE/GF and IABE/CF composites were listed in Table. 5-2.

Table. 5-2 Formula of IABE/GF and IABE/CF composites

Composite	Areal density of fabric (g/m^2)	Number of plies	Thickness (mm)	Fibre volume fraction (%)
IABE/GF	300	8	2.05	46.2
IABE/CF	300	8	2.43	54.9

5.3 Characterization

All composites were non-destructively tested by C-scan using a MISTRAS UPK-T36 ultra-sonic scanner (USA) with a 5 MHz transducer prior to mechanical test.

DMA measurements were carried out on a Perkin Elmer DMA8000 equipment (Perkin-Elmer Corporation, USA). The IABE/GF and IABE/CF composites were cut to the dimensions of 40*10 mm^2. The tests were carried out by using a single cantilever system. The fixed frequency was 1 Hz, the heating rate was 3 ℃/min and the temperature range was 30-160 ℃.

The mechanical test parameters and standards for IABE/GF and IABE/CF composites were summed up in Table. 5-3. The tensile tests were carried out using same machine as flexural test based on ASTM D-3039 standard, the sample size was 250*15*2 mm^3 and the crosshead speed was 1 mm/min. The span during test was 150 mm due to there were 50 mm long end tabs adhered to two ends of samples.

The flexural properties of samples were tested by an electronic universal testing machine (MTS Systems Corporation, Shenzhen, China) according to ASTM D-790-03 standard, the crosshead speed, sample dimension and span were 1 mm/min, 84*12.5*2 mm^3 and 32 mm, respectively.

The compressive tests were carried out according to ASTM D-6641 standard. The sample size was 140*13*2 mm^3 and the crosshead speed was 1.3 mm/min.

The interlaminar shear strength (ILSS) of samples was characterized according to ASTM D-2344 standard. The sample size was 12*4*2 mm^3 and the span was 8 mm, the test speed was 1 mm/min.

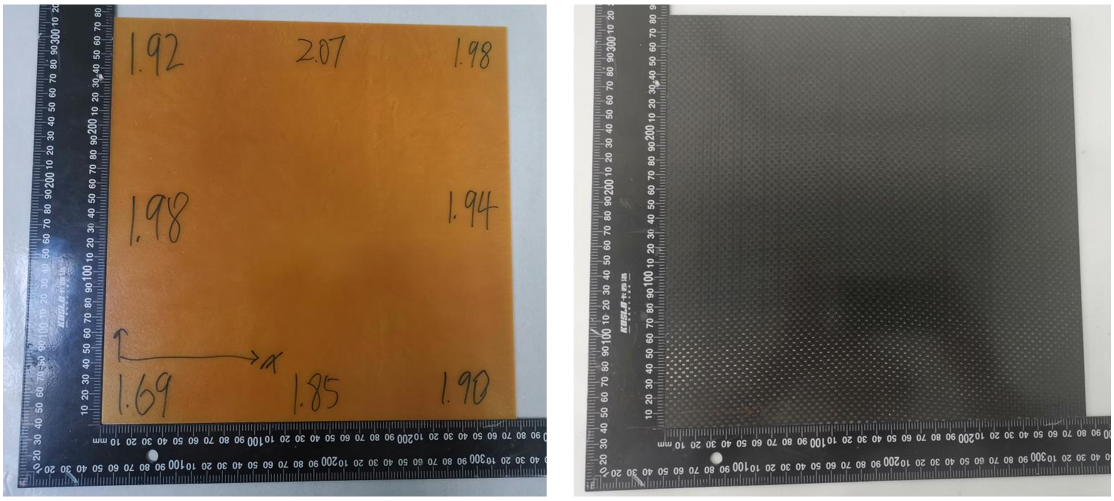
Table. 5-3 Mechanical test parameters and standards for IABE/GF and IABE/CF composites

Test	Size (mm)	Span (mm)	Cross head speed (mm/min)	Standard
Tensile	250*15	150	1	ASTM-D790
Flexural	84*12	64	1	ASTM-D3039
Compressive	140*13	13	1.3	ASTM-D6641
Interlaminar shear	12*4	8	1	ASTM-D2344

5.4 Results and Discussion

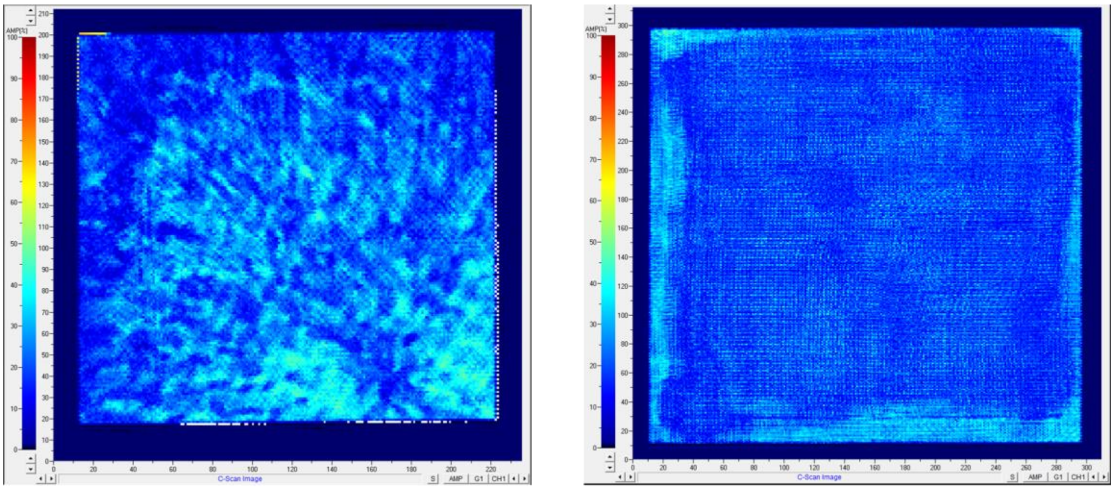
5.4.1 Sample quality of IABE/GF and IABE/CF composites

The digital images of composite surface and C-scan results of IABE/GF and IABE/CF composite samples were displayed in Figure. 5-7 and Figure. 5-8. The surface of both IABE/GF and IABE/CF samples were smooth and even. There was no obvious defects from C-scan results of samples. The samples were with promising quality and the fabric was sufficiently infiltrated by IABE resin, the void content of samples was in a quite low level as well.



(a) (b)

Figure. 5-7 Digital images of (a) IABE/GF and (b) IABE/CF composites



(a) (b)

Figure. 5-8 C-scan results of (a) IABE/GF and (b) IABE/CF composites

5.4.2 Dynamic mechanical analysis results of IABE/GF and IABE/CF composites

The DMA results of (a) storage modulus and (b) loss factor of IABE/GF and IABE/CF composites were displayed as Figure. 5-9. The IABE/CF composite showed higher storage modulus than IABE/GF composite, which was ascribed to the higher strength of CF than GF. The glass transition temperature of IABE/GF and IABE/CF were 114 ℃ and 130 ℃ respectively, the loss factor at glass transition temperature of IABE/CF composite was also higher than that of IABE/GF composite, which implied better compatibility between CF and IABE.

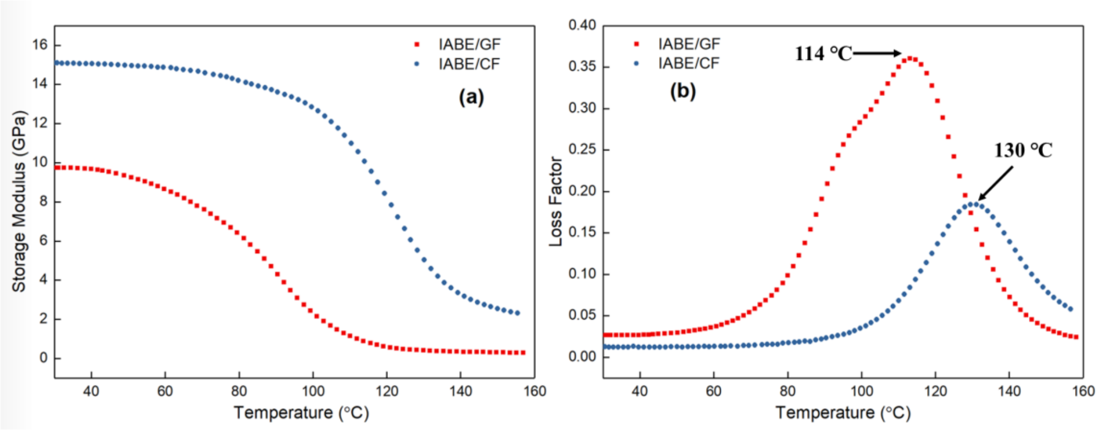


Figure. 5-9 The DMA results of (a) storage modulus (b) loss factor of IABE/GF and IABE/CF composites

5.4.3 Mechanical performance of IABE/GF and IABE/CF composites

The tensile, flexural, compressive and interlaminar shear test results of IABE/GF and IABE/CF composites were plotted in Figure. 5-10 and Figure. 5-12, respectively. The relevant mechanical performance was summarized as Table. 5-4 and Table. 5-5. The mechanical performance of IABE/GF and IABE/ CF composites were compared with the results from relevant work which studied GF or CF reinforced composite based on rosin-sourced epoxy matrix [87]. The comparison of mechanical performance between IABE/GF with rEP/GF and IABE/CF with rEP/CF composites were depicted as Figure. 5-11 and Figure. 5-13. The tensile, flexural, compressive and ILSS properties of composites with IABE matrix were comparable to counterparts based on rosin-sourced epoxy matrix.

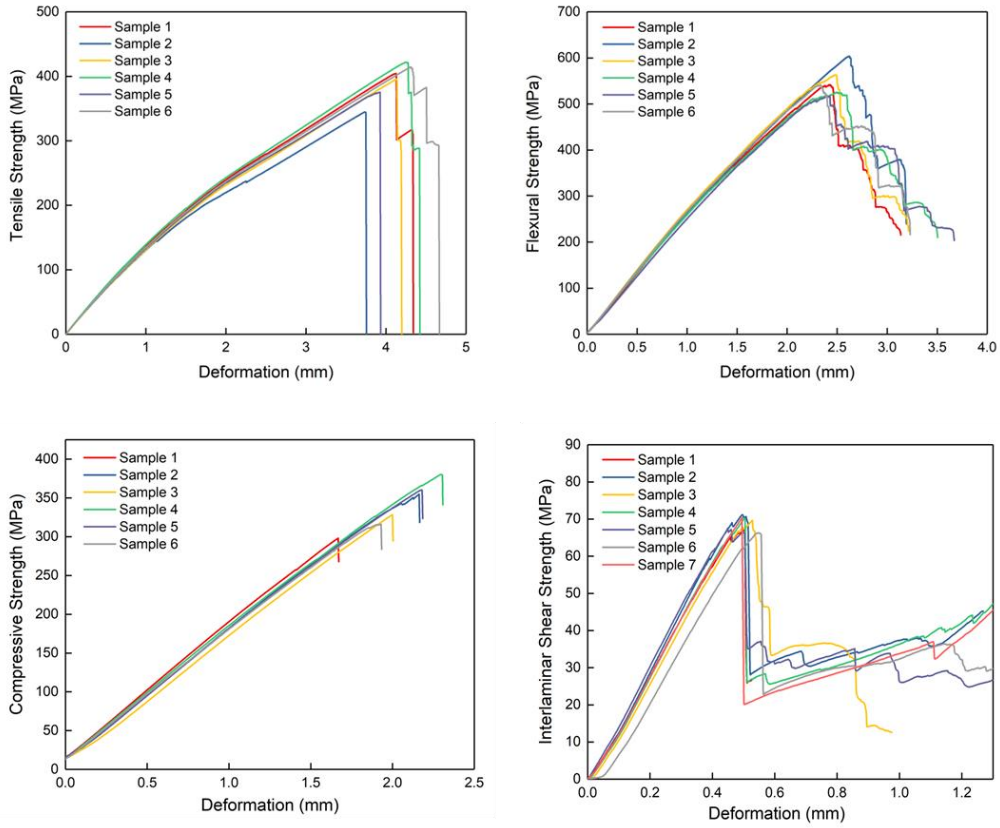


Figure. 5-10 Mechanical properties of IABE/GF composites

Table. 5-4 Mechanical properties of IABE/GF composite

	IABE/GF	**Reference[1]**
Tensile strength (MPa)	392.4±28.3	510
Tensile modulus (GPa)	20.2±0.5	24.4
Flexural strength (MPa)	547.7±32.2	687
Flexural modulus (GPa)	22.9±0.3	23.4
Compressive strength (MPa)	339.6±30.7	456
Compressive modulus (GPa)	22.3±0.4	25.8
Interlaminar shear strength (MPa)	68.8±1.9	59.1

1 The reference was GF reinforced rosin-sourced epoxy (rEP/GF) resin composite, the volume fraction of GF was 47% [87]

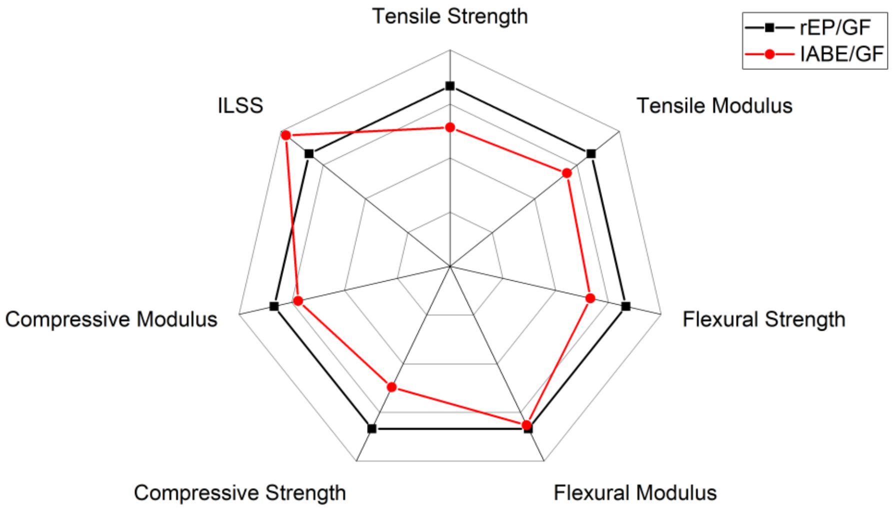


Figure. 5-11 The comparison of mechanical performance between rEP/GF and IABE/GF

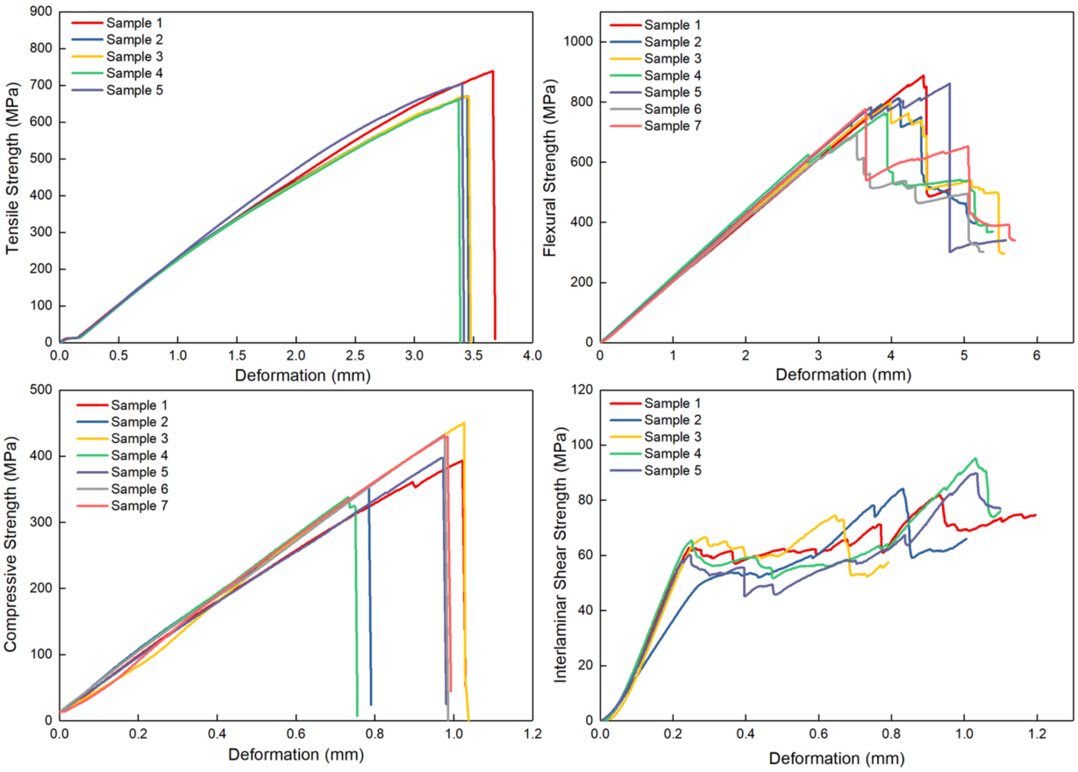


Figure. 5-12 Mechanical properties of IABE/CF composites

Table. 5-5 Mechanical properties of IABE/CF composite

	IABE/CF	Reference[2]
Tensile strength (MPa)	689.3±32.1	667
Tensile modulus (GPa)	38.9±0.8	54.6
Flexural strength (MPa)	799.3±64.9	947
Flexural modulus (GPa)	58.5±3.4	51.4
Compressive strength (MPa)	399.2±41.9	651
Compressive modulus (GPa)	60.9±4.8	53
Interlaminar shear strength (MPa)	82.1±9.0	74.8

2 The reference was CF reinforced rosin-sourced (rEP//CF) epoxy resin composite, the volume fraction of CF was 42% [87]

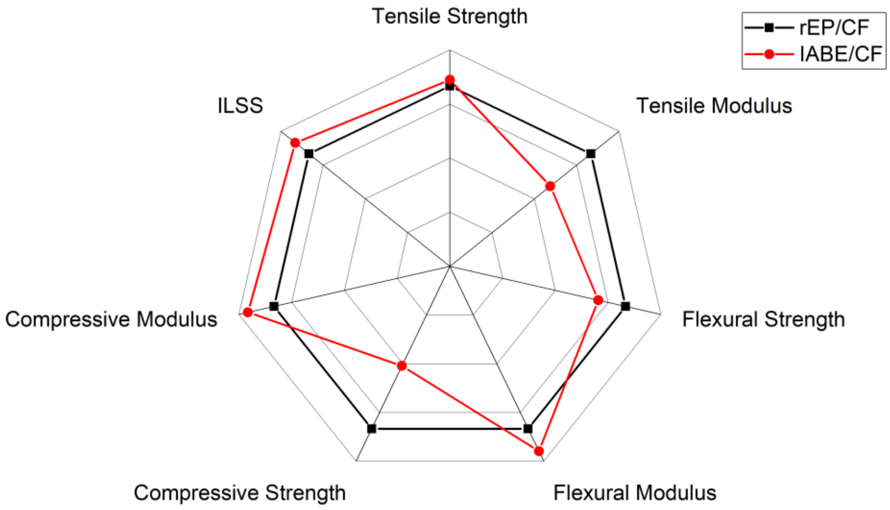


Figure. 5-13 The comparison of mechanical performance between rEP/CF and IABE/CF

5.5 Conclusion

IABE/GF and IABE/CF composites were fabricated via compression molding process from corresponded prepregs. Both the IABE/GF and IABE/CF composites samples achieved acceptable matrix infiltration to fabric. The glass transition temperature of IABE/GF and IABE/CF composites were 114 ℃ and 130 ℃ respectively. The tensile, flexural, compressive and interlaminar shear properties of the composites were characterized and possessed comparable mechanical performance to GF or CF reinforced composite with rosin-sourced epoxy matrix. The current work attempted to get some basic information about mechanical performance of fibre reinforced IABE composite. The results have proved the potential of IABE resin as alternative to traditional petroleum-based resin.

Chapter 6 Overall summary of the thesis and future works based on research findings

6.1 Overall summary of the thesis

The aim of this work is to fabricate fully-green composites composed of ramie fabric and rosin-sourced epoxy resin. Due to the intrinsically high flammability of both natural fabric and bio-sourced epoxy resin, FR additives are introduced into the composite system to improve the flame retardancy and extend the application of the NFRP composite. However, in the cases of fibre reinforced epoxy composite, the exist of fibre reinforcement in composite system possesses candle-wick effect which restrains the efficiency of directly mixing FR additives into epoxy matrix. Therefore, a possible idea is to simultaneously modify fabric and polymer with FR additives, the RF was modified with OP while rEP was modified with APP, the combined effect of simultaneously modification to fabric and epoxy on FR property of composite was investigated.

To furtherly study the combined effect, different FR additives (APP, ATH, ZnB and EG) were applied to modify the rEP, the modified rEP were still reinforced by OP@RF. By comparing the mechanical and FR behaviors of the composites, the combined effect of different FR additives in rEP matrix with OP@RF was evaluated and the corresponded FR mechanism was discussed.

Furthermore, during the manufacturing of rEP/RF composites, the high viscosity of rEP system caused the processibility problem which decreased the final mechanical performance of the composite. To cope with the viscosity problem, an ex-situ LCM process was developed, the rosin-sourced curing agent was preloaded onto RF firstly, and epoxy monomer was then applied to infiltrate the RF in a RTM process. The infiltration of matrix and mechanical properties of composites were characterized.

In addition, GF and CF reinforced composites based on itaconic acid based epoxy resin were fabricated and tested. This was a preliminary study as an extension of previous work to evaluate the possibility of other fibre reinforcements and bio-sourced epoxies.

6.2 Findings of this work

- In the cases of flame retardant fibre reinforced composites, simultaneous FR modification to both matrix and fabric is a promising strategy to improve the flame retardancy of the composite. The combined effect of the two FR modification can significantly reduce the combustibility and heat release of composite during combustion. The APP@rEP/OP@RF and EG@rEP/OP@RF composites achieved excellent flame retardancy.
- The FR modification to rEP matrix is more effective than FR modification to fabric for NFRP composite. The first reason is that the heat release of combustion of rEP is much higher than that of natural fibre, the second reason is that the combustion majorly occurs at the upper surface of composite, this area is also a resin-rich region and the combustion is mainly related to pyrolysis of resin polymer. Therefore, FR modification to resin is necessary to ensure the inflammability of resin matrix. However, the candle wick effect of RF will decrease the efficiency of FR modification to rEP, thus FR modification to fabric is also important to improve integral fire safety performance for NFRP composite.
- Dip coating process is a facile method to coat water-soluble OP onto RF and the OP modification can effectively improve the inflammability of RF. However, the hydrophilicity of OP will cause compatibility problem, while OP will generate phosphorous-containing group and promote the dehydration and carbonization of cellulosic fabric at high temperature. Therefore, the introduction of OP has significantly reduced the mechanical performance of composite reinforced by OP@RF. In contrast, the mixing of APP, ATH, ZnB or EG additives into resin matrix showed less influence on mechanical performance of composites. To solve the decreased mechanical performance of flame retardant NFRP composite caused by incompatibility between P-containing FR additive and ramie fibre, there are three

possible approaches. Firstly, the dehydration reaction between the P-containing group and cellulose led to the decrease of mechanical property of natural fibre, maybe another flame retardant additive is more proper by comprehensively considering the effectiveness and difficulty of FR modification. Secondly, another possible way is to balance the content of flame retardant additives in matrix and on fabric, the thesis has proved that FR modification to resin matrix was more effective than FR modification on fabric surface, so an experiment can be designed to investigate the best composition ratio of two modification. At last, due to the decomposition of cellulose in natural fibre at high temperature, reducing the curing temperature during curing process is a feasible method to enhance the final mechanical performance of NFRP composite, the employment of another bio-sourced resin matrix with lower curing temperature is a possible idea.

- As reinforced element, there is an nonnegligible gap in mechanical properties between NFRP composites and composites reinforced by GF or CF due to the nature of natural fibres. Accordingly, it is not reasonable to pay too much attention to improve mechanical performance of NFRP composites and NFRP composite is not suitable to be utilized as structural material. However, NFRP composites possess some other functions such as damping and sound absorption property due to the unique lumen structure of natural fibre. The future work should focus more on functional application of NFRP composites, rather than pursuing higher mechanical properties.
- There are still many issues in the development and utilization of bio-sourced epoxy resins. The current work tried to cope with the processibility problem caused by high viscosity of epoxy system based on rosin-sourced anhydride and an ex-situ liquid composite molding was carried out. The anhydride curing agent was pre-loaded onto RF and the RF after modification was infiltrated by non-reactive resin in RTM process. The separation of curing agent and epoxy monomer solved the poor infiltration problem that rosin-sourced epoxy system are not suitable for LCM process. The next step may be to optimize the process parameters and open up a new LCM for

more two-component resin system with high viscosity.

- At last, the IABE/GF and IABE/CF composites were fabricated and the mechanical performance of the composites were tested. This is a preliminary work to provide fundamental properties of fibre reinforced IABE composites for future work and to extend the range of fibre reinforcement type and bio-sourced epoxy type for current work.

6.3 Future works

6.3.1 The combined effect of FR modification to matrix and FR modification to fabric

The combination of FR modification to both fabric and resin was proved to be an effective strategy to improve the flame retardancy of fibre reinforced composites. The problem was that phosphorus-containing FR additives on RF caused visibly negative effect on mechanical performance of composite. Therefore, it is significant to develop FR additives which balance the compatibility and flame retardancy for FR modification to fabric. FR additives based on silane coupling agent [176, 211] or nanocarbon materials [160] may be an acceptable solution.

Furthermore, the FR modification to resin matrix can be optimized, the APP, ATH, ZnB and EG were respectively mixed with epoxy resin. If more than one kind FR additives are introduced into resin matrix, the synergistic effect between different FR additives are worth to be studied as well.

In addition, the FR mechanism of the combined effect of two modifications was not comprehensively studied. The role of FR modification to fabrics in the combustion of fibre reinforced composites should be furtherly investigated to understand the combined effect.

6.3.2 The influence of fibre hybridization on flame retardancy of fibre reinforced composite

NFRP is taking the place of composite reinforced by conventional synthetic fibres, as non-structural material, there is still a gap between the strength of natural fibres and synthetic fibres. Thus fibre hybridization with higher strength synthetic fibres is an important strategy to improve the mechanical properties of NFRP composites. This strategy is especially effective to composite with natural fabric reinforcements, part of the natural fabric can be replaced by CF or GF and the hybridization of high strength fibre can enhance the overall mechanical performance of the composite.

Most of the fibre hybridization for NFRP composite is aim to improve the mechanical property of composite, while few studies have focused on the effect of fibre hybridization on flame retardancy of composite. Compared with natural fibres, GF and CF are intrinsically inflammable, based on the protective char layer FR mechanism, it can be speculated that hybridization of GF or CF on the surface of NFRP composite can possibly improve the flame retardancy of composite. Also, the investigation of influence of fibre hybridization on flame retardancy of NFRP composite can provide some information to furtherly understand the role of fibre in flame retardant fibre reinforced polymer composite and candle wick effect of different fibre type.

6.3.3 Development of green composite with flame retardancy

In recent year, some FR additives derived from natural sources have been developed for green composite. The representative examples are phytic acid [141] based and lignin [140] based FR additives.

Another potential strategy to achieve FR and green composite is to adopt bio-sourced intrinsically epoxy as matrix. In general, intrinsically FR bio-sourced epoxy resin can be achieved via two methods: selecting bio-sourced percussor with higher proportion of aromatic structures in molecular chain; or introducing groups containing characteristic elements such as phosphorus, silicon, etc. into the molecular structure [212]. The employment of intrinsically FR bio-sourced epoxy can solve the dispersion problem compared to directly mixing FR additives into resin.

Strictly speaking, rosin-sourced epoxy and itaconic acid based epoxy are only bio-sourced materials, they are derived from natural feedstock but the degradability of them are not ideal. There is an increasing trend of using bio-sourced and biodegradable polymer as matrix for FR and green composite, an representative example is polylactic acid [213].

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